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Polymer formation, deactivation, and ethylene selectivity decline in Pd/Al₂O₃ catalyzed selective acetylene hydrogenation

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Rice University, 1989
POLYMER FORMATION, DEACTIVATION, AND ETHYLENE SELECTIVITY DECLINE
IN Pd/Al₂O₃ CATALYZED SELECTIVE ACETYLENE HYDROGENATION

by

STEPHEN C. LEVINESS

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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APPROVED, THESIS COMMITTEE

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ABSTRACT

The removal of acetylene by selective hydrogenation is a critical step in the purification of ethylene feeds for industrial polyethylene production. Hydrogenation of 0.35-1.0% acetylene in ethylene over Pd/Al₂O₃ catalysts is accompanied by the formation of significant amounts of surface oligomers/polymers. During the initial stages of CSTR operations at 40-120°C and P=1 atm these accounted for 8 to 50% of the acetylene consumed. Ethylene selectivities calculated ignoring these polymers are incorrect.

Approximately 30% of these products are volatile and soluble in hydrocarbon solvents. They consist of even carbon numbered chains from C₈ to at least C₅₀. Normal paraffins are the major species at each carbon number, although branched paraffins, linear and branched mono- and di-olefins, and alkylbenzenes are also produced. The remainder is nonvolatile and insoluble in any known solvent; its degradation products are consistent with those of polyacetylenes of carbon number greater than 24. A mechanism involving polymerization in regions of low surface hydrogen concentrations and terminated by hydrogenation is proposed.

The accumulation of the liquids in catalyst pores imposes diffusion limitations on the acetylene reaction; both the rate of acetylene consumption and its selectivity to ethylene decrease. These effects are reversible upon removing the liquid polymers.

The decrease in surface polymer selectivity observed during operation is compensated by an increase in gas phase oligomer
selectivity; the total oligomer/polymer selectivity does not change appreciably. In conjunction with previous investigations showing nearly constant ethane production only from acetylene, this suggests that the product distribution from acetylene hydrogenation does not change significantly.

All catalysts exhibited an induction period where the activity increased and the ethylene selectivity decreased, the latter due only to an increase in the rate of ethylene hydrogenation. The duration of this period increased sharply with decreasing catalyst metal loading, which is proposed to be inversely related to metal dispersion. The increasing duration of activation is therefore a form of structure sensitivity. Activation was only reversible upon moderate temperature hydrogen or oxygen/hydrogen treatments and represents the formation of some active surface species.
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Stephen C. LeViness
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I TEGO ARCANA DEI
I. INTRODUCTION

Ethylene production in the U.S. was approximately 33 to 35 billion pounds in 1987 (1,2), which represented a 6.6% increase over 1986 (1). Production in the last 10 years has increased at an average annual rate of 4.5% (1); current production levels represent nearly 100% of nameplate capacity (1,3,4,5). Prices have risen accordingly, from 13¢/lb in early 1987 to nearly 20¢/lb at the end of the year (3,6); they reached 26¢/lb by the end of the second quarter of 1988 (5,7) and stabilized at 31¢/lb in July and August (8). A fluid catalytic cracker explosion at Shell’s Louisiana refinery in May wiped out 6% of the total U.S. ethylene capacity and exacerbated the existing price squeeze (9). Prices are predicted to remain high or perhaps to rise even further (5), possibly to 40¢/lb by next year (8).

In response Advanced Extraction Technologies has recently developed the Mehra process for extracting ethylene directly from refinery fuel gas streams containing 15 to 20% ethylene (10). Plans to construct 47 new ethylene plants worldwide have been announced in the last 3 years (2); in the U.S. Phillips, Quantum Chemical, Dow, and Union Carbide are considering or have made plans for expanding ethylene production capacity (5,11). More recent announcements would increase ethylene production by about 29% in the next five years (12,13). More than 3 billion lb/year will be added between 1991 and 1993 alone, when total capacity should reach 45-47 billion lb/year (11,12,14).

Several companies including Pace Petrochemical, Union Texas Petroleum, Chevron, and Ethyl are considering importing ethylene to the U.S. Gulf Coast (!) to meet increased demand without restarting idled
U.S. capacity or constructing new production facilities (15). A series tracking Gulf Coast ethylene operating margins for plants utilizing a variety of feedstocks has recently been announced (16).

In 1987, polyethylene (PE) production of 17.17 billion pounds (9.35 low density PE (LDPE) plus linear low density PE (LLDPE), and 7.82 high density PE (HDPE)) consumed 17.4 billion pounds, or approximately 52% of total ethylene production (1,2,12,14). This represented an increase of 8% and 11% in 1987, and an increase of 4 and 8% in the last 10 years, for LDPE/LLDPE and HDPE, respectively (1). Further growth of 4.6 and 6.9% between 1986 and 1990, and 3.2 and 4.7% between 1991 and 1995, is predicted (14). The production of ethylene oxides (5.1 billion pounds ethylene), vinyl chlorides (4.2 billion pounds), ethylbenzenes (2.6 billion), and α-olefins (2.0 billion) accounted for most of the remaining ethylene consumed (2,14).

The price of polyethylene has increased from 27.5–30¢/lb in early 1987, to 46–47¢/lb in mid 1988 (7,17,18) and to more than 50¢/lb in August (11). Worldwide, 34 new polyethylene plants have been announced in the previous 3 years (2). In the U.S, PE suppliers are planning to add 2.9 billion pounds capacity by 1991 (5,19). Total U.S polyethylene capacity should exceed 23.5 billion lb/year by the end of 1991 (11).

Current PE production is severely limited by the shortage of ethylene discussed above (8,11,12). This in turn has led to an increase in interest in possible PE recycling schemes (20).

In addition to the older, more common PE processes, such as the Hoechst HDPE process (21), the Phillips HDPE process (22), the Imhausen LDPE process (23), and the Stamicarbon "compact" PE solution process
(24), a new gas phase process for the production of new types of polyolefin copolymers covering a broad range of very low tensile modulus polymers, called "flexomers", has recently been developed by Union Carbide (25). This may put further pressure on already tight ethylene supplies.

Ethylene streams produced by pyrolysis of heavy hydrocarbons are invariably contaminated by small amounts (0.2–2.0%) of acetylene (26–29). Typical pyrolysis yields of ethylene plant feedstocks are shown in table 1. Depending on further processing conditions, it may be necessary to remove this acetylene impurity. Current ethylene product specifications, particularly for high quality polyethylene feedstocks, require a maximum acetylene content of 1–10 ppm (22,26,27,29,30–41).

Acetylene may be removed from ethylene streams by physical separation, usually selective solvent extraction (42) with acetone (30,34,38,40,43), dimethylformaldehyde (DMF) (30), dimethylformamide (34,38,40,43) or n-methyl pyrrolidone (34,40), or by sorption on Cu(I) and Cu(II) salt solutions (44). Physical separation is rarely economically feasible unless a demand for only moderate amounts of acetylene exists, in which case acetylene recovery facilities can be located between the de-ethanizer and the ethylene-ethane fractionator, or downstream of the latter (34,40).

Selective catalytic hydrogenation of either the cracked gas in the compression train (front-end mixtures) or the ethylene-ethane product stream from the de-ethanizer overhead (tail-end mixtures), usually over low loaded (0.04 wt%) Pd/Al₂O₃ catalysts at 30–80°C and 15–25 bar pressure seems to be the most practical process and is in general
commercial use (29,33,40), although Stiles (45) reports the use of sulfided Ni/alumina at 200-250°C, 200-1000 psi. A typical process configuration is shown in figure 1.

Table 1. Typical Pyrolysis Yields of Ethylene Plant Feedstocks (in mass percent) Petroleum Fractions (34)

<table>
<thead>
<tr>
<th>Severity</th>
<th>Naphtha</th>
<th>Kerosene</th>
<th>Gas Oil</th>
<th>Vacuum Gas Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>H₂</td>
<td>0.63</td>
<td>0.8</td>
<td>0.63</td>
<td>0.65</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.7</td>
<td>15.3</td>
<td>11.4</td>
<td>10.6</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.3</td>
<td>0.75</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>24.0</td>
<td>29.8</td>
<td>23.2</td>
<td>24.0</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>3.9</td>
<td>3.75</td>
<td>3.4</td>
<td>3.25</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.76</td>
<td>1.1</td>
<td>0.85</td>
<td>1.0</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>5.75</td>
<td>14.1</td>
<td>13.8</td>
<td>14.45</td>
</tr>
<tr>
<td>C₃H₁₀</td>
<td>0.41</td>
<td>0.25</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>C₄H₄</td>
<td>4.6</td>
<td>4.85</td>
<td>4.4</td>
<td>4.7</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>6.85</td>
<td>4.2</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>C₄H₁₀</td>
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<tr>
<td>C₅</td>
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<td>2.3</td>
<td>3.0</td>
<td>3.3</td>
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<tr>
<td>C₆H₆</td>
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<td>6.3</td>
<td>7.2</td>
<td>5.8</td>
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<tr>
<td>C₆H₁₀</td>
<td>4.4</td>
<td>4.9</td>
<td>4.0</td>
<td>3.15</td>
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<tr>
<td>C₇H₆</td>
<td>2.65</td>
<td>2.0</td>
<td>2.2</td>
<td>1.2</td>
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<tr>
<td>C₇H₁₀</td>
<td>0.52</td>
<td>0.7</td>
<td>0.75</td>
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<td>C₆-C₈/PON</td>
<td>8.83</td>
<td>2.0</td>
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<tr>
<td>C₇-200°C</td>
<td>3.75</td>
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<td>4.85</td>
<td>2.4</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>1.8</td>
<td>3.8</td>
<td>13.5</td>
<td>17.6</td>
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</table>

The selective removal of acetylene by hydrogenation over metal catalysts apparently depends upon the energetics of the surface process. However, in spite of stronger alkyne adsorption on most metal surfaces (46-48), particularly acetylene on Pd, the selectivity in the half hydrogenation of acetylene to ethylene rarely reaches the required low concentrations of acetylene without notable formation of ethane, even
Figure 1. Flow Diagram of a C₂ Cut Selective Hydrogenation Process (33)

on the best Pd catalysts (49,50). Improper operation of the acetylene hydrogenation process, resulting in an ethylene loss of 2 to 3%, would produce a loss of about $3 million per year (in 1979 dollars and at 1979 ethylene prices) for a billion pound per year olefin plant (51). For this reason the addition of selective poisons such as CO, Pb, and/or sulfur is common practice (31,33,36). The process itself is very sensitive to a number of reaction variables, including feed temperature, space velocity, and C₂H₄, CO, H₂, and C₂H₂ feed concentrations (51). The problem of computer control of a selective acetylene hydrogenation plant has recently become a field in itself (52-54).

Selective hydrogenation of trace acetylene only to ethylene, without simultaneous ethylene hydrogenation to ethane, is the ideal, desired process. However, in addition to the production of ethane from both acetylene and ethylene, oligomers ranging from C₄ to higher molecular weight "green oil" are also produced (32-38). The
accumulation of these oligomers results in a continual decrease in catalyst activity, requiring a gradual increase in reactor temperature throughout the operation. The catalysts are typically regenerated in steam/air mixtures at 400°C every 6 months (33-38). Catalyst service life is about 5 years (33-35, 37, 38).

While the selective hydrogenation of acetylene on Pd catalysts is of great industrial significance, this is not the entire story. The reaction has been known for over 100 years, and has been the subject of many investigations during this time span. Yet the nature of the reaction mechanism and the causes of observed changes in catalyst activity and product selectivities during continuous operation remain unclear. These questions will be considered in the following section.
II. BACKGROUND - LITERATURE REVIEW

A. Acetylene Hydrogenation Over Transition Metal Catalysts

In 1874 Von Wild first reported the hydrogenation of acetylene to form ethylene, ethane, and higher molecular weight products over Pt catalysts (55). Throughout the latter nineteenth and early twentieth centuries, the reaction was studied over Ni (56), Pt (57), Pd (58), Fe (59), and Cu (60) with limited success. Much of this early work has been reviewed by Sabatier (61), Nieuwland and Vogt (62), Miller (63), and Bond (64,65).

In 1944 and 1945, Sheridan conducted the first systematic study of acetylene hydrogenation over Ni (66-68), Pt (69), Pd, Fe, Co, and Cu (70), all supported on pumice carriers at 2-20 wt% metal loadings. The results of these investigations, plus further experiments over Rh and Ir catalysts, were summarized in 1952 by Sheridan and Reid (71).

In a batch reactor system they observed a constant rate, constant product selectivity reaction over each catalyst up to the point corresponding to essentially complete acetylene conversion, when rapid ethylene hydrogenation began. The values of activity, expressed as moles of acetylene consumed per gram metal per second, and the various product selectivities, expressed as moles produced per mole acetylene consumed, varied with the different metals employed. Added ethylene acted as an inert diluent, which the authors assumed was due to the much greater strength of adsorption of acetylene on these metals (66-71). The reaction was generally first order in hydrogen and slightly
negative, 0 to -1, in acetylene. The activation energy over each metal was 12-16 Kcal/mole.

The specific activities, expressed as moles of acetylene consumed per gram metal per second, were in the order:

\[ \text{Pd} > \text{Pt} > \text{Ni} = \text{Rh} > \text{Fe}, \text{Cu}, \text{Co}, \text{Ir} > \text{Ru} = \text{Os} = 0 \]

and were qualitatively related to the crystal structures of the metals (71).

Ethylene selectivities, defined as moles of ethylene produced per mole acetylene consumed, were of the order:

\[ \text{Pd} > \text{Ni} > \text{Rh}, \text{Pt}, \text{Ir} \]

and were tentatively related to the interatomic distances of the particular crystal faces present in each metal (71). The authors also suggested that the selectivity might be related to magnetic properties, especially the paramagnetic susceptibility, of the metals. The extent of higher hydrocarbon formation was of the order:

\[ \text{Co}, \text{Ni}, \text{Cu} > \text{Fe} > \text{Rh} = \text{Pd} > \text{Ir} = \text{Pt} \]

and appeared to be associated with metals of small(er) atomic size.

Pd catalysts were the most active and ethylene selective of those studied. They also deactivated fairly rapidly, the reaction rate falling to 1/20 of its initial value after 8 experiments (\(H_2/C_2H_2 = 3.0\), \(P = 600\) torr, \(T = 36^\circ\text{C}\)); thereafter the activity remained constant (70). This was attributed to surface contamination by nonvolatile polymeric residues. During deactivation, ethylene selectivity, expressed as the per cent ethylene of the total ethylene plus ethane formed, decreased from an initial value of about 93 to 70%. However, it continued to decrease after the activity had reached a steady state. The authors
found no apparent explanation for this behavior, although they suggested that surface contamination was itself selective, due to the existence of different sites for ethylene and ethane formation. Aging had little or no effect on the per cent of acetylene converted to higher hydrocarbons.

In 1950 Tamaru (72-74) studied acetylene hydrogenation over 1% Pd on alumina (72,73) and 0.13, 0.40, 1.0 and 2.0% Pd on kieselguhr (74). The reaction proceeded in two distinct stages. First all acetylene was hydrogenated or polymerized; after complete acetylene consumption ethylene was hydrogenated to ethane at a higher rate than the previous reaction of acetylene. The fraction of acetylene forming products other than ethylene and ethane (polymers) was about 45%. Acetylene deposited on the catalyst surface as polymer caused a decrease in the rate constants of both acetylene and ethylene hydrogenation, although ethylene was affected much more severely (table 2). Polymer loadings as low as 90 cc (N.T.P.)

<table>
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<tr>
<th>Deposited C₂H₂ (cc. (NTP)/g cat)</th>
<th>K₁ (C₂H₂ + H₂)</th>
<th>K₂ (C₂H₄ + H₂)</th>
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<tr>
<td>0</td>
<td>0.63</td>
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<td>30</td>
<td>0.58</td>
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<td>300</td>
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per gram catalyst (96 mg/g) caused a decrease of about 25% and 80% in the rate constants for acetylene and ethylene hydrogenation, respectively. The author suggested that although these results might be
due to the existence of different active regions on the catalyst where acetylene and ethylene adsorption and reaction take place independently, it appeared unlikely as the presence of acetylene could completely terminate the ethylene reaction (73). In studies on the effect of metal loading, and by implication the metal dispersion, Tamaru (74) observed that while the acetylene reaction rate constant decreased linearly with increasing metal loading, the ethylene hydrogenation rate constant passed through a maximum at 1.0% Pd. The author had no real explanation for this unexpected observation.

In 1958 Bond (75,76) reported that in the reaction between dideutero-acetylene (C₂D₂) and hydrogen over Ni, all possible deuterocethylenes were formed, strongly suggesting some degree of dissociative acetylene adsorption to form surface C₂ units and free deuterium, both of which were active in subsequent reaction steps forming ethylene.

Also in 1958 Bond, et al (77) studied acetylene hydrogenation over α-Al₂O₃ supported Rh, Pt, and Pd (5 mol% metal loadings). The activity and ethylene selectivity trends between the different metals were identical to those reported earlier by Sheridan (71). However, in direct contradiction to the results of Sheridan (70), they found that the ethylene selectivity of Pd increased from an initial value of 85% of the total C₂ compounds formed to 95% during the first 5 batch reactions conducted - all at identical initial reactant pressures - and thereafter remained constant. During this time, the catalyst activity decreased to a steady state value of 0.40 times the initial one.
They also reported that at some point during each reaction, usually corresponding to complete acetylene consumption, the rate of pressure fall in their batch reaction system, and hence the rate of reaction, sharply accelerated, signaling ethylene hydrogenation. Curiously, they observed that this point occurred at higher acetylene pressures with increasing hydrogen and/or ethylene pressures, signaling ethylene hydrogenation in the presence of acetylene, which was believed to be impossible due to the higher adsorption strength of acetylene. No real explanation for this behavior was made.

In 1960, Anderson, et al (37) studied the selective hydrogenation of acetylene in excess ethylene streams over Pd catalysts at typical industrial conditions for that time (P = 100-550 psig, T = 212-392°F). Differential conversion experiments over a wide range of pressures, temperatures and reaction gas compositions did not fit any simple kinetic expression, although experiments at 1 atm and 212°F, with 0.1% C₂H₂ and 0.3% H₂ in ethylene, yielded a pseudo-first order relationship between conversion and space velocity. Polymer formation was observed at all conditions, ranging from about 5% of the inlet acetylene at H₂/C₂H₂ = 3 to 28% at H₂/C₂H₂ = 1.2. The composition of this polymer fraction was not completely ascertained, but IR analysis showed a large concentration of hexenes. While the presence of CO in the inlet gas stream caused a decrease in catalyst activity at all conditions, it also caused an increase in the outlet ethylene concentrations in hydrogen rich mixtures.

During continuous operation, catalyst lifetime was inversely related to the inlet acetylene concentration. The authors concluded
that the deactivation was generally due to accumulation of polymers on
the catalyst, which was directly related to acetylene concentration.
Catalysts operated at 392°F were regenerated in O₂/N₂ = 15 mixtures at
1022°F after acetylene conversions fell from about 90% (initial) to 50%.
After each regeneration, the operation time necessary to reach 50%
conversion increased. On one catalyst sample, the conversion fell to
50% in 250 hrs. initially, in 650 hrs. after the first regeneration, and
to only 84% in 1128 hrs. after the second regeneration.

In the early 1960's Bond (78), Bond and Wells (47), Wells (80,81),
and Bond, et al (82,83) reviewed earlier work on the hydrogenation of
unsaturated hydrocarbons, and first presented the concepts of
thermodynamic and mechanistic factors controlling selectivity. The
thermodynamic factor here refers to the difference in acetylene and
ethylene adsorption strengths which allows for the hydrogenation of
acetylene only, even in a large excess of ethylene, over a catalyst,
such as Pd, that may have significant ethylene hydrogenation activity in
the absence of acetylene (a similar effect was observed by Hamilton and
Burwell (84) during 2-butyne hydrogenation on Pd/Al₂O₃ in the presence of
cis-2-butene and 1-pentene). The mechanistic factor refers to the
possible formation of ethylene, ethane, or higher hydrocarbons during
acetylene hydrogenation. The overall selectivities shown by any
catalyst therefore depend on a combination of both factors.

In 1965 and 1966 Bond and Wells released a detailed series of
studies on acetylene hydrogenation over α-Al₂O₃ supported Pt (85), Pd
(86), Rh and Ir (87), and a study of acetylene deuteration over all 4
metals (88). Metal loadings were 5 mol% in all cases, and all reactions
were conducted in a batch reaction system. Although the general behavior and trends between metals were identical to those reported earlier (74,77), these investigations went into much greater depth.

On Pd (86) at temperatures of 0-30°C and initial acetylene pressures of 50 torr, they reported 4 distinct types of reaction behavior: (i) with \( \text{H}_2/\text{C}_2\text{H}_2 \leq 1.0 \), ethylene selectivity was high, 93-98\% of the total \( \text{C}_2 \) products formed, throughout the reaction, (ii) with \( \text{H}_2/\text{C}_2\text{H}_2 = 2.0 \), high ethylene selectivity was maintained throughout the reaction until complete acetylene conversion, which was then followed by much more rapid ethylene hydrogenation, (iii) with \( \text{H}_2/\text{C}_2\text{H}_2 \geq 2.0 \), the initial reaction was highly selective to ethylene, but rapid ethylene hydrogenation began before complete acetylene acetylene conversion, and (iv) with \( \text{H}_2/\text{C}_2\text{H}_2 \geq 8 \), the reaction was completely nonselective, with rapid ethylene hydrogenation throughout. At moderate \( \text{H}_2/\text{C}_2\text{H}_2 \) ratios - regime (iii) - added ethylene hastened the onset of nonselective behavior; such addition had no effect on regimes (i) and (ii).

Increasing temperature had a similar effect.

This behavior is analogous to that reported earlier by these authors (77). Here they proposed that ethylene hydrogenation in the presence of acetylene may begin when the hydrogen concentration on the surface is sufficiently high to allow for the direct interaction of ethylene from the Van der Waals layer with hydrogen adsorbed on the surface. However, following the suggestion of LeViness (89), we have recalculated their reported data assuming that acetylene pore diffusion effects caused surface Pd sites to become available for ethylene adsorption and hydrogenation in regimes (iii) and (iv). These
calculations appear in Appendix A (p. 500) and provide strong evidence that this was indeed the case. During the selective period of the reaction, the selectivity for ethylene decreased slightly with increasing conversion and hydrogen pressure and decreasing acetylene pressure.

Substantial C4 production, some 37% of the total acetylene consumed, was observed at 160°C and H2/C2H2 = 1.0. This fraction had the composition 4% 1,3-butadiene, 54% 1-butene, 24% trans-2-butene, 14% cis-2-butene, and 4% butane; these values are very far from thermodynamic equilibrium. The mechanism for C4 production was discussed in terms of that originally proposed by Sheridan for this reaction over Ni (67). Unfortunately, the effects of hydrogen pressure, feed ratios, temperature, and added ethylene on both the total C4 production selectivity and composition were either not investigated or not reported. They also observed traces of C6 products, mostly hexenes, as did Sheridan (67).

In the study of the acetylene deuterium system (88), no exchange of acetylene – formation of C2HD or C2D2 – was observed over any of the metals studied, while hydrogen exchange – the formation of HD – was rapid over Rh and Ir, slow over Pt, and negligible over Pd. Although all possible deuteroethylenes were observed, as previously (75,76), dideuteroethylene was always the major product. Deuterium distributions of the ethane produced were not reported.

In 1968 Taylor, et al (90–92) conducted a series of investigations on the adsorption and retention of 14C labeled hydrocarbons on 5 mol% Pd, Pt, and Rh on α-Al2O3 catalysts. In all adsorption measurements on
Pd, a fraction of the adsorbed hydrocarbon was permanently retained on the catalyst, and with ethylene and acetylene a small amount of ethane was observed in the gas phase. The fraction retained was in the order:

acetylene >> alkenes > cyclopropane > alkanes

This retention was interpreted as the result of dissociative adsorption - C-H bond breaking - or C-C bond fission. However, at temperatures less than 200°C, no evidence for the latter was observed.

From CO site titration measurements, the retained alkenes corresponded to approximately monolayer coverage of the metal sites. In contrast, acetylene was retained in amounts larger than that necessary for monolayer coverage. This excess acetylene retention appeared to be due to its ability to undergo polymerization, assuming that, once formed, the polymers could migrate to the support. The nature of this retained acetylenic species was not studied in such detail as to allow for a precise definition of its structure.

The injection of inactive (12C) ethylene to a previously 14C ethylene covered Pd surface resulted in no radioactivity in the gas phase ethylene, or in the small amounts of ethane formed. Hydrogen treatment had the same result. It was also possible to hydrogenate inactive ethylene on this catalyst without producing any radioactive products.

More importantly, acetylene adsorbed to form strongly bound species, and inactive ethylene and ethane, on a 14C ethylene covered surface in approximately the same amount as it did on a clean surface (one not pre-exposed to ethylene), suggesting to the authors distinctly different sites for the adsorption of each hydrocarbon. The
implications of this observation on acetylene hydrogenation are large, but it appears to contradict their earlier observation of essentially complete monolayer coverage by adsorbed ethylene and greater than monolayer coverage by adsorbed acetylene.

On all three catalysts studied, hydrogen uptake was much larger than that required for monolayer coverage, and was attributed to hydrogen migration, or spillover, from the metal to the Α-Al₂O₃ support, where it may have been associated with surface -OH groups. They also observed that during treatment with He at 200°C, only hydrogen associated with the metal was removed, while that with the support was retained.

McCarroll and Thomson (93) observed that although part of previously adsorbed ethylene was quickly displaced from Pd films by molecular acetylene beams, and another part slowly desorbed, the majority (60-80%) was permanently retained on the catalyst surface. The authors concluded that this retained species probably consisted of high polymers in ring or chain forms.

Komiyana and Inoue (94,95) studied the effects of catalyst particle size on acetylene hydrogenation over Na₂S₂O₃ poisoned, supported Ni catalysts. Using mixtures with hydrogen/acetylene = 2, they observed a constant ethylene selectivity over catalyst particles of 0.097-0.74 mm diameter, followed by a steady decrease in ethylene selectivity as the particle size was increased to 3.5 mm. The authors interpreted these results in terms of a micro-macro pore model in which acetylene pore diffusion effects became pronounced with increasing particle size (379).
During a study on the effects of aging and deactivation on ethylene selectivities (94), they observed that although over some of the larger catalyst particles ethylene selectivities decreased slightly as catalyst activity began to decay, during further operation all ethylene selectivities increased sharply, approaching 100% as further deactivation occurred. While the authors successfully modeled this behavior in terms of Langmuir-Hinshelwood kinetics and a modified shell poisoning model, these results appear to be due to the sulfur poisoning carried out prior to operation, assuming that the presence of sulfur rendered the catalyst inactive for ethylene hydrogenation at any time.

In a study of the adsorption of $^{14}$C acetylene on coldworked Pd foil, Inoue and Yasumori (96) recognized and classified 4 different adsorbed species on the surface (figure 2). These were acetylene which is: A. desorbed during evacuation, B. removed during hydrogenation, C. removed by hydrogen treatment at 150°C, and D. left on the surface after reduction and only removed by high temperature oxidation. The relative amounts of these species changed markedly with variations in foil annealing temperature, except for species D, which was essentially constant throughout the temperature range investigated.

The activity of the catalyst also changed with annealing temperature. Although this change was not regular, the activity expressed per molecule of adsorbed species B behaved in a very regular fashion (figure 3). From this information, 2 types of B sites were proposed. The first, type (I), existed only after annealing at T < 300°C, were more active than type (II) sites (whose number increase greatly upon annealing at T > 555°C), and were not affected by CO
Figure 2. Effects of Annealing Temperature on the Number of Different Types of Acetylene Adsorption Sites (96).

Figure 3. Changes in Specific Activities with Annealing Temperature (96).

adsorption to 20% coverage. Type (II) sites poisoned linearly with CO adsorption and were completely inactive at 80% coverage. The behavior
of these different sites during pressure jump and isotope replacement studies has been reported in greater detail by Inoue and Yasumori (97).

In 1974 Takeuchi, et al (98,99) studied the effects of preadsorbed \( \text{H}_2\text{S} \) on the hydrogenation of acetylene and ethylene over Ni wire. In all cases, acetylene hydrogenation proceeded with high selectivity for ethylene. After complete acetylene conversion, ethylene hydrogenation began, but slowed and finally stopped "in a very short time". A fresh sample of sulfurated catalyst had no activity for ethylene hydrogenation at any time.

These results were interpreted as a reversible formation of active sites on the surface. Initially, \( \text{H}_2\text{S} \) adsorbs on the surface and blocks the active sites. Due to its higher strength of adsorption, acetylene may displace this \( \text{H}_2\text{S} \) and react. Upon complete acetylene consumption, \( \text{H}_2\text{S} \) moves back onto the active sites, blocking them for ethylene adsorption (due to its higher adsorptive strength than ethylene). \( \text{H}_2\text{S} \) was not observed in the gas phase during acetylene hydrogenation, indicating that although it was displaced from the active sites it remained on the catalyst. Similar behavior was observed with CO pre-adsorption, except that CO was observed in the gas phase upon admission of acetylene. Therefore additional CO was necessary to terminate ethylene hydrogenation after complete acetylene consumption.

Oudar (100) observed the displacement of preadsorbed sulfur during butadiene adsorption and hydrogenation over Pt(110) catalysts. In addition, the presence of a butadiene overlayer on the surface decreased the Pt-sulfur binding energy by between 15 and 22%. Similarly, Berenblyum, et al (101) observed that Pd/Al\(_2\)O\(_3\) catalysts poisoned by
various sulfur compounds \((C_4H_3SH, C_6H_5CH_2SH, (C_6H_5CH_2)S, (C_6H_5S)_2, S_8, \) and \(C_2H_5SC_2H_5\) were reactivated during hydrogenation of phenylacetylene, 1,3-pentadiene, and 1-hexene. These authors concluded that this reactivation was due to the reduction of the sulfurized palladium species to lower valent states by reaction with the alkadienes/alkynes in a \(H_2\) atmosphere.

In 1976 Thomson and Webb proposed a new interpretation for olefin hydrogenation on metal catalysts (102). They suggested that the reaction proceeds through the transfer of atomic hydrogen through a strongly bound surface species, rather than through direct addition to the adsorbed hydrocarbon. This species was represented as \(M-C_yH_x\), where \(M\) represents a surface metal site \((y = 2 \text{ and } x \leq 4 \text{ for ethylene hydrogenation})\). In this scheme, hydrogenation is seen as an extension of self-hydrogenation, which, although self poisoning, remains continuous in the presence of hydrogen.

Also in 1976, Inoue, et al (103) studied the effects of preadsorbed acetylene on the formation of benzene and the hydrogenation of acetylene and ethylene on polycrystalline Pd-black surfaces.

Acetylene adsorbed at 195 K produced benzene during desorption at 220 to 310 K, and hydrogen above 400 K. This was reversible upon subsequent adsorption-desorption cycles, although only about 20% of the adsorbed acetylene desorbed as benzene. The remainder appeared to exist as a strongly bound surface species. Ethylene adsorbed on a clean surface desorbed as ethylene at 270 K, ethane at 320 K, and hydrogen above 400 K. In sharp contrast, ethylene adsorbed on an acetylene
adsorbed-benzene desorbed surface showed only a small ethylene desorption peak below 270 K. No ethane or hydrogen desorption occurred.

The reaction of acetylene and hydrogen at 300 K was also investigated. An induction period was observed during the initial run, but was absent in subsequent ones, suggesting to the authors that a surface template formed from strongly bound acetylenic species during the first run. Sulman, et al (104) observed a similar induction period in the selective hydrogenation of C₅, C₁₅, and C₂₀ acetylenic alcohols on a modified Pd/Al₂O₃ catalyst, and proposed an identical surface reactive complex formation during this period. An induction period during which the formation of an organometallic surface complex was observed has also been reported by Bai, et al (105) and Ghosh and Kevan (106) during ethylene dimerization over Pd-Y and Pd-X zeolite catalysts.

During a study on the effects of added acetylene to Pd ethylene hydrogenation catalysts, Inoue, et al (107) observed that upon successive ethylene hydrogenation reactions over the same catalyst, the activity decreased to less than 1/50 of its initial value on a clean surface, but then increased linearly with the amount of adsorbed acetylene, reaching a new maximum of about 1/5 of the initial value. These results clearly show the difference in catalytic properties of the bare Pd surface and one previously exposed to acetylenes.

In 1977 and 1978 McGown, et al studied the hydrogenation of 2% acetylene in ethylene on 0.04 wt% Pd/γ-Al₂O₃ catalysts in both static (108) and spinning basket (109) reactor systems.

In a static system with H₂/C₂H₂ = 2.0, P = 55 torr, and T = 20°C, they observed 4 distinct types of reaction behavior. These were: (i)
until 10 minutes reaction time, the rate was high while the selectivity for ethylene was very poor (prior admission of hydrogen increased the total amount of ethane produced in this region); (ii) a steady state constant rate period, which was unaffected by catalyst age, observed from 30 to 250 minutes reaction time, during which the selectivity for ethylene was both constant and high. However, the selectivity in this region, here defined as the rate of ethylene production over the rate of ethane production, decreased regularly from an initial value of about 20 to 2-3 during the fourth experiment. Between runs the catalyst was either treated with hydrogen or evacuated overnight, and no difference was observed between these two treatments; (iii) from 250 to 355 minutes, the rate of ethylene production slowed, reaching negative values as all of the acetylene was consumed. Rapid ethylene hydrogenation followed. This region is analogous to the acceleration point selectivity breakdown reported earlier by Bond and Wells (77,86); and (iv) after 355 minutes, the rate of ethylene hydrogenation decreased, reaching zero as all of the system hydrogen was consumed.

In an experiment using 25% ^14C acetylene, 75% light ethylene, \( \frac{H_2}{C_2H_2} = 2.0 \), and \( P = 73.4 \) torr, they found that during the steady state rate period (ii above), about 85% of the total ethane formed was produced from ethylene. Unfortunately, the overall selectivity and the prior history of the catalyst used in this experiment was not reported. Assuming an ethylene/ethane production ratio of 20 (fresh catalyst) yields an ethylene selectivity of > 98% of the total \( C_2 \) compounds formed only from acetylene, while an ethylene/ethane ratio of 3 (aged catalyst) yields a value of about 94%. The authors also found evidence for
substantial acetylene exchange with deuterium, directly contradicting the results of Bond and Wells (88).

The influence of added CO was also investigated. Amounts < 578 ppm had little effect on the rate of acetylene hydrogenation, but sharply lowered the rate of ethane production in region (ii), while amounts > 1155 ppm resulted in a very slow rate of ethylene hydrogenation after all acetylene had been consumed (region (iii)).

The authors interpreted these results in terms of 2 distinct types of surface Pd sites, one on which both acetylene and ethylene could adsorb and react, but on which acetylene is adsorbed some 2200 times stronger than ethylene. Only ethylene could adsorb and react on the other. The second type was believed to be easily poisoned by CO, thereby increasing the overall ethylene selectivity by preventing ethylene hydrogenation. They therefore concluded that the selectivity was controlled by the relative number of these two types of sites.

Experiments in a spinning basket (perfectly backmixed flow) reactor showed that the rate of acetylene hydrogenation was acetylene pore diffusion controlled at low acetylene pressures, and independent of acetylene (zero order) at high acetylene pressures. The acetylene pressure at which the transition to surface reaction control occurred generally increased with increasing surface reaction rate (figure 4).

The surface reaction rate was first order in hydrogen, zero order in acetylene, depended upon temperature in a typical Arrhenius fashion ($E_{act} = 11.2$ Kcal/mole), and was inversely proportional to the square root of the gas phase CO concentration. The selectivity in the non-diffusion controlled regime was independent of both acetylene and
Figure 4. Influence of Ethylene and CO on the rate of Acetylene Hydrogenation at 343 K in the presence of 25% Hydrogen (109).

ethylene partial pressures, which the authors felt was consistent with the 2 site mechanism proposed earlier (108).

They also found that 5-20% of the acetylene consumed was dimerized to form \( C_4 \) hydrocarbons of similar composition to those reported earlier by Bond and Wells (86). However, in the presence of CO, negligible n-butane was formed. In experiments with acetylene-propylene mixtures, no \( C_5 \) compounds were detected, which the authors interpreted as evidence that such products are formed only through the dimerization of two acetylene molecules. The mechanism of this dimerization was interpreted according to the scheme originally proposed by Sheridan for the same reaction over Ni (67).

After several weeks of continuous operation with CO in the gas phase, a brown oil was observed in the reactor outlet line. GC analysis showed at least 16 different compounds. Infrared (IR) spectra indicated
carbonyl groups and suggested the presence of a small amount of olefinic unsaturation. Ultraviolet (UV) spectra confirmed the presence of carbonyl groups. Mass spectra (MS) detected chains up to 22 carbon atoms in length.

In 1978 and 1979 Al-Ammar and Webb conducted a series of studies of acetylene hydrogenation over 5 wt% Pd/α-Al₂O₃ and 5 wt% Pd, Rh, Ir (110-112), and 25.4 wt% Ni (113) on SiO₂ catalysts, and of allene (methyl acetylene) hydrogenation over 5 wt% Rh on SiO₂ (114), all in a static reactor system.

In part 1 (110), they investigated the adsorption and retention of both ¹⁴C labeled acetylene and ethylene, and found that both adsorbed in 2 distinct phases (figure 5). The first was a steep, primary phase which they interpreted as direct adsorption on the surface Pd sites. The second was a more gradual, linear increase, interpreted as a secondary overlayer adsorbed upon the primary species. They concluded that the transition point represented monolayer surface coverage. As this behavior was identical after the support was treated with hexamethyl-disilazane, the migration, or spillover, of adsorbed species to the support was ruled out. However, direct adsorption on the support was not considered, and adsorption on support blanks was apparently not conducted.

When acetylene and ethylene preadsorbed catalysts were employed in acetylene hydrogenation, the activity declined to a steady state of about 1/8 of its initial value after a number of experiments. After this steady state had been reached, further experiments with ¹⁴C
Figure 5. Adsorption Isotherms for $^{14}$C labelled Species on Freshly Reduced (A) 0.10 g Pd/silica and (B) 0.10 g Pd/alumina (110).

acetylene were conducted. A part of the adsorbed species was removed during hydrogenation, and a further fraction could be removed by allowing the catalyst to stand under hydrogen for 6 hours. Re-
adsorption of $^{14}$C acetylene showed that the primary adsorption layer on the steady state catalyst was about 50% lower, and adsorbed much less CO, than fresh catalysts.

These results were discussed in terms of the mechanism proposed by Thomson and Webb (102), where the primary species that could be removed by hydrogen treatment corresponds to the $M-C_2H_x$ species they had proposed. As the number of these hydrogen transfer species decreases with catalyst age, the activity also declines. However, the activity decline of about 8 times was much larger than the 50% reduction in the amount of this adsorbed species. This sensitivity was not discussed.

Most importantly, ethylene admitted to acetylene precovered catalysts showed the same adsorption capacity as in the absence of acetylene, providing very strong evidence to the authors for the existence of more than 1 type of Pd surface site. They concluded that 2 types of metallic sites existed on the catalyst surface, one of which may adsorb and hydrogenate only acetylene, the other only ethylene. The difference in the rates of ethylene hydrogenation in the presence and absence of acetylene was assumed due to different hydrogen availabilities at the two types of sites in the presence of acetylene.

It should also be noted that these authors made no mention of the presence or absence of C$_4$ and higher hydrocarbons produced during the hydrogenation of acetylene, and indeed their data would seem to indicate that it did not occur. During batch reactions over supported Pd catalysts, they reported that the rate of pressure fall in their reactor accelerated after essentially all acetylene had been consumed. In reaction between 12.5 torr acetylene and 37.5 torr hydrogen, this
acceleration occurred after a pressure fall of 13.2 torr. If all acetylene (12.5 torr) had been consumed at this point and no higher weight hydrocarbons were produced, then the remaining 0.7 torr pressure drop must represent extra hydrogen consumed to form ethane. Assuming that this is the case yields an ethane selectivity of \( \frac{0.7}{12.5} = 5.6\% \), and therefore an ethylene selectivity of 94.4\%. As this is the value quoted by the authors for ethylene selectivity over this catalyst, we must rule out the formation of any oligomeric species in this reaction. However, it seems odd that the authors do not even mention this rather remarkable fact, as all previous studies cited in this paper report the formation of higher weight products.

In addition, at about the same time as this report was published, one of the authors published a detailed review of hydrogenation phenomena (115), which contained a discussion of the formation of C\(_4\) products during acetylene hydrogenation over group VIII metals; over Pd a C\(_4\) selectivity of 37\% was reported. It appears that the assumption that the acceleration occurred after complete acetylene consumption was incorrect (which would agree with the observations of Bond and Wells (86) over similar catalysts and hydrogen/acetylene ratios (p. 13)). We have investigated these problems in more detail (Appendix B, p. 510). From this information we conclude that the selectivities they reported are also incorrect.

Part 2 of this study (111) dealt with further investigations of the type reported in part 1. Here, using \( \frac{H_2}{C_2H_2} = 3.0 \) and \( P = 50 \) torr, they reported that the steady state reaction rate was reached after 8 to 10 batch experiments (figure 6), and related the decline in activity to
Figure 6. Variation of the First Order Rate Constant With Reaction Number for 0.10 g catalyst at 298 K (111).

the build-up of permanently retained species (a reduction of M-C₆H₆) possibly due to surface polymer formation. Ethylene selectivity values were unaffected by this deactivation and were about 95% of the total ethylene plus ethane formed. Reaction orders remained first in hydrogen and zero in acetylene. They also reported that the total amount of acetylene adsorbed in the primary layer remains the same throughout deactivation, although the fraction of permanently retained species increased. Consequently, the amount of M-C₆H₆ must have decreased. A further development of the model of Thomson and Webb (102) was made.

Part 3 of this study (112) showed that during deactivation, the ethylene selectivity, again defined as the % ethylene of the total ethylene plus ethane formed, did in fact decrease from an initial value of 94% to a steady state value of about 92%. However, ¹⁴C acetylene experiments showed that the intrinsic selectivity - of products formed
only from acetylene - remained constant at about 94% (again, because C\textsubscript{4} compounds were ignored, we must conclude these values are erroneous). The observed decline in overall selectivity was a function only of an increase in the rate of ethylene hydrogenation, which was found to vary linearly with ethylene partial pressure, in clear contradiction of the results of Sheridan (70), Bond and Wells (86), and McGown, et al (109).

This they interpreted as evidence for 3 distinct types of surface sites, the first on which acetylene reacts to form ethylene, the second, acetylene to form ethane, and the third, ethylene to form ethane. No mention of possible sites for the polymerization of acetylene to C\textsubscript{4} and higher hydrocarbons was made. The relative activities of each site were proposed to be controlled by the hydrogen availability at each, so that in the presence of acetylene, hydrogen for ethylene hydrogenation sites was unavailable due to complete occlusion. Monitoring the surface count rate during acetylene hydrogenation in the presence of \textsuperscript{14}C ethylene further supported this conclusion, as the count rate showed no large increase upon acetylene consumption and the onset of rapid ethylene hydrogenation.

The simultaneous adsorption of CO, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4} with a different species labeled with \textsuperscript{14}C during each experiment was investigated on catalysts under hydrogenation conditions. Contrary to the observations of McGown, et al (108), all 3 compounds adsorbed in approximately the same amounts, regardless of the presence or absence of either, or both, of the others. Hydrogen adsorption, however, was drastically reduced by prior CO adsorption and resulted in the displacement of a small amount of the preadsorbed CO. Thus the selectivity promoting effect of CO was
interpreted as a competitive adsorption between CO and hydrogen. This results in a reduced surface hydrogen concentration which blocks hydrogen from ethylene adsorption sites.

In part IV of this study (113), using a 25.4 wt% Ni on SiO₂ catalyst, they reported results that were in substantial agreement with those published earlier over Pd, Rh, and Ir catalysts. The adsorption of acetylene on fresh catalysts again showed 2 distinct regions, the first of which they concluded corresponds to the M-C₆H₆ species. The amount of this species and the catalyst activity decreased with batch reaction number. However, although the amount of adsorbed acetylene assumed to represent M-C₆H₆ decreased by a factor of about 4, the catalyst activity reached a steady state of only 1/6 of the initial value. Again, this sensitivity was not discussed. Here they concluded that four distinct types of sites exist on the catalyst surface. The first is active only for acetylene selfhydrogenation, the second only for acetylene hydrogenation to ethylene, the third only for acetylene to ethane, and the fourth only for ethylene hydrogenation to ethane. ¹⁴C labeling showed that the predominant route for ethane formation was direct hydrogenation of acetylene, without an ethylene intermediate.

In a study of the hydrogenation of allene (methyl acetylene) over 5 wt% Rh on SiO₂ catalysts (114), similar results were again reported. The adsorption of allene over fresh and deactivated catalysts was not investigated in this case, apparently due to the instability of the ¹⁴C labeled species. Labeled propylene, however, showed no primary adsorption layer on freshly reduced catalysts in the presence of allene, or on deactivated catalysts regardless of the presence of allene.
Propylene was also observed to adsorb and hydrogenate to propane over steady state catalysts in the presence of allene. The authors concluded that 3 separate sites were present on the catalyst surface: the first for allene hydrogenation to propylene, the second for allene to propane, and the third for propylene hydrogenation to propane.

While generally developing the mechanism for acetylene hydrogenation in terms of the model of Thomson and Webb (102) as discussed above, the review by Webb (115) also made an attempt to reconcile the different experimental results and conclusions of Al-Ammar and Webb (110-112) and McGown, et al (108-109). However, because during reaction in the presence of $^{14}$C labelled ethylene Al-Ammar and Webb (112) observed no abrupt increase in the catalyst surface count rate upon complete acetylene consumption, as would be expected if acetylene and ethylene competed for and reacted on the same Pd sites, this effort was perhaps unsuccessful.

In order to reconcile these different models we must conclude that the number of ethylene only sites is much greater than the number of sites for either acetylene or ethylene adsorption (so that the increase in ethylene adsorption when these sites become available is masked by the much greater amount of ethylene previously adsorbed on the ethylene only sites), and that the ethylene only sites are inherently much less active (as the rate of ethylene hydrogenation was always lower than the rate of acetylene hydrogenation in the presence of acetylene), or that their activity is greatly reduced in the presence of acetylene due to almost complete hydrogen occlusion from them by adsorbed acetylene.
The adsorption experiments of Al-Ammar and Webb (110-112) have consistently shown that the number of ethylene only sites is much smaller than the number of acetylene only sites, while the batch experiments of McGown, et al (108) have shown that the reaction of ethylene in the absence of acetylene is much faster than the reaction of acetylene. Thus, it would appear that the only way to reconcile these differences lies in the assumption of almost complete hydrogen occlusion from the ethylene sites by acetylene, as proposed by Al-Ammar and Webb (110-112). At the present time, no mechanism explaining this occlusion, and the necessary physical separation between the two types of sites implied by it, has been proposed.

At the same time that Webb (115) published this review of hydrogenation reactions, Wells (116) reported the results of a study on the role of hydrogen occlusion and its influence on selectivity during butadiene hydrogenation on Ru, Rh, Os, Ir, Pt, Au, and Co powder catalysts. He observed that the capacity of these metals to occlude hydrogen parallels the extent of butane formation during butadiene hydrogenation. This result was interpreted in terms of cavitated zones where large reservoirs of hydrogen were occluded. Away from these zones, butadiene is hydrogenated to butenes very selectively (S→100%) and little or no butene hydrogenation to butane occurs; at the edges of these zones hydrogen availability is sufficiently high to convert essentially all butadiene to butane (S→0%). The overall selectivity was therefore determined by the extent of these zones of occluded hydrogen. The order of the metals for both hydrogen occlusion and butane formation was:
$0 = \text{Au} < \text{Co} < \text{Pt} < \text{Ru} < \text{Rh} < \text{Os} < \text{Ir}$

Unfortunately, neither Pd nor Ni, well known hydrogenation catalysts which are capable of forming metal hydride phases (117), was included in this study, and it is unclear how the existence of large amounts of absorbed hydrogen might affect these properties. If, however, this model is correct, then we would expect very little hydrogen occlusion over either Pd or Ni, as butane production during butadiene hydrogenation over both is very small (118-131). This model may support the proposal of Al-Ammar and Webb (110-112) that different sites are responsible for ethylene vs. ethane production from acetylene, but adds nothing to the proposed role of hydrogen occlusion away from ethylene only sites on Pd in the presence of acetylene.

Also recently, Guczi, Weiss, and various co-workers conducted a series of studies on acetylene hydrogenation over both Pd-black and Pd on various supports (132-144).

In a study of trace (0.35%) acetylene deuteration in excess ethylene over 0.1 wt% Pd/$\gamma$-Al$_2$O$_3$ in a flow reactor at 0°C and P = 3 - 5 atm (132), they observed aging effects very similar to those reported by McGown, et al (108) on 0.04 wt% Pd/$\gamma$-Al$_2$O$_3$ catalysts. Although the reaction rate of acetylene remained constant during aging, the selectivity for ethylene production decreased from an initial value of about 80% of the total C$_2$ products to a value of ~40% after 700 hours of continuous operation. That is, a net consumption of ethylene was observed at acetylene pressures where the reaction would not be expected to be acetylene pore diffusion limited (figures 7). As in Al-Ammar and Webb (110-112), these authors calculated ethylene selectivities assuming
ethylene and ethane were the only products; these values are also wrong. However, ethane selectivities are correct and negative ethylene selectivities were still observed (see Appendix B, p. 510). This

![Graph showing the effect of aging on ethylene production](image)

**Figure 7. The Effect of Aging Uniformly Deposited 0.1 wt% Pd/Alumina Catalysts on Ethylene Selectivity at 273 K (132).**

necessitates the conclusion that ethylene hydrogenation can occur in the presence of acetylene, as observed by McGown, et al (108), and by Al-Ammar and Webb (112). Since $^{14}$C labeling was not used here, the relative rates of ethylene hydrogenation and acetylene hydrogenation to ethylene and ethane are unknown.

As the acetylene rate remained constant while the selectivity decreased, the activity of the catalyst, measured by the deuterium reaction rate, actually increased as a function of time. Alternatively, if we assume a first order hydrogen dependence for this reaction, the reaction rate constant increased with time, as the hydrogen partial pressure decreased to accommodate the changing reaction stoichiometry.
This result would appear to be incompatible with the mechanism proposed by Thomson and Webb (102), for it would require a large increase in the number of M-C\textsubscript{2}H\textsubscript{x} sites during aging, unless by some unknown mechanism, the occlusion of hydrogen away from ethylene only sites is gradually reduced during catalyst operation, allowing ethylene hydrogenation to take place.

Effects of the nature of the support and the metal impregnation profile were investigated on 0.35 wt% Pd on α-Al\textsubscript{2}O\textsubscript{3}, carbon fiber, carbon sieve, and silica fiber supports, and on 0.1 wt% Pd both uniformly and peripherally deposited on γ-Al\textsubscript{2}O\textsubscript{3} (132). Although the supports had no hydrogenation activity of their own at reaction conditions, a large support effect was observed. The highest selectivity for ethylene was observed with the α-Al\textsubscript{2}O\textsubscript{3} supported catalyst, followed, in decreasing order, by uniformly and peripherally deposited Pd on γ-Al\textsubscript{2}O\textsubscript{3}, which were essentially equal, then carbon fiber, silica fiber, and finally carbon sieve, on which negative selectivity values were observed. As no differences in activity and selectivity between the uniform and peripheral 0.1 wt% Pd catalysts were observed, they concluded that on these catalysts acetylene pore diffusion was not a controlling factor.

However, as only this catalyst, which contained about 70% less Pd than the others and had a different pore size distribution, was checked for diffusion control effects, it is impossible to rule out the possibility that diffusion control effects caused the observed differences in selectivity on the 0.35 wt% Pd catalysts. Changes in C\textsubscript{4} selectivities (which were ignored) would also cause apparent changes in
calculated ethylene selectivities. In addition, no such support effect on fresh catalysts in the absence of pore diffusion effects has been reported before. Ethylene selectivities have all been approximately the same, regardless of the nature of the support.

In a study of the deuteration of 90% acetylene 10% $^{14}$C ethylene with $D_2/(C_2H_2+C_2H_4) = 4.0$ and $P = 63$ torr over Pd-black catalysts, Gucci, et al (133) found that at high acetylene pressures, the reaction of ethylene did not occur, but acetylene was hydrogenated to form both ethylene and ethane, in addition to various $C_4$ products. Ethylene was also hydrogenated to ethane at low acetylene partial pressures. This the authors interpreted as evidence for only one type of surface site, on which either acetylene or ethylene may adsorb and react, but which acetylene monopolizes until it disappears to a sufficient extent for sites to become available for ethylene adsorption and hydrogenation. This interpretation differs from the conclusions of McGown, et al (108) and Al-Ammar and Webb (112), but so does the catalyst used (Pd-black vs. Pd on $Al_2O_3$ or $SiO_2$). Also contrary to the results of McGown, et al (108), no acetylene exchange with deuterium was observed at any time.

Margitfalvi, et al (134,135) extended these investigations on Pd-black with various mixtures of $^{14}$C/$^{12}$C acetylene, $^{14}$C/$^{12}$C ethylene, hydrogen, and deuterium in a continuous back-mixed flow reactor. They observed that the reaction order in acetylene changed from essentially zero at high acetylene pressures to negative (between 0 and -1) to zero again, where the rate passed through a maximum, then to positive as the acetylene pressure approached zero (figure 8). Ethylene hydrogenation
began at about the same acetylene pressure that the rate reached a maximum but was completely terminated at higher acetylene pressures.

![Graph showing Acetylene Reaction Rate vs. Acetylene Pressure](image)

**Figure 8. Acetylene Hydrogenation Rate Dependence on Acetylene Partial Pressure in the Presence (A) and Absence (B) of Ethylene.** Pd black catalyst. P_D$_2$=14.6 torr. P_C$_2$H$_4$=7.6 torr (134).

All possible deuteroethylenes and ethanes were observed in the gas phase products of the reaction between acetylene and deuterium, again suggesting some degree of dissociative acetylene adsorption, as reported earlier by Bond and Wells (88) and McGown, et al (108).

Here, Margitfalvi, et al (134,135) first proposed a special form of the ethylidene species originally proposed by Oliver and Wells (145), ethylidyne, which could be responsible for the direct formation of ethane from acetylene (figure 9). This species had been previously observed by Somerjai, et al (146) during acetylene adsorption on Pt crystals.

More importantly, they recognized that acetylene hydrogenation yields ethylene, ethane, and C$_4$ hydrocarbons under all experimental
conditions, and at low acetylene partial pressures, such as those found near the outlet of commercial hydrogenation reactors (1 to 10 ppm (22,30-38)), the hydrogenation of both acetylene and ethylene proceed simultaneously. This behavior could be only moderately affected by changes in operational parameters, suggesting that in the search for a more selective catalyst, further research should be directed at altering the catalyst itself.

![Chemical Reactivity Diagram](image)

Figure 9. The Formation of Ethyldene (A) and Ethylidyne (B) During Acetylene Adsorption on Pd (134,135,145).

Moses, et al (136) studied the effects of catalyst pretreatment on the hydrogenation of 9/1/40 of C2H2/C2H4/D2 mixtures, P = 52 torr, over 0.04 wt% Pd/γ-Al2O3 catalysts in a batch reactor.

They observed that although the ethylene selectivity decreased with reaction number for catalysts treated with hydrogen between runs, as did McGown, et al (108), when these catalysts were treated for 1/2 hour in flowing O2 at 200°C prior to hydrogen treatment, the selectivity remained constant. This they related to the removal by oxidation of a strongly bound acetylenic species, which was responsible for the observed selectivity decline. Similar results were reported by Al-Ammar and Webb (110-112), except that in their case the build-up of strongly
bound species caused a decrease in activity, not selectivity. Reasons for this discrepancy were not discussed, although the 100 fold difference in metal loading may be responsible in some way.

They also observed that using catalysts after initial reduction without subsequent high temperature evacuation resulted in an initial period of high reaction rate and low ethylene selectivity during the succeeding experiment (McGown, et al (108) observed similar behavior during the initial stages of batch reactions). Such an effect was absent after evacuation for 1/2 hour at 450°C. This was interpreted in terms of the formation of a $\beta$-phase Pd-hydride, which Jenko, et al (147) had recently shown to be some 10 times more active, and much less ethylene selective, than the more common $\alpha$-phase in acetylene hydrogenation. They postulated that the additional hydrogen present in the $\beta$-phase was active in the formation of the ethylidyne species, which Margitfalvi, et al (134,135) had earlier proposed as the species leading to direct ethane formation from acetylene. Similarly, they postulated that the existence of strongly bound acetylenic or polymeric deposits increased the surface hydrogen concentration, which also contributed to the formation of ethylidyne, yielding the ethylene selectivity decline found on aging here, by McGown, et al (108), and by Weiss, et al (132). This effect of surface carbon residues was shown by Boudart, et al (148) on the Pt-carbon system.

However, using $^{14}$C acetylene McGown, et al (108) observed that the selectivity of products from acetylene remained essentially constant during aging, and Weiss, et al (132) ultimately reached conditions of net ethylene consumption at high aging times (>700 hours). These
results indicate that the observed decrease in selectivity can not be
due only to a higher percentage of acetylene hydrogenated to ethane, but
must be at least in part due to an increase in the catalysts activity
for ethylene hydrogenation, even in the presence of acetylene.

In experiments using deuterium rather than hydrogen, Moses, et al
(136) found that using hydrogen as a reactant resulted in rates 8 times
greater than using deuterium. This is much larger than the 1.4-1.6
isotope effect reported by Inoue and Yasumori (97) for the same reaction
on Pd foil. There was no significant difference in using hydrogen or
deuterium for reduction after catalyst regeneration (oxygen treatment),
but initial catalyst reduction in hydrogen resulted in a rate 5 times
greater than with deuterium. Curiously, there was no effect on ethylene
selectivity, effectively ruling out the existence of a β-phase hydride
as the explanation for these phenomena. Rather than simply accepting
the fact that the isotope effect was this large, the authors proposed
that this might be due to the formation of some other type of hydride,
though not the β-phase itself, as the deuteride could not exist at these
experimental conditions (149).

They also observed that when ethylene was exposed to a freshly
regenerated catalyst for 1 hour, after a subsequent regeneration cycle
the activity was only 1/3 of its initial value, and the ethylene
selectivity had dropped by about 2% (which is probably not significant).
However, after another regeneration cycle, both the activity and
ethylene selectivity had returned to their initial values. This
behavior is similar to the results of Inoue, et al (103,107), reported
earlier. These results, however, directly contradict the adsorption
studies of Al-Ammar and Webb (110-112), who have repeatedly found that acetylene and ethylene adsorbed in the same amount and in the same way regardless of the absence or presence of the other.

LeViness, et al (138) studied the hydrogenation of 0.4-1% acetylene in the presence of both 0.4 and 18 vol% hydrogen in balance ethylene mixtures, P = 1 atm, over 0.04 wt% Pd/γ-Al₂O₃ catalysts containing 0:100, 30:70, and 80:20 atoms Cu/atoms Pd.

They also observed a steady decrease in ethylene selectivity during catalyst aging, while the activity for acetylene hydrogenation remained constant. However, on freshly prepared catalyst samples, ethylene hydrogenation to ethane (measured using ¹⁴C ethylene) was terminated at acetylene pressures greater than the pressure corresponding to the maximum rate of acetylene hydrogenation found by Margitfalvi, et al (135) on Pd-black. The acetylene reaction order fit this same curve (figure 8, p. 38). Experiments using ¹⁴C labeled ethylene also showed that the percentage of acetylene forming ethylene was high (91-95% of the C₂ products formed from acetylene) at all times, and the observed overall ethylene selectivity decrease observed was due only to an increase in the catalyst activity for ethylene hydrogenation, at acetylene pressures where ethylene hydrogenation was terminated on fresh catalyst samples.

The weight of the catalyst sample, measured in a microbalance, increased concurrently with the ethylene selectivity decline, although these measurements were not carried out during all experiments due to equipment limitations. As they had previously found no ethylene selectivity decrease on catalysts treated with oxygen between reactions
(136), the authors concluded that the decrease in overall ethylene selectivity is directly related to the build-up of high molecular weight oligomeric products on the catalyst surface, which can only be removed by thermal oxidation. This suggested to the authors that on supported, aged Pd catalysts, which showed significant ethylene hydrogenation activity in the presence of acetylene sufficient to terminate ethylene hydrogenation on Pd-black or fresh supported samples, a second type of hydrogenation site must exist. However, in contrast to the conclusions of McGown, et al (108,109), and Al-Ammar and Webb (110-112), they concluded that this second type of hydrogenation site was the Al₂O₃ support itself.

In addition, they proposed that the surface oligomeric species acted as a promoter of hydrogen spillover from the surface Pd sites, where hydrogen is dissociated, to the support, where it may react with adsorbed ethylene, analogous to the results of Boudart, et al (148) on the Pt-carbon system. In the absence of the surface oligomers (such as on fresh samples), where hydrogen spillover cannot take place, or of support sites for ethylene adsorption (such as on Pd-black), ethylene hydrogenation does not occur.

The addition of small amounts (60 ppm) of CO in the gas phase sharply decreased the rate of ethylene hydrogenation to ethane, while increasing amounts (>500 ppm) completely terminated it; the observed ethylene selectivity values approached those observed (with ¹⁴C ethylene) from acetylene hydrogenation only. In agreement with the observations of Al-Ammar and Webb (111), the authors concluded that this CO effect is due to hydrogen displacement from the metal surface, but
then proposed that this greatly decreased the amount of hydrogen spillover to the support.

Cu addition decreased somewhat the catalyst activity and increased its stability (reduced the extent of ethylene selectivity decline during operation), resulting in a significant decrease in the rate of ethane production and a marginal decrease in the amount of acetylene converted to C_4 and higher gas phase products. The authors concluded that this was due to incorporation of Cu into the Pd matrix, decreasing the number of multiple Pd sites responsible for dissociative adsorption, which the authors concluded leads to the formation of both oligomers and ethylidyne (which can only desorb as ethane).

Weiss, et al (139) continued to study the effects of adding Cu to 0.04 wt% Pd catalysts, and of adding CO to the inlet reactant stream. Because added Cu had only a small effect on the selectivity to C_4 and higher gas phase hydrocarbons (in the absence of CO), they concluded that the observed increase in ethylene selectivity (i.e. decrease in the rate of ethylene hydrogenation to ethane) upon the addition of Cu was due to the Cu providing desorption sites for spillover hydrogen (reducing the hydrogen concentration on the Al_2O_3 support), and not due to a decrease in the amount of polymer formation (reducing the dissociative adsorption of acetylene).

Experiments on the effects of CO in gas mixtures containing a large excess of hydrogen (H_2/C_2H_2 > 15) showed that while 800 ppm reduced the rate of acetylene consumption by almost 2 orders of magnitude, it had little or no effect on the percentage of acetylene converted to C_4 and higher hydrocarbons. This they took as conclusive evidence that CO
competes with and displaces hydrogen from the catalyst surface, for if the reduction in rate was due to competition with acetylene, they would have expected the fraction polymerized to C₄ and higher compounds - assumed to require 2 neighboring adsorbed acetylene molecules - to be greatly diminished. Further results supporting these conclusions are reported by Gucci, et al (140).

Sarkany, et al (141) studied the effects of aging with a tail-end mixture (0.29% C₂H₂, 0.44% H₂, balance ethylene) over Pd-black and Pd on various Al₂O₃ supports. They again observed that on supported catalysts, ethylene selectivity decreased with time on stream for the first 40-60 hours, while acetylene conversion activity remained essentially constant. ¹³C labeled acetylene showed that the product distribution from acetylene also remained unchanged, again indicating that the observed decrease in ethylene selectivity was due only to an increase in the catalyst activity for ethylene hydrogenation. On Pd-black the opposite trend in ethylene selectivity was observed.

They concluded that initially on Pd-black there are sites active only for the hydrogenation of ethylene, but as polymer forms on the catalyst surface, it first blocks these sites (increasing the observed ethylene selectivity by terminating direct ethylene hydrogenation). Acetylene was able to compete with this polymer until a much greater amount had formed, after which time acetylene conversion also decreased. On supported Pd, however, the polymer acted as a transfer medium, supplying atomic hydrogen to Al₂O₃ sites for ethylene hydrogenation.

TGA measurements showed that the polymer on supported catalysts amounted to 6-30 mg per gram catalyst and was sufficient to induce
substantial activity for ethylene hydrogenation, assumed to occur on the support. In contrast, loadings of > 140 mg per gram catalyst of squalane or hexadecane had no appreciable effect on either catalyst activity or selectivity, indicating that the polymer responsible for promoting hydrogen spillover was not a simple paraffin film. The nature of the actual polymer formed remained unknown.

Sarkany, et al (142) investigated the composition of samples of industrial "green oil" (polymer produced during acetylene hydrogenation in the presence of CO) using NMR, IR and MS, and the effects of added green oil on the activity and selectivity of 0.04 wt% Pd/γ-Al₂O₃ catalysts. They observed two distinct green oil phases, one dissolving in methanol, the other precipitating paraffins upon mixture with methanol. The paraffin phase contained an average of 8 to 10 carbon atoms, with 7-8% olefinic protons. The other phase was shown to contain carboxylic acids, due to the incorporation of CO into the polymer chain. Only traces of aldehydes and alcohols, and no ketones, were detected.

Green oil loadings of 29-103 mg per gram catalyst decreased the catalyst activity by 40-70%, while loadings of 1.5 ml per gram catalyst decreased activity by more than 1 order of magnitude. In all cases ethylene and ethane selectivities were only moderately affected. They concluded that this decrease in catalyst activity was caused not by the oil physically blocking pores and/or covering active sites with a thin film, but by direct poisoning of the Pd sites, perhaps by the formation of surface carboxylates - from the observed carboxylic acids - which might be strong enough to inhibit acetylene chemisorption.
Sarkany, et al (143) also investigated the effects of catalyst dispersion on acetylene conversion activity and product selectivities over various Pd catalysts. As the dispersion of Al₂O₃ supported Pd catalysts increased from about 6% to about 50%, the turnover number (TON) increased by a factor of about 4, while the amounts of ethane formed from both acetylene and ethylene (again using ¹⁴C labeled acetylene) decreased by a factor of about 4. They concluded that at low dispersions, the ease of dissociative acetylene chemisorption, the formation of surface alkylidyne species, and possibly the formation of a β-phase Pd-hydride accounted for the higher rate of ethane formation, while at higher dispersions more efficient acetylene complexing inhibited the adsorption of ethylene. However, we have recalculated their values to correct for different hydrogen pressures in each experiment (Appendix C, p. 520). The results of these calculations shed doubt on this conclusion and instead suggest that the apparent trends in Sarkany, et al (143) may be artifacts resulting from experimental error.

Tamaki and Imanaka (150) have recently observed a large increase in both catalyst activity and initial ethylene selectivity with increasing film thickness during acetylene hydrogenation over thin Pd films. They also observed a steep increase in the Pd(220) X-ray diffraction (XRD) intensity and a decrease in the Pd(111) intensity during the same treatment. These authors concluded that while the Pd(220) surface exhibited a high ethylene selectivity (96%), the Pd(111) face was not suitable for selective acetylene hydrogenation.

It should be noted that the impetus for the proposal of Thomson and Webb (102) that hydrogenation takes place on an adsorbed
hydrocarbonaceous layer (M-C_{y}H_{x}, discussed earlier) was the fact that remarkably little structure sensitivity had been reported in the hydrogenation literature up to that time (151-158). At the same time very little information about catalyst dispersion values, particularly for those of very low (< 0.1 wt%) Pd loadings, was available. There is considerably more evidence at this time that the hydrogenation of acetylene and other similar compounds is more structure sensitive than previously believed (127-130,150,158-189). This is not to rule out any role of active surface hydrocarbonaceous species, for the results of Moses, et al (136) and Inoue, et al (103,107) clearly show the importance of the initial hydrocarbon species formed on Pd catalysts, and the marked differences in behavior between such precovered catalysts and those consisting of bare Pd metal only.

Kranich, et al (144) attempted to capitalize upon the previous observations of Sarkany, et al (143) by incorporating Pd into the very small pores of various types of zeolites, which might ideally increase the Pd dispersion to near unity. 0.008 wt% Pd on ZSM-5 showed no ethane production at all, versus an ethane selectivity of 3% over an industrial 0.04 wt% Pd/γ-Al_{2}O_{3} catalyst (ICI-38-3). The oligomer selectivities of this Pd on ZSM-5 catalyst and of a 0.024 wt% Pd on Na-mordenite catalyst were somewhat lower than over the industrial catalyst (19 and 13%, versus 24%). However, many other types of Pd on zeolites showed substantially worse product selectivities, and lower acetylene hydrogenation activities were observed in all cases. The authors concluded that zeolite supported catalysts of small channel size and in
which Pd is incorporated into the structure during synthesis looked promising.

More recently Plante and Weiss (190) studied the deactivation during operation of a series of 0.035 wt% Pd catalysts supported on α-Al₂O₃ and various zeolites (silicalite S-115, ALPO-5, and ZSM-5). During selective acetylene hydrogenation in a plug flow reactor at 10 atm, 80°C, and H₂/C₂H₂ given variously as 1.20, 1.39, and 1.50, they observed a steady decrease in activity over each catalyst. During this deactivation oligomers of molecular weights up to at least 200 g/gmole of composition 90% C₄ and 10% C₆+, corresponding to about 10% of the acetylene consumed, were observed in the gas phase products. The alumina supported catalyst exhibited the highest average oligomer molecular weight, while its activity decreased the least, casting some degree of doubt on the authors' contention that the accumulation of higher molecular weight oligomeric products caused the observed deactivation. They postulated that the lower average oligomer molecular weights observed during reaction over zeolite supported catalysts were due to the cracking activity of the zeolites.

Compared at equal weight hour space velocities, the order of activity was alumina > ZSM-5 > S-115 >> ALPO-5. However, since Pd dispersions were not measured it is unclear if this is a result of support modification of the Pd activity, or simply differences in the number of active Pd sites on each catalyst sample. It should be noted that Landau, et al (191) observed that the presence of strongly acidic proton centers on Pd-faujasite hydrogenation catalysts strongly increased the catalyst resistance to sulfur poisoning. They concluded
that this effect was due to the metal acquiring an electron-deficient character through interaction with electron-acceptor (H) centers, which hindered its reaction with electron-acceptor sulfur atoms.

In contrast to the observations of Sarkany, et al (143), Gigola, et al (192) observed that the specific activity of a series of 0.04 and 0.06 wt% Pd/α-Al₂O₃ catalysts, used in acetylene hydrogenation at industrial conditions (P = 15 atm), decreased by 1 order of magnitude as the catalyst dispersion increased from 10 to 76%. At the same time, catalysts of dispersions < 20% were very selective up to 95% acetylene conversion, while those of dispersions > 20% were selective only up to 20-30% conversion. Because the ethylene selectivity was high on catalysts of low dispersions, they concluded that the higher activity shown was not due to the formation of a β-phase Pd-hydride. In addition, the lack of any decrease in catalyst activity during operation led them to conclude that differences in the formation of surface polymers on samples of different dispersions was not a likely explanation for these trends either. They concluded that changes in the strength of acetylene complexation with changing dispersion might play an important role, though they left this role unspecified. In addition, they suggested that the possible existence of higher local temperatures at the surface of small metal crystallites than the bulk measurements in exothermal reactions (193) might have caused a change in the thermodynamic factor of selectivity control and led to the subsequent selectivity breakdown. We have investigated this behavior in more detail (Appendix C, p. 520) and tentatively conclude that Pd deposition throughout the support pellets in the high dispersion samples led to
acetylene pore diffusion control. Rapid ethylene hydrogenation then led to nonisothermal conditions in the pellets and subsequent reaction runaway.

Yajun, et al (194) studied acetylene hydrogenation over a series of 0.033 to 0.045 wt% Pd/Θ-Al₂O₃ catalysts at industrial conditions (T = 30-85°C, P = 5 atm (\(\theta\)), 0.38-0.42% C₂H₂, 82-83% C₂H₄, 16-17% C₂H₆, and \(H₂/C₂H₂ = 1.5-4.0\). They observed an induction period during which the conversion of acetylene increased from essentially zero to nearly 100%, lasting approximately 100 hours. After this induction period the conversion, and hence acetylene hydrogenation activity, decreased almost linearly with time until the experiment was terminated after 800 hours operation. Both the induction period and subsequent deactivation were accompanied by a significant rate of heavy polymer production (4 X 10⁻⁴ g per gram catalyst per hour (figure 10)).

After 600 hours operation, a 0.035 wt% Pd catalyst contained 0.385 g polymer per gram catalyst (corresponding to 40.5% heavy polymer retention), while its surface area had decreased to only 7.2% of the original value. Lighter polymers, such as C₄ olefins and diolefins, and various C₆ species, were observed in the gas phase. The structure of heavy polymer from several catalyst samples was investigated by a number of techniques, including NMR (table 3).
Figure 10. Dependence of Acetylene Conversion and Polymer Formation Rate on Operation Time. 0.035 wt% Pd/alumina. $T = 35-40^\circ C$ (194).
Table 3. Reaction Conditions and the Structure of Liquid Polymer (194).

<table>
<thead>
<tr>
<th>Reaction Conditions and Analytical Data</th>
<th>Sampling Localities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Side Stream A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>C2-037</th>
<th>C2-037</th>
<th>C31-1A</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of Catalyst Bed</td>
<td>single</td>
<td>single</td>
<td>double</td>
</tr>
<tr>
<td>Operating time, hr.</td>
<td>427</td>
<td>after 5300</td>
<td>regenerated in operation</td>
</tr>
<tr>
<td>in operation after 1 yr. op.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Space vel., hr⁻¹</th>
<th>3000</th>
<th>2000-3000</th>
<th>2000-4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tₐ₀, °C</td>
<td>55</td>
<td>45-55</td>
<td>29</td>
</tr>
<tr>
<td>Tₘ, °C</td>
<td>85</td>
<td>75-85</td>
<td>63</td>
</tr>
<tr>
<td>H₂/C₂H₂, molar ratio</td>
<td>3.5-4</td>
<td>3.5-4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

2. Structure and properties of polymer

<table>
<thead>
<tr>
<th>Specific Gravity</th>
<th>0.821</th>
<th>0.823</th>
<th>0.826</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. of distill., °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Point</td>
<td>161</td>
<td>264</td>
<td>232</td>
</tr>
<tr>
<td>10% Distilled</td>
<td>197</td>
<td>277</td>
<td>245</td>
</tr>
<tr>
<td>20% Distilled</td>
<td>219</td>
<td>285</td>
<td>260</td>
</tr>
<tr>
<td>40% Distilled</td>
<td>246</td>
<td>298</td>
<td>291</td>
</tr>
<tr>
<td>60% Distilled</td>
<td>264</td>
<td>310</td>
<td>300</td>
</tr>
<tr>
<td>80% Distilled</td>
<td>296</td>
<td>326</td>
<td>310</td>
</tr>
<tr>
<td>End Point</td>
<td>304</td>
<td>346</td>
<td>323</td>
</tr>
<tr>
<td>Mean Molecular Wt.</td>
<td>196</td>
<td>220</td>
<td>231</td>
</tr>
<tr>
<td>C/H wt. ratio</td>
<td>6.44</td>
<td>6.45</td>
<td>6.48</td>
</tr>
<tr>
<td>Mean Formula</td>
<td>C₁₄H₂₆.₃</td>
<td>C₁₅H₂₉.₅</td>
<td>C₁₆.₇H₃₀.₉</td>
</tr>
<tr>
<td>General Formula</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMR Data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatic-H/alkyl-H</td>
<td>0.016</td>
<td>0.008</td>
<td>0.007</td>
</tr>
<tr>
<td>Olefinic-H/alkyl-H</td>
<td>0.12</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>α-olefinic-H/internal olefinic-H</td>
<td>0.25</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>Branchiness Index</td>
<td>0.28</td>
<td>0.30</td>
<td>0.28</td>
</tr>
</tbody>
</table>
B. The Formation of \( \text{C}_4 \) and Higher Hydrocarbons

As discussed in the previous section, the hydrogenation of acetylene produces not only ethylene and ethane, but also \( \text{C}_4 \) and higher (\( \geq \text{C}_{22} \)) oligomeric products (63, 109, 142, 194-196). This is very undesirable, not only because ethylene is the desired product of the reaction, but also because the build-up of these products on the catalyst surface appears to be related to, and perhaps responsible for, observed decreases in catalyst activity (37, 38, 67, 70, 72-74, 86, 89, 94, 110-112, 138, 142, 190, 194, 197, 198), selectivity (70, 109, 132, 136-139, 197), or both, perhaps by blocking surface sites and/or increasing the surface hydrogen concentration. It is therefore important to develop an understanding of the reaction mechanism which forms these products so that it may be suppressed. The general phenomenon of catalyst deactivation by coke formation is, however, well known (199-206) and will not be considered here.

In a study of acetylene hydrogenation over Ni catalysts, Sheridan (67) proposed a free radical mechanism for the polymerization of acetylene to \( \text{C}_4 \) and higher hydrocarbons, which has since been referred to as the Sheridan Mechanism (figure 11). He chose to represent adsorbed ethylene, which was not observed to polymerize, as species (I). Adsorbed acetylene was represented as species (II) and (III), although species (III) was assumed to be unable to form in the absence of hydrogen. Species (III) is the precursor to \( \text{C}_4 \) formation, as shown in (IV), and would explain the absence of acetylene polymerization in the absence of gas phase hydrogen (67, 194). An identical mechanism was
proposed by Bond and Sheridan (207,208) for polymerization during the hydrogenation of methylacetylene and allene.

![Chemical structure](image)

Figure 11. The Sheridan Polymerization Mechanism (67).

Bond and Wells (86) assumed this mechanism for the formation of \( C_4 \) products during acetylene hydrogenation over Pd catalysts, and further postulated that adsorbed acetylene dimerized in this way to form adsorbed 1,3-butadiene which could then either desorb or undergo hydrogenation to a butene or \( n \)-butane. They made this conclusion because the distribution of \( C_4 \) products was consistent with that observed during 1,3-butadiene hydrogenation over Pd (118-120). The results of Young, et al (120) for this reaction (table 4) compare well with the \( C_4 \) distribution observed by Bond and Wells (p 14, or (86)). Distributions over Pd-BaSO\(_4\) were very different than those over Pd alone due to the high activity of BaSO\(_4\) for butene isomerization (120). The low values of the cis/trans ratio observed led Bond and Wells (86) to assume that the packing of acetylene on the Pd surface was more likely
Table 4. Composition of Butenes Obtained From Partial Hydrogenation of Butadiene in 95% Ethanol (120).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. °C</th>
<th>% Hydrogenation</th>
<th>% 1-butene</th>
<th>% trans-2-butene</th>
<th>% cis-2-butene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-12</td>
<td>68</td>
<td>72.1</td>
<td>18.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Pd</td>
<td>-12</td>
<td>50</td>
<td>48.5</td>
<td>40.1</td>
<td>11.4</td>
</tr>
<tr>
<td>Pd-BaSO₄</td>
<td>28</td>
<td>55-75</td>
<td>5.0</td>
<td>67.5</td>
<td>25.7</td>
</tr>
<tr>
<td>Pd-BaSO₄</td>
<td>-8</td>
<td>78</td>
<td>6.0</td>
<td>75.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>55-75</td>
<td>21.5</td>
<td>61.0</td>
<td>17.5</td>
</tr>
</tbody>
</table>

that represented by (A) in figure 12 rather than (B), which would yield predominantly cis-2-butene upon hydrogen addition on the surface.

![Diagram](image)

Figure 12. Acetylene Packing and Dimerization on Pd (86).

McGown, et al (109) have also proposed that the Sheridan Mechanism accurately describes the behavior they observed, although they concluded that while the staggered packing of acetylene on the surface, (A) in figure 13, was the favored arrangement at low acetylene coverages, at complete acetylene coverage the arrangement shifted to a closer packing geometry (B). They reached this conclusion based upon the results of experiments which showed that the production rate of cis-2-butene increased significantly at the point where acetylene zero order behavior begins. However, this rate then decreased at higher acetylene
pressures, as did the production rates of trans-2- and 1-butene, with a correspondingly large increase in the rate of 1,3-butadiene production, which does not support this conclusion. They also concluded that this increase in 1,3-butadiene production was due to an increasing intensity of acetylene bombardment on the surface, which displaced the butadiene molecules before they had time to hydrogenate.

![Acetylene Packing on Pd (109)](image)

Figure 13. Acetylene Packing on Pd (109).

Margitfalvi, et al (135) reported that over Pd-black catalysts the cis/trans ratio was greater than 1, perhaps indicating a different, more compact, surface packing arrangement in this case.

It must be emphasized that the free radical precursors of acetylene polymerization as proposed in the Sheridan Mechanism have not yet been directly observed by any method, spectroscopic or otherwise. The fact that acetylene polymerization in the absence of gas phase hydrogen has been observed by Taylor, et al (90,91), Altham and Webb (209), and Al-Ammar and Webb (110-112) could be taken as evidence that this species is not necessary for polymerization to occur. However,
Yajun, et al (194) have observed that polymerization is negligible in the absence of hydrogen (only 0.00034% of the total C₂ fraction after 354 hours, versus 0.01 to 0.02% in its presence), while Bryce-Smith (210) has observed that although a wide variety of acetylenic compounds, such as phenylacetylene and 1-octyne, polymerized readily over Pd, acetylene itself was a poison. Still, the possibility remains that surface hydrogen produced by the dissociative adsorption of acetylene could be active to form the free radical.

At temperatures higher than 400°C acetylene undergoes rapid free radical polymerization and condensation reactions (62,211,212). The activation energy is generally about 40 kcal/mole. The products of this homogeneous reaction are mainly aromatic (principally benzene, but styrene, naphthalene, anthracene, toluene, biphenyl, xylenes, and manner others have been detected (62,211)).

LeViness, et al (138) reported that in the absence of gas phase CO, 1,3-butadiene is the predominant initial product, although 1-,trans-2- and cis-2-butenes, and n-butane were also produced initially. With decreasing acetylene pressures, butadiene is rapidly hydrogenated to mainly 1-butene, with smaller increases in the other C₄ species. Weiss, et al (139) reported similar C₄ product distributions formed in the presence of 800 ppm CO, although 1,3-butadiene was not completely hydrogenated until much lower acetylene pressures had been reached and n-butane was not observed at all. Similar C₄ distributions have been reported by Webb (115).

Sarkany, et al (141,142) investigated the composition of the total gas phase oligomeric products (table 5). From these data, it appears
that the polymer is some 10 times more likely to desorb than to undergo further acetylene addition. This may not actually be the case, as they also report substantial surface polymer formation (table 6), and we

Table 5. C₄⁺ Product Distribution (141).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>time on stream (hrs.)</th>
<th>C₄</th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mol%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/γ-Al₂O₃</td>
<td>97</td>
<td>86.3</td>
<td>11.9</td>
<td>1.8</td>
<td>0.02</td>
</tr>
<tr>
<td>ICI-38-1</td>
<td>95</td>
<td>87.7</td>
<td>10.3</td>
<td>0.9</td>
<td>0.01</td>
</tr>
<tr>
<td>Pd/α-Al₂O₃</td>
<td>106</td>
<td>94.5</td>
<td>5.3</td>
<td>0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6. Amount of Surface Polymer (141).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time on Stream (hrs)</th>
<th>mg polymer/gₜₐₜ</th>
<th>Rate of polymer formation</th>
<th>Rate of polymer formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg polymer/gₜₐₜ</td>
<td>mg polymer/gₜₐₜ*hr</td>
<td>mg polymer/gₜₐₜ*hr</td>
</tr>
<tr>
<td>Pd/γ-Al₂O₃</td>
<td>12</td>
<td>3.68</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>10.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>227</td>
<td>36.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICI-38-1</td>
<td>140</td>
<td>17.13</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Pd/α-Al₂O₃</td>
<td>150</td>
<td>6.17</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>95 at% Cu +</td>
<td>77</td>
<td>12.76</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>ICI-38-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

might conclude that the decrease in gas phase concentration observed with increasing carbon number may be due at least in part to an increase in surface retention, due to a simultaneous increase in boiling point with carbon number.
Bond (64) reported that over Ni/pumice catalysts operated at 200-250°C, acetylene hydrogenation yielded significant polymer production, including substantial amounts of C_{31} and higher compounds (table 7). It is important to note the identical amounts of both C_4 and C_6 compounds, which together made up only 50% of the total oligomeric products. This is clearly different from the results of Sarkany, et al (141,142), for although they only measured the gas phase products, we would expect essentially all of the C_6 species to vaporize and exist in the gas phase at the given reaction conditions. Exact reasons for this difference are not clear, but are likely due to the higher operation temperatures used by Bond (64) and the use of Ni vs Pd catalysts, as Sheridan (71) had previously shown that the formation of higher hydrocarbons was significantly greater over Ni than over Pd.

Table 7. Yields of Higher Hydrocarbons From Acetylene Hydrogenation Over Ni at 200 to 250°C (64).

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Approximate Percentage Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_4</td>
<td>25</td>
</tr>
<tr>
<td>C_5</td>
<td>2</td>
</tr>
<tr>
<td>C_6</td>
<td>25</td>
</tr>
<tr>
<td>C_7</td>
<td>2</td>
</tr>
<tr>
<td>C_8</td>
<td>5</td>
</tr>
<tr>
<td>C_9-C_14</td>
<td>7</td>
</tr>
<tr>
<td>C_{15}-C_{30}</td>
<td>17</td>
</tr>
<tr>
<td>C_{31}-C_x</td>
<td>17</td>
</tr>
</tbody>
</table>

In light of these results of Bond (64), those of Yajun, et al (194) (that significant amounts of very high molecular weight compounds may form on the catalyst surface), the catalyst weight increase observed
during continuous operation by LeViness, et al (138) and Sarkany, et al (141,142), and the \( \text{C}_4 \) composition studies described above showing the formation and presence of 1,3-butadiene (which is a low weight precursor and may undergo polymerization itself (213)), we must consider the possibility of polyacetylene production on the surface during acetylene hydrogenation.

Polyacetylene has been the focus of a great deal of recent attention (214-218) due to its ability to conduct electricity, particularly after doping with \( \text{AsF}_5, \text{SbF}_5, \text{ClO}_4, \text{PF}_5, \) or halides such as \( \text{Br}, \text{Cl}, \) and \( \text{I} \) (217). The formation of polyacetylene has been observed over catalysts such as both pure and fluoridated alumina (219,220), Co(II) and Ni(II) exchanged zeolites (221), various Ni and Co complexes (41), and homogeneous \( \text{Ti(OCH}_3)_4-\text{Al(C}_2\text{H}_5)_3 \) Ziegler-type catalysts (41,222, 223). We should note that \( \text{PdCl}_2 \) in acetic acid is also an active polyacetylene catalyst at 120\(^\circ\)C (41). The polymer may exist as all-cis, all-trans form, or some mixture of the two. Ito, et al (222) observed the formation of all cis-polyacetylene during polymerization at \( T \leq 78^\circ\)C, and all trans at \( T \geq 150^\circ\)C. The cis form isomerized to the trans between 75 and 115\(^\circ\)C (223). In the absence of hydrogen and oxygen, Ito, et al (223) observed the decomposition of polyacetylene between 325 and 420\(^\circ\)C, which yielded benzene, hydrogen, ethane, ethylene, propylene, butane, and a brown colored viscous liquid, although benzene was always the dominant product. In the presence of oxygen, polyacetylene reacted readily to form oxygenated material, even at low temperatures (222). In addition, it is not soluble in any known solvent (41,220,222).
At the present time experimental techniques successfully used to investigate its structure and properties, and perhaps to test for its presence in unknown samples, are resonance Raman spectroscopy (221,224,255), electron microscopy - either direct transmission or scanning - (222,223), IR spectroscopy (221,224), magic angle spinning (MAS) $^{13}$C NMR, various magnetic resonance methods (226), or direct measurement of electrical conductance (227) (which can be several orders of magnitude higher than those of other nonconducting hydrocarbons (41, 214-218)). These results show the difficulty that might be present in trying to identify small amounts of polyacetylene produced on a selective hydrogenation catalyst, and may explain why it could be produced under these conditions and yet not be observed during any previous investigations. The polymerization of acetylene to cyclooctatetraene has also been reported (228).

Although the selectivity of surface polymer formation from acetylene (the percentage of reacting acetylene forming surface polymers) has been reported by Sarkany, et al (141), there are several problems involved with these data. They report in the experimental section that the amounts of polymer formed corresponded to approximately 2% of the acetylene consumed, and were thus ignored in subsequent selectivity calculations. However, it appears that this number was arrived at by dividing the total amount of polymer formed in an experiment by the total amount of acetylene reacted in it. Since the authors observed no catalyst deactivation during aging, all acetylene consumption rates remained constant throughout each experiment. Yet it is equally apparent that the rate of surface polymer formation does
decrease with time, and substantially at that. Over 0.04 wt% Pd on γ-Al₂O₃, they report 3.68 mg polymer after 12 hours on stream (0.30 mg/hr average rate at 6 hours), 10.2 mg at 47 hours (0.19 mg/hr at 29.5 hours), and 36.3 mg at 227 hours (0.15 mg/hr at 137 hours). It appears that even if the overall selectivity to surface polymer is about 2%, in the very early stages of the reaction the value may be significantly higher.

In addition, the temperature at which the polymer data in table 6 were collected is not reported (141). If we assume a polymer production rate of 0.10 mg per gram catalyst per hour, and assume a mean polymer structure of \((C_2H_4)_n\), we calculate a rate of \(3.85 \times 10^{-6}\) moles per gram catalyst per hour. If we next assume the polymer measurements were conducted at 295 K, where the rate of acetylene consumption was \(1.39 \times 10^{-8}\) moles per gram catalyst per second, we find that selectivity for polymer formation is about 7% of the reacting acetylene. If we assume a higher temperature of 366 K, where the acetylene rate was \(5.01 \times 10^{-7}\), the surface polymer selectivity is only about 0.2%. Again, if we take a polymer accumulation rate of 0.30 mg per gram catalyst per hour, from table 6, we calculate the surface selectivity to be between 0.6 and 21%. Clearly, it would be very desirable to know which of these values is correct, for if the higher - 7 to 21% - values are accurate, much of the recent data on the selectivity values of acetylene hydrogenation in excess ethylene must be suspect. To the best of my knowledge all of these TGA experiments were conducted at 30°C (303 K), and hence the correct initial surface polymer selectivity is in the range 5-20%. 
Nair (229) measured the weight of various 0.04 wt% Pd on alumina catalysts before and after 60 to 400 hours of continuous acetylene hydrogenation; catalyst weight increased by 1.2-2.5%. However, it appears that the catalyst pellets were not dried before initial weight measurements, and the well known tendency for aluminas to adsorb water probably limits the usefulness of these data. Yajun, et al (194) observed that polymer on the catalyst surface reduced subsequent water adsorption by around 50%, so these values of 1.2-2.5% are very much minima, and the actual weight increases were probably higher.

Yajun, et al (194) reported that 0.01-0.02% of the C_2 fraction was converted to heavy polymers at industrial conditions. As the feed gas was about 0.4% acetylene, this yields an average surface polymer selectivity of 2.5-5%, assuming 100% acetylene conversion. However, as the rate of polymerization decreased with operation time, and the conversion of acetylene was always less than 100% (after several hundred hours it was less than 60%), the selectivity as defined here must have been significantly higher than this value.

Similarly, Derrien (33) reports a commercial reactor employing a feedstock with 1.0% acetylene would typically have about 0.03% oligomers in the gas phase at essentially 100% acetylene conversion, and concludes that the formation of oligomers is negligible (6-9% of the reacted acetylene formed gas phase oligomers, assuming they are predominantly C_4 and C_6 species). No quantitative information about the amount of surface polymer formed is reported, but the usual catalyst lifetime between regenerations is given as about 6 months. From the inlet composition and flow rate data, along with the reactor catalyst loading,
which are given, we can make several tentative calculations. If we assume that the catalyst must be regenerated when about 50% of the pores are plugged (after 6 months), the catalyst porosity is about 0.35, the mean density of the surface polymer is 0.8 g/cc, and the mean polymer formula is \((\text{C}_2\text{H}_4)_n\), we find that about 0.2% of the total reacted acetylene has formed surface polymers during the 6 months operation time. Once again, we might suspect that the rate of polymer formation on the surface decreases during operation, and thus this average selectivity to polymer would not be very representative of the actual reaction conditions, particularly during the initial period of operation.

In contrast to the results above, Weiss, et al (132) conducted solvent extractions of used 0.1 wt% Pd/Al\(_2\)O\(_3\) catalysts with heptene, and found no long chain polymer precursors present in detectable quantities (< 0.4–1.86 mg per gram catalyst). These catalysts were operated at 0°C and 3 to 5 atm total pressure for up to 700 hours. It is not at all clear why no surface polymers were detected, for we would expect no sharp decrease in polymer selectivity with decreasing temperature, and the increase in pressure should favor increased conversion to polymer. While there may not have been any significant amount of polymer formed, it seems more likely that either the polymer species present were not soluble in heptene (such as polyacetylene), or the analytical procedure employed to detect them was not appropriate (see Appendix B, p. 510).

One of the authors (190) has subsequently claimed that surface polymeric species were indeed observed during this heptene extraction (they were not (132)).
In many recent investigations of trace acetylene hydrogenation (132,137-142), the ratio of ethylene to acetylene in the feed stream is sufficiently high (34.5 in (138) to 290+ in (141)) that the production rate of ethylene cannot be measured accurately. In these cases, the consumption rate of acetylene consumption is measured, and the selectivities for all products other than ethylene are calculated from the rate of production of each and the acetylene consumption rate. As these selectivities are based on the molar rate of acetylene forming each product, and not the molar rate of production of each (eg. C4 selectivity is 2 times the rate of C4 production over the rate of acetylene consumption), if all species production rates are known, the selectivities should sum to 100%. Because the rate of ethylene production cannot be accurately measured, the selectivities of all other species are summed and subtracted from 100% to give the apparent ethylene selectivity.

The problem with data calculated in this way, which ignores the formation of surface polymers, should now be apparent. In addition, several earlier investigations (110-112,132) have even failed to include measurement of the gas phase polymerization products, although one of the authors had previously reported substantial C4 production (115). The total reported range of C4+ selectivities is 5-40%, but most investigations have found values of 20-40% (table 8), and most only included C4 species, as higher carbon numbered species were assumed to be negligible. Even in cases where the acetylene to ethylene ratio was low enough to measure the rate of ethylene production (85-88,110-112), ethylene selectivities calculated as the rate of ethylene production
over the rate of production of ethylene plus ethane may not be very meaningful, as 25-60% of the total products are ignored.

Similarly, Plante and Weiss (190) studied deactivation and oligomerization during high pressure (10 atm) acetylene hydrogenation. Ethylene was present in a 50:1 excess over acetylene, and while the production of oligomeric species was investigated, only those in the gas phase were collected.

Table 8. C₄ Selectivities Reported For Different Pd Catalysts (89).

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>SC₄</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 wt% Pd/pumice</td>
<td>20 - 30%</td>
<td>Sheridan (70)</td>
</tr>
<tr>
<td>10 wt% Pd/pumice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 mol% Pd/α-Al₂O₃</td>
<td>37%</td>
<td>Bond &amp; Wells (86)</td>
</tr>
<tr>
<td>ICI-38-3</td>
<td>5 - 20%</td>
<td>McGown, et al (109)</td>
</tr>
<tr>
<td>(0.04 wt% Pd/γ -Al₂O₃)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04 wt% Pd/γ -Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICI-38-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0.04 wt% Pd/α-Al₂O₃)</td>
<td>20 - 40%</td>
<td>Sarkany, et al (141)</td>
</tr>
<tr>
<td>Pd-Black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04 wt% Pd + X at% Cu/</td>
<td>18 - 40%</td>
<td>LeViness (89)</td>
</tr>
<tr>
<td>γ -Al₂O₃ (X=0,30,50,80,90,99)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The production of these species corresponded to a 9% selectivity for C₄ and 1% for C₆ and higher species. The build-up of surface oligomers was not investigated, in spite of the claim that they had previously observed such species. In addition, reported acetylene conversion,
product selectivity, and initial composition values often correspond to hydrogen conversions greater than 100%. Depending on the composition of the surface polymer, hydrogen consumption may be either greater or smaller than that calculated ignoring its formation. In this case, we might assume the hydrogen/carbon ratio is somewhat less than 2, so that hydrogen conversions will remain less than 100%.

These figures clearly show the importance of including the gas phase, and quite possibly also the surface, polymer production rates in order to close the overall material balance in all future acetylene hydrogenation studies, particularly as the presence of surface polymer is assumed to play an important role in catalyst deactivation and/or selectivity decline, and ethylene selectivities calculated ignoring these will be incorrect.

The data in table 8 may be contrasted to those in table 9, from the hydrogenation of methyl acetylene over various transition metal catalysts (230). Although it is not clearly stated in this work, it appears that these values represent gas phase polymerization products only, as no experimental details for the measurement of surface species are given. Although Pd catalysts were not employed in this work, from the order of these metals for decreasing polymer formation observed by Sheridan and Reid ((71), or p. 8), we would suspect Pd to exhibit a value of perhaps 5%. The large difference in the percent polymerization over Pd for acetylene vs. methylacetylene is not unreasonable in light of the likely structural inhibition of the polymerization of methylacetylene, compared to acetylene.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Propylene Selectivity</th>
<th>% Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-powder</td>
<td>95</td>
<td>0.52</td>
<td>1.0</td>
</tr>
<tr>
<td>Pt-powder</td>
<td>95</td>
<td>0.93</td>
<td>2.9</td>
</tr>
<tr>
<td>Pt-pumice</td>
<td>95</td>
<td>0.91</td>
<td>2.9</td>
</tr>
<tr>
<td>Ni-pumice</td>
<td>97</td>
<td>0.96</td>
<td>3.7</td>
</tr>
<tr>
<td>Ni-powder</td>
<td>75</td>
<td>0.85</td>
<td>3.7</td>
</tr>
<tr>
<td>Ir-pumice</td>
<td>95</td>
<td>0.79</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe-powder</td>
<td>179</td>
<td>0.96</td>
<td>7.6</td>
</tr>
<tr>
<td>Rh-pumice</td>
<td>55</td>
<td>0.93</td>
<td>10.0</td>
</tr>
<tr>
<td>Ir-powder</td>
<td>95</td>
<td>0.71</td>
<td>10.0</td>
</tr>
<tr>
<td>Co-powder</td>
<td>75</td>
<td>0.88</td>
<td>18.0</td>
</tr>
<tr>
<td>Cu-powder</td>
<td>173</td>
<td>1.00</td>
<td>46.9</td>
</tr>
</tbody>
</table>

All researchers who have observed the oligomerization of acetylene have assumed that the necessary prerequisite, regardless of the actual reaction mechanism chosen, is two neighboring adsorbed acetylene molecules. McGown, et al (109) investigated this dependence in a CSTR under conditions similar to those appearing in figure 4, and observed behavior which strongly support this conclusion (table 10). Values of \( n \), as defined in table 10, are generally very close to 2, indicating that two acetylene molecules must indeed be adsorbed on adjacent sites.

However, LeViness (89) has suggested that this may not always be the case. LeViness, et al (138) have reported that the addition of up to 80:20 atoms Cu/atoms Pd had no effect on the \( C_4^+ \) selectivity observed in the absence of gas phase CO. However, LeViness (89) also reports that these same catalysts showed a reduction in \( C_4^+ \) selectivity from 25-32% to 18-25% upon the addition of Cu in the presence of 800 ppm CO. Similarly, no abrupt change in \( C_4 \) selectivity was observed during the
Table 10. Dependence of the Rate of C₄ Production on the Surface Coverage of Acetylene at 343 K (109).

<table>
<thead>
<tr>
<th>Inlet gas composition</th>
<th>nᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ (%)</td>
<td>C₂H₄ (%)</td>
</tr>
<tr>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>35</td>
</tr>
</tbody>
</table>

ᵃRate of C₄ production = k(ΦC₂H₂)^n

transition to acetylene pore diffusion controlling conditions in the absence of CO, as would be expected from the data of McGown, et al (109). As McGown, et al (109) conducted the experiments shown in table 10 in the presence of CO, LeViness (89) has suggested that in the absence of CO acetylene oligomerization may proceed through the interaction of gas phase or physisorbed acetylene with a dissociatively adsorbed or surface free radical acetylenic species. The data are presently inconclusive.

Based upon the small amounts of branched polymerization products observed (67,194), it appears that acetylene addition to surface species occurs mainly at chain ends, perhaps by insertion into an existing Pd-C bond, while internal C-C bonds, including the olefinic bonds observed by McGown, et al (109), Sarkany, et al (142), and Yajun, et al (194), cannot participate in subsequent additions to a great extent. We might agree with Yajun, et al (194), that α-olefins present the greatest possibility of further polymerization. Surprisingly, the α-olefin
present in the greatest concentration, ethylene, has never been observed to participate in the surface polymerization reaction \(109,134,135,141\), in spite of its well known tendency to polymerize rapidly and poison Pd and other transition metal catalysts in the absence of acetylene \(106,107,231-241,656\). Yajun, et al \(194\) report that polymer was also formed from ethylene, but give no details about the method used to determine this or the percentage formed from ethylene.

The effects of CO on the amount, structure and resulting properties of the oligomeric products formed are at present poorly understood. Of course, carbonyl groups and carboxylic acids, which McGown, et al \(109\) and Sarkany, et al \(142\) have observed in the products of acetylene oligomerization in the presence of CO, cannot exist in oligomers formed in its complete absence. The question of whether ethylene/acetylene mixtures produced from feed gas pyrolysis can ever be truly free of CO may well be worthy of consideration, particularly if polymer produced in its supposed absence are found to contain carboxylic acids or other oxygenated species.

The extent of deactivation produced by a specific amount of polymer is higher for polymers produced in the presence of CO. While all authors studying acetylene hydrogenation in the absence of CO over catalysts containing > 1% Pd have observed substantial activity declines (from 2.5 to 20 times lower than initial activities \(70,86,110-112,135\)) only Yajun, et al \(194\) and Plante and Weiss \(190\) have reported an activity decline over catalysts containing < 0.35% Pd, although they operated at higher pressures than all other studies except those of Weiss, et al \(132\) and Gigola, et al \(192\). In addition, it is not at
all clear that the industrial feedstocks used by Yajun, et al were at least nominally free of CO.

In the presence of gas phase CO, McGown, et al (109), LeViness (89), Weiss, et al (139) and Sarkany, et al (141,142) have reported substantial catalyst deactivation on 0.04% Pd catalysts. Sarkany, et al (141) reported that polymer loadings as high as 36.3 mg per gram catalyst formed in the absence of CO caused only an ethylene selectivity decline, while Sarkany, et al (142) reported that polymer loadings of 29 mg per gram catalyst formed in the presence of CO caused an activity decline of about 75%, but did not substantially effect the product distribution pattern. This greater sensitivity to polymer formed in the presence of CO may be due to the presence of carbonyl groups, perhaps through the formation of surface carboxylates which might be able to compete favorably with acetylene for surface adsorption sites, as proposed by Sarkany, et al (142).

The reason for difference between catalysts of low versus high Pd loadings in the absence of CO (constant activity versus deactivation) is currently unknown, but is most likely directly related to the differences in Pd/support ratios and/or changes in the metal crystallite size - dispersion - with the same.

Moses, et al (136) reported that on used catalysts showing lowered ethylene selectivities, 1/2 hour oxidation at 200ºC prior to reduction was sufficient to restore the ethylene selectivity to its initial value. Sarkany, et al (141) reported that in flowing air, "most" of the polymer, as measured by TGA, was removed between 120 and 400ºC. Differential Scanning Calorimeter (DSC) measurements showed an
endothermic peak in the 30 to 120°C range and a strongly exothermic peak between 240 and 360°C, which they felt represented oxidation of the surface species. Although the time scales of these TGA and DSC experiments were not reported, it seems likely that the treatment described by Moses, et al (136) may not be sufficient to remove all of the polymer from the catalyst surface. The question of why this treatment was then sufficient to restore the ethylene selectivity deserves consideration. Sarkany, et al (141) also reported that treating the catalyst with up to 200 mg C₁₆ paraffin per gram catalyst had no effect on either the rate of acetylene consumption or the various product selectivities.

We might therefore conclude that the decrease in ethylene selectivity is caused by either an unknown species of surface polymer (which would cause a decrease in ethylene selectivity when put on fresh catalyst samples) which is destroyed in oxygen at 200°C, or an unknown species, although possibly a paraffin in this case, that increases the rate of ethylene hydrogenation due to its precise location on the catalyst surface. This location must then allow for its rapid oxidation at the conditions reported by Moses, et al (136). In this latter case, the area of the Pd-alumina interface would seem to best explain the above observations, and might further support the proposed role of polymer assisted hydrogen migration to the support in the observed ethylene selectivity decline (137-142).

In contrast to the above results, Sokol'skii and Ualikhanova (242) observed that while colloidal Pt and Pd catalysts were stable in the hydrogenation of 1-, 2-, and 3-hexynes, the catalyst activity for
hydrogenation of the resulting alkene gradually decreased during operation. The net result was an increase in alkene selectivity.

During dehydrocyclization of n-heptane and n-hexane over Pt/Al₂O₃ catalysts Lietz, et al (243) observed that only the small fraction of the total carbonaceous residue located on, or in the immediate vicinity of, Pt particles causes deactivation. This fraction could be burned off during oxygen treatment, restoring the initial catalyst activity. The majority of the surface species, located on the alumina support away from Pt had no influence on activity and was only oxidized slowly at conditions where the harmful species was completely removed. Similarly, Fujimoto, et al (244) observed that coke on Ni-Mo/SiO₂-Al₂O₃ hydrocracking catalysts is burned off at much lower temperatures in the presence of Pt, which promoted oxygen spillover to the catalyst surface.

It should be noted that Amariaglio, et al (245) have challenged the interpretation that oxygen treatment improves catalytic activity by burning off carbonaceous residues. These authors observed a strong activation in ethylene hydrogenation induced by pretreatment of Rh ribbons with oxygen/helium mixtures which was not dependent on the oxygen content but increased with both the length and temperature of pretreatment. They concluded that the main variable in this activation was the flux of oxygen back-diffusing to the Rh surface during subsequent reduction by hydrogen or the reactant mixture.

While this may be true, it appears that they confused two different effects which can independently increase catalyst activity during oxygen treatment. There is simply too much evidence, including that presented in this section, that oxygen treatments can and do remove
carbonaceous residues that poison the surface activity to conclude that this is not possible. However, at the same time there is evidence that moderate temperature oxygen treatment can redisperse a sintered metal catalyst (246-248), apparently by stress induced deformations caused by the change in lattice parameter upon going from the metal to the metal oxide. Similarly, ion bombardment can increase the "roughness" of metal single crystals and films (249,250). Both of these treatments create more active sites by increasing the percentage metal exposed (dispersion) and thus increase catalyst activity. These treatments can be reversed by high temperature hydrogen treatment (sintering) of supported catalysts (246-248,251-252), or high temperature annealing of films (96,249,250). It seems likely that such an effect was observed in this work, but that in no way invalidates the residue removing enhancement of oxygen treatment on other catalysts.

Sarkany, et al (253) studied the formation of carbonaceous deposits on Pt and Pt-Sn catalysts formed during methane, n-hexane, 1-hexene, 1,5-hexadiene, and benzene adsorption at 573-773 K. Strongly bonded, partly dehydrogenated hydrocarbon species, which they referred to as "DP-1", formed in 45 to 120 minutes at 573 K from all hydrocarbons and could only be removed by hydro-desorption in the temperature range 653 to 723 K. DP-1 was regarded as the main precursor to coke formation. At temperatures greater than 663 K, two new types of unreactive deposits appeared, referred to as "DP-2" and DP-3". DP-2 formed from all hydrocarbons, but DP-3 was not formed from methane. The authors concluded that DP-2 represented coke formed on the metal surface or in the vicinity of the metal support interface, while DP-3
represented coke present on the support. Sarkany (254) has investigated this behavior in more detail using Pt-black samples placed in a microbalance, and described the effect of irreversibly adsorbed hydrocarbons and the surface hydrogen availability on the various product selectivities during n-hexane conversion.

Hegedus and Petersen (255) proposed that during cyclopropane hydrogenation over Pt/Al₂O₃ catalysts support hydrogen was depleted to some extent by reaction with adsorbed hydrocarbons, creating a concentration gradient away from Pt islands on the surface. The reduced hydrogen concentrations promoted the formation of carbonaceous deposits around the Pt particles and accelerated spillover to the support, further reducing the hydrogen concentration in the region of the Pt-support interface. This caused further deposit formation and finally complete deactivation as the active surface was covered with hydrogen deficient, strongly sorbed carbonaceous residues.

Frusteri, et al (256) observed the self-regeneration of deactivated Pt/Al₂O₃ reforming catalysts by the hydrogenation of surface residues with hydrogen previously spilt over to the support. The presence of Cl on the support was a prerequisite for this spillover. The concentration of support hydrogen, and thus the extent of regeneration, was maximized by a Cl content of 0.5%.

Niemantsverdriet and van Langeveld (257) recently investigated the formation of coke on Pt, Ir and Rh foils during exposure to ethylene at temperatures between 325 and 775 K. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) indicated the presence of four different types of surface carbonaceous deposits: molecular,
carbidic, amorphous, and graphitic. At 325 K, the deposits consisted mainly of molecular forms, which the authors felt was consistent with ethylidyne formation. However even at this temperature graphitic or amorphous carbon was present on all samples. The relative amounts of each type of species was discussed in terms of the known catalytic behavior of each metal.
C. The Adsorption of Acetylene and Ethylene on Transition Metals

The reaction mechanism proposed by Bond and Wells (85-88) for acetylene hydrogenation appears in figure 14. They observed complete surface monopolization by acetylene, so that ethane was only formed directly from it. No ethylene hydrogenation was observed prior to the reaction acceleration point (see p. ), although $^{14}$C labeling was not conducted. It should be noted that these authors observed a decrease in catalyst activity, and a significant increase in ethylene selectivity, upon catalyst aging (77,86).

\[
\begin{align*}
H_2(g) + 2(\ast) & \iff 2H \\
C_2H_2(g) + 2(\ast) & \iff HOC=CH \\
HOC=CH + H_2 & \iff HC=CH_2 + H \\
HOC=CH + H & \iff HC=CH_2 + (\ast) \\
HC=CH_2 + H & \iff H_2C=CH_2 + 2(\ast) \iff C_2H_4(g) + 3(\ast)
\end{align*}
\]

Figure 14. Acetylene Hydrogenation Mechanism (85-88).

McGown, et al (108,109) proposed that the selectivity is controlled by the relative number of 2 types of surface sites, one on which either acetylene or ethylene may adsorb, but on which acetylene is adsorbed some 2200 times stronger than ethylene; the other on which only ethylene may adsorb.
Al-Ammar and Webb (110-112) have proposed that 3 types of surface sites are involved in this reaction, one on which acetylene is hydrogenated to ethylene, one on which acetylene is hydrogenated to ethane, and third on which ethylene is hydrogenated to ethane. They proposed that the selectivity is controlled by the hydrogen availabilities at each type. Catalyst activity, they concluded, is related to the proportion of dissociatively adsorbed acetylene which exists on the surface as the M–C\textsubscript{2}H\textsubscript{x} species, originally proposed by Thomson and Webb (102).

Weiss, et al (132-142), on the other hand, tended to agree with the above mechanism of Bond and Wells, expanding it to the one appearing in figure 15. They also concluded that ethylene selectivities decline due to polymer assisted hydrogen migration to the alumina support, where it may react with adsorbed ethylene to form ethane (137-142).

There is adsorption and spectroscopic evidence supporting each of these theories.

Eischens and Pliskin (258) have presented a large body of IR spectra of adsorbed molecules, for hydrocarbons principally on silica supported Ni. During ethylene adsorption on bare Ni, they observed spectra characteristic of H\textsubscript{2}C–CH\textsubscript{2}, H\textsubscript{2}C-CH, and in some cases a surface carbide. However, during adsorption on a hydrogen precovered surface, spectra suggested mainly the associatively adsorbed species, H\textsubscript{2}C–CH\textsubscript{2}. In both cases, the spectra indicated that most species were saturated, although the H/C ratio was low; carbon atoms were bonded to multiple metal sites. All species could be hydrogenated to adsorbed alkyl radicals, H\textsubscript{2}C–CH\textsubscript{3}, at 35°C and 1/2 atmosphere hydrogen, although there
was some evidence that the associatively adsorbed species could be hydrogenated at lower hydrogen pressures than the more dehydrogenated species.

![Chemical Reaction Diagram]

**Figure 15. Acetylene Hydrogenation Mechanism (134).**

Similar spectra were observed during acetylene adsorption on both hydrogen precovered and bare Ni at 35°C. Ethyl radicals formed over bare Ni were assumed to be produced from acetylene self-hydrogenation, supported by the coexistence of a surface carbide phase. Evidence suggesting the surface polymerization of both acetylene and ethylene, most likely forming adsorbed butyl groups, \( \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \), was also observed. Nash and DeSieno (259) also found evidence for saturated species from IR spectra during acetylene adsorption on Ni powders produced from electrically exploded wires, as did Sheppard and Ward (260) during acetylene adsorption on silica supported Pt and Ni. Both surface carbide and adsorbed butyl species were observed, although the extent of both was greater on Pt than Ni.
Morrow and Sheppard (261) found IR evidence of both associative and dissociative adsorption of ethylene on Ni and Pt, and the formation of surface carbides, although these were easily hydrogenated to ethane on Pt. They observed no evidence for $\pi$-bonded species, as envisioned by Bond and Wells (86).

Little, et al (262) observed the existence of both olefinic and saturated species upon ethylene adsorption on silica supported Ni, Cu, and Pd. However, upon acetylene adsorption on Pd, only olefinic species were observed. They interpreted this result, in agreement with Eischens and Pliskin (258), as a suggestion that self-hydrogenation, which must occur to give rise to saturated species, occurs more readily on Ni than on Pt, and by implication does not occur at all during acetylene adsorption on Pd. Kojima, et al (263) also reported the dissociation of ethylene upon adsorption on Pd(ll1) at 295 K, while acetylene adsorption was mainly nondissociative. More recently, Hasse, et al (264) observed that although ethylene adsorbed dissociatively on Ni(ll1) at low pressures (less than 1/2 monolayer coverage), at higher pressures (coverages) self-hydrogenation with hydrogen previously dissociated from adsorbed ethylene became important. Many of these investigations are included in the reviews by Little (265,266).

The reviews of Bond and Wells (79) and of Bond (267) present other early evidence for their choice of representing adsorbed ethylene and acetylene as $\pi$-bonded rather than di-$\sigma$-adsorbed species. This conclusion is further supported by the results of Soma (268) from low temperature (195 K) IR spectra of ethylene adsorption on alumina supported Pt, Pd, and Rh.
Chesters, et al (269) reported that a \( \pi \)-complex formed during ethylene adsorption on Pd(110) at 110 K, although they also observed a small amount of di-\( \sigma \)-adsorbed species. Demuth and Eastman (270) observed both \( \pi \)- and \( \sigma \)-orbital shifts during acetylene and ethylene adsorption on Ni(111), while Demuth (271) observed a \( \pi \)-bonded structure over Pd(111) and Pt(111) at low temperatures (\( T \leq 180 \) K) which rehybridized upon warming to room temperature to a surface complex involving both \( \pi \) and di-\( \sigma \)-adsorption bonds to the surface. In a study of hydrogen diffusing through a Pd membrane to react with adsorbed ethylene and acetylene, Zubarev, et al (272) observed ethane formation from acetylene by a reversibly adsorbed ethylene \( \pi \)-complex intermediate. Ito, et al (273) observed changes in bond hybridization, from sp to sp\(^2\) for acetylene and from sp\(^2\) to sp\(^3\) for ethylene, upon adsorption on Pd, and concluded both di-\( \sigma \)- and \( \pi \)-bonded structures exist on the surface. In addition, they found that most of the adsorbed acetylene remains associatively adsorbed, while only a small amount actually dissociates. Kojima, et al (274) found that while ethylene adsorbed dissociatively, at room temperature the adsorption of acetylene was mainly associative on various Pt surfaces. The Pt(211) surface was particularly active in promoting ethylene polymerization due to an increased rate of formation of ethyl radicals.

In a study of \(^{14}\)C ethylene adsorption and hydrogenation on Ni films, Thomson and Wishlade (275) found that some preadsorbed ethylene participated in subsequent hydrogenation reactions, while the remainder was unreactive and strongly retained. They postulated that ethylene is immobile after chemisorption, as observed by Arthur and Hanson (276)
during Field Emission Microscope (FEM) studies of Ir surfaces, and that
certain crystal faces are inactive for hydrogenation.

Taylor, Thomson and Webb found similar results on alumina
supported Pd, Pt, and Rh catalysts (90,91), as did Inoue, et al, on Pd foil (96,263,277), Gentle and Muetterties on Pd single crystals (278),
and Altham and Webb (209) during $^{13}$C ethylene and tritium tracer studies
on alumina and silica supported Pt. These authors also found evidence
suggesting that hydrogen migration between the metal and the support is
of importance in this reaction system.

The previously discussed results of Al-Ammar and Webb (110-112)
and the static capacitor technique studies of Dus and Lisowski (279,280)
are also strong evidence for the simultaneous existence of at least two
types of adsorbed ethylene on platinum metals. Frolov and Novikova
(281) have also reported an apparent inhomogeneity of active sites
during the hydrogenation of cyclopentadiene/isoprene mixtures over
Pd/Al$_2$O$_3$ catalysts. Siegel, et al (282) have modeled the surface of
platinum metal catalysts during reactions between hydrogen and various
hydrocarbons assuming three different types of surface sites,
differentiated by the coordinative unsaturation of each type. Similar
conclusions have been reached by Ledoux (283).

Dalmai-Imelik and Massardier (284) have reported that for ethylene
hydrogenation, the Ni(100) face was inactive, while the activities of
the Ni(111) and Ni(110) faces differed by a factor of two. The rate of
benzene hydrogenation, however, was not significantly different on the
three faces, even though the type of adsorption was not the same on each
face. More recently, Massardier, et al (285) observed that although the
butadiene hydrogenation selectivity for butenes was nearly equal to one on both the Pd(111) and Pd(110) crystal faces, the more open Pd(110) face was one order of magnitude more active. Smith, et al (286) found that CS₂ caused a linear decrease in the rate of (+)-apopinene hydrogenation on silica supported Pt and Pd catalysts. The number of CS₂ molecules required to completely poison the catalyst was always less than the number of surface atoms and correlated well with the number of edge sites.

Kojima, et al (250) studied the damage produced by argon ion bombardment and the elimination of this damage by thermal annealing of a Pt surface used in acetylene adsorption and hydrogenation. The temperature region in which surface defects along the [110] zone through the (100), (311), (211) and (111) planes disappeared (473 to 573 K) was identical with that at which the catalyst activity for acetylene decreased drastically. The authors concluded that surface vacancies, displaced atoms, or their assemblies around the [110] zone form the catalytically effective sites for the reaction. Similarly, Poppa and Soria (249) found the annealing to about 600 K drastically reduced the adsorption of CO and H₂ on Pd(111), while low-dose argon ion bombardment introduced surface imperfections which restored a high adsorption probability.

Muettterties, et al (287) exposed acetylene adsorbed on Pt(111) and Pt(100) surfaces to hydrogen pressures of 10⁻⁷ - 10⁻¹¹ torr in the temperature range 20 to 135°C. On Pt(100) the net reaction was hydrogen exchange, whereas on Pt(111) the only reaction was hydrogenation. This difference was discussed in terms of the topographical differences
between the two surfaces. Recently Tamaki and Imanaka (150) observed a steep increase in catalyst activity and selectivity with increasing film thickness of a thin Pd film. At the same time, the intensity of the Pd(111) XRD intensity decreased and the Pd(220) intensity increased steeply. Van Strien and Nieuwenhuys (288) found that both C-H and C-C bond breaking during ethylene adsorption and decomposition on Pt surfaces occurred easiest (at a lower temperature, or at a faster rate at equal temperatures) on the Pt(210) and Pt(110) faces, followed by the stepped Pt(533) face and finally the close packed Pt(111) face.

In 1969, Morgan and Somorjai (289) first found evidence for the formation of ordered surface structures during ethylene and acetylene chemisorption on Pt(100) and Pt(111) single crystals using Low Energy Electron Diffraction (LEED) analysis. Similar results have been reported by Freyer, et al (290) during acetylene and ethylene adsorption on Pt. The formation of these ordered structures and their effects on metal catalysis have been reviewed by Somorjai (291–294). Davis, et al (295) have found that disordered carbonaceous deposits formed from hydrocarbons on a series of Pt single crystals acted as non-selective poisons which block surface sites from incident reactant molecules, store and exchange hydrogen with reactant surface species, and provide desorption sites for product molecules.

In 1979, Somorjai, et al (146) first found evidence, by LEED investigations, for the existence of the ethylidyne species during both acetylene and ethylene adsorption on Pt(111) single crystals, although in an earlier study (296) they observed acetylene attachment to three metal atoms during adsorption, as had Fischer and Kelemen (297) on both
Pt(111) and Pd(111), but neither group was able to identify its structure. They suggested that the vinylidene species, $\text{C}=$CH$_2$ (observed by Eley (298) upon ethylene adsorption on Ni) was the intermediate structure of both acetylene and ethylene reactions to form ethylidyne. These results were confirmed during adsorption and thermal desorption studies on Pt(111) by Salmeron and Somorjai (299).

Davis, et al (300) have also studied the subsequent role of this ordered ethylidyne structure during ethylene hydrogenation on Pt(111). Ethylidyne produced during adsorption between 300 and 400 K was stable with respect to hydrogenation at room temperature, while at atmospheric hydrogen pressure and temperatures above 350 K it was easily removed from the Pt surface by hydrogenation. During ethylene adsorption above 450 K, both active and inactive forms of partially dehydrogenated carbonaceous deposits were formed. The inactive forms showed much lower activity for hydrogenation of ethylene and hydrogen transfer to reactant molecules, and increased with increasing adsorption temperature as the surface became progressively more hydrogen deficient. A similar loss of activity with decreasing hydrogen content in surface carbonaceous residues was reported by Mardaleishvili and Rapoport (301) during acetylene cyclotrimerization to benzene over NbO$_2$ catalysts. The active ethylidyne form observed by Davis, et al (300), could always be removed by hydrogen treatment. The authors concluded that the hydrogenation reaction takes place over this ordered metal-organic layer, which acts as the hydrogen transfer mechanism and is thus analogous to the M-C$_x$H$_x$ species of Thomson and Webb (102).
Similar conclusions were reached by Godbey, et al (302) from studies of ethylene adsorption on Pt, and by Ibach, et al (303). They observed an identical formation and subsequent role of ethylidyne during Surface Vibration Spectroscopy investigations of acetylene and ethylene adsorption on Pt(111), although Ibach and Lehwald (304) had previously identified ethylidene (not ethylidyne) during a similar investigation on Pt(111) in the absence of preadsorbed hydrogen. With preadsorbed hydrogen, ethylidyne formed. Ibach, et al (303) further concluded that as ethylidyne was observed during acetylene adsorption in the absence of hydrogen, a more dehydrogenated form of acetylene such as \( \overset{\text{C-CH}}{\wedge} \) or carbon deposits must also exist, and suggested that intermediate species such as \( \text{HC-CH}_3 \) or \( \text{H}_2\text{C-CH}_2 \) would be expected to polymerize and might give rise to the formation of even numbered polymerization products during subsequent reactions.

In contrast to these conclusions, Beebe and Yates (305) have observed that ethylidyne formation and hydrogenation rates are 2-3 times lower than the rate of ethylene hydrogenation on 10% Pd/Al\(_2\)O\(_3\) catalysts. In addition, the rate of ethylene hydrogenation was the same over catalysts with and without preadsorbed ethylidyne. These authors concluded that ethylidyne is not a necessary species in the mechanism of hydrogenation. Moshin, et al (306) report similar observations and conclusions during ethylene hydrogenation on 3% Pt/Al\(_2\)O\(_3\).

Ethylidyne has also been observed during ethylene adsorption on Pt(111) by Steininger, et al (307), who observed a di-\( \sigma \)-adsorbed species during adsorption below room temperature, but only ethylidyne above 300 K. Albert, et al (308) found that during the adsorption of
both ethylene and acetylene on Pt(111) at low temperatures, both formed species with the C-C bond parallel to the surface, again shifting to ethylidyne formation between 300 and 400 K. Ogle, et al (309) observed the formation of ethylidyne from ethylene and propylidyne from propylene during adsorption on Pt(111), while Creighton, et al (310) observed that this ethylidyne was active for H-D exchange, possibly through ethylidene intermediates. Freyer, et al (311) observed the formation of ethylidyne and several hydrocarbon fragments intermediate between ethylidyne and a dehydrogenated C₂ species or graphitic carbon during ethylene and acetylene adsorption on Pt(111).

Ethylidyne was calculated to be the most stable surface structure of acetylene adsorbed on Pt(111) by Anderson and Hubbard (312) using atom superposition and electron delocalization techniques, and by Gavezzotti and Simonetti (313,314) using the Extended Huckel Molecular Orbital Theory.

On Pd(111), Demuth (315) observed two classes of structures by He II photo-emission spectroscopy of acetylene adsorption. One class was weakly distorted, while the other was strongly distorted (sp².₅ hybridization). No species corresponding to these structures were proposed. Similarly, by inelastic electron tunneling spectroscopy, Bayman, et al (316) observed five different species formed during acetylene adsorption on Pd. One was weakly bound acetylene, two were very strongly bound, while the last two were rehybridized. Again, no corresponding structures were proposed.

In contrast, by angle dependent EELS, Kesmodel and Gates (317) observed the formation of ethylidyne, ethylidene, and a HC-CH₂ species
during ethylene adsorption on Pd(111) crystals. Using high resolution EELS and LEEDs, these authors later found surface bonding geometry involving acetylene co-ordination at three-fold sites on the Pd(111) surface during acetylene adsorption (318).

Further EELS observations of the low temperature phase of ethylene adsorbed on Pd(111) (319) indicated that it was more weakly bound than on Ni(111) and Pt(111), and suggested hydrogen bond-like interactions between the adsorbed ethylene and the metal surface. Thermal evolution of acetylene studied by high resolution EELS on Pd(111) indicated that acetylene forms mainly ethylidyne, and a small amount of residual acetylene, in the presence of hydrogen on the surface (320). Evidence also suggested a vinylidene intermediate. Although ethylene also formed some ethylidyne upon adsorption, much of it desorbed as ethylene during heating from 150 to 300 K. Kesmodel, et al (321) observed that while ethylidyne was the major species formed during acetylene adsorption on Pd(111), a C=CH species with both carbons bonded to the surface was also formed, while on Pd(100), only the latter species formed. During acetylene adsorption on Pd(100), Kesmodel (322) observed only a strongly distorted (~sp$^3$ hybridization) chemisorbed acetylene species, which was not positively identified. Lloyd and Netzer (323) also observed ethylidyne formation from ethylene adsorption on Pd(111). Beebe and Yates (324) observed the formation of ethylidyne during ethylene adsorption on 10% Pd/alumina, and found that it decreased subsequent CO adsorption by 30%. They concluded that ethylidyne only formed on the Pd(111) surface, which represented about 30% of the total catalyst Pd.
Gay (325) has recently questioned the applicability of low pressure adsorption studies on Pt single crystals to polydisperse supported Pt catalysts. During high resolution solid-state $^{13}$C NMR studies of ethylene adsorption on 5 and 10 wt% Pt on alumina and silica catalysts he observed a $\pi$-bonded olefin on each catalyst. Additional evidence suggested both a $\sigma$-adsorbed species with an intact C=C double bond, and surface alkyls. Little evidence of nonprotonated carbon was found, and the existence of either $=\text{C-CH}_3$ or $=\text{C-CH}_2$ was excluded. Beebe, et al (324,326) observed the presence of ethylidyne upon adsorption of ethylene or acetylene on 10% Pd/Al$_2$O$_3$ catalysts. This ethylidyne was stable to 400 K. Similarly, Galuszka and Amenomiya (327) have recently reported the formation of a species similar to surface ethylidyne and a benzene type species during acetylene adsorption on 5 wt% Ni/Al$_2$O$_3$ catalysts from room temperature to 250°C. Both species were stable in hydrogen up to 250°C.

During low temperature acetylene adsorption on Pd and Cu, Sesselmann, et al (328) observed the formation of ethylidyne at low acetylene coverages, while at high exposures adsorbed benzene was observed on the surface. They later reported the same low temperature (150 K) benzene formation from acetylene adsorption on Pd, but on increasing the temperature to 300 K, a reactive $\pi$- or di-$\sigma$-adsorbed species and another unreactive, unknown species were formed (329). Tysoe, et al (330,331) observed that at temperatures below 220 K, adsorbed acetylene lay flat on the Pd surface, and readily trimerized to form benzene. At higher temperatures, olefinic bonds perpendicular to the surface were formed, possibly by partially hydrogenated
intermediates. Preadsorbed hydrogen increased the production of ethylene at the expense of benzene. Ethylene production was apparently initiated by the formation of adsorbed vinyldene. Bandy, et al (332), on the other hand, observed only a di-σ-adsorbed species upon acetylene adsorption at 110–120 K on Cu, Ni, and Pd.

Marchon (333) observed the formation of acetylene species on bridged sites perpendicular to the Pd-Pd surface axis. Further adsorption of acetylene induced this species to cyclotrimerize to adsorbed benzene at 153 K. This benzene desorbed at 248 K. Higher temperatures caused the adsorbed acetylene to decompose to C=CH and/or C=CH₂ or undergo cyclotrimerization to benzene. Stuve, et al (334) observed that ethylene adsorption at 80 K on Pd(100) formed both di-σ- and π-bonded species. Between 100 and 300 K, the π-bonded species desorbed, while the di-σ-adsorbed species dehydrogenated to HC=CH₂ and finally to =CH at 300 K. Adsorbed oxygen blocked the formation of the di-σ-adsorbed species, but the π-bonded species was stable up to 0.5 monolayer oxygen coverage. Two oxygen atoms were necessary to block one ethylene molecule from the surface. Kojima, et al (263) studied acetylene and ethylene adsorption on Pd(111) by Field Emission Microscopy (FEM) and found substantial ethylene dissociation, while acetylene adsorbed mainly non-dissociatively.

Much of these recent UHV spectroscopic investigations have been reviewed by Bertolini and Massardier (335) and Simonetta and Gavezzotti (336).

At this point, it is not possible to say which, if any, of the various proposed mechanisms for acetylene hydrogenation is correct.
Based upon the evidence presented here, we can only say what we believe could be possible, and this includes all of the proposed mechanisms.

It must also be stressed that although many of these structures presented here and assumed to exist during acetylene and/or ethylene hydrogenation do exist upon acetylene/ethylene adsorption, this in no way ensures their existence under hydrogenation conditions, for the great majority of these studies were conducted under very special conditions, often on very special metal samples, which are very different from the conditions and catalysts used during hydrogenation. This question is discussed in more detail by Sermon (337) and Shustorovich (338).
The behavior of reactions involving hydrogen as a reactant, intermediate, or product species over Pd catalysts is complicated by the high diffusivity of hydrogen atoms in Pd (339) and the possible existence of 2 distinct types of Pd hydrides, termed the $\alpha$ and $\beta$ phases, respectively (figure 16). The existence of these phases is

![Diagram](image)

Figure 16. Hydrogen Absorption Isotherms in Palladium (340).
determined by the temperature and hydrogen pressure. The α-phase is formed by the absorption of small amounts of hydrogen, with a maximum composition of about PdH_{0.03} at room temperature. The lattice parameter of the α-phase at these conditions is only slightly larger than that of pure Pd (3.889 Å). Upon further hydrogen absorption, the α-phase becomes unstable and the lattice expands to about 4.018 Å at PdH_{0.7}, to form the β-phase (340).

Worsham, et al (341) have shown by neutron diffraction that hydrogen atoms occupy about 70% of the octahedral interstices in the face-centered cubic Pd lattice of the β-phase hydride, giving a NaCl-type structure that is hydrogen deficient. From calculations of the lattice stretch per unit hydrogen uptake, Scholten and Konvalinka (340) have found no evidence for a difference in hydrogen positioning between the two phases. Proton Magnetic Resonance (PMR) studies by Burger, et al (342) point to identical modes of binding for both phases. Based on these results, Scholten and Konvalinka (340) have concluded that in the β-phase, hydrogen tends to cluster in such a way that 4 out of 6 of the octahedral interstices are filled, while in the α-phase the hydrogen is randomly distributed over all octahedral interstices. Flanagan and Oates (343) have investigated the dilute region of primary solubility, and obtained excess enthalpies of solution which were independent of hydrogen content.

Palladium and deuterium also form similar α- and β-phase deuterides, although in general higher deuterium pressures and/or lower temperatures are necessary to achieve equal D/Pd ratios. Foltz and Melius (344) have observed a large difference in the rate of hydrogen
exchange with a β-phase Pd-deuteride compared to deuterium exchange with a β-phase hydride. Nicol, et al (345) found a preferential hydrogen occupation of subsurface sites for dilute hydrogen in deuterium on Pd black. The thermodynamics of both the Pd-hydrogen and Pd-deuterium systems over bulk Pd have been extensively reviewed by Lewis (149,346, 347), Stoneham (348), Tanaka and Azofeifa (349) and Wicke, et al (350). The structural and electronic properties of implanted metal hydrides are discussed by Traverse and Bernas (351).

The existence of these two types of adsorbed hydrogen in Pd complicates the procedure of hydrogen adsorption measurements of Pd surface areas and particle dispersions, although Sermon (352,353) and Aben (354) have reported methods that avoid this complication for Pd-blacks and supported Pd catalysts, respectively. Paseka, et al (355) have recently reported a potentiometric titration method that allows for the simultaneous measurement of both adsorbed and absorbed hydrogen over Pd-black and supported Pd catalysts containing at least 5% Pd.

While the behavior of the Pd-H system in the presence of hydrogen only and on relatively large Pd particles has been studied extensively, its behavior on supported Pd catalysts, particularly during reactions involving hydrocarbons, is still poorly understood. It should be noted that because of the geometry of the Pd-hydrides, with hydrogen occupying interstices in the Pd crystal structure, the formation of both hydride phases is progressively more difficult as the Pd dispersion approaches unity, and is impossible at atomic dispersion, as no Pd cubic structure can exist. This effect has been demonstrated by Boudart and Hwang (356) and by Nandi, et al (357,358). Similarly, Jobic and Renouprez (359)
observed a decrease in the intensity of the β-phase neutron spectrum peak during low pressure (1.5, 25, and 200 mbar) hydrogen adsorption and absorption on small Pd crystallites (d<15Å) encaged in the large cavities of a Y-zeolite. Everett and Sermon (360) have challenged the suggestion of Suzuki and Suzuki (361) that hysteresis observed during the α-β and β-α phase transformations should vanish with decreasing metal crystallite size due to the decreased hydrogen capacity of small Pd crystallites. They observed a halving in the area of the hysteresis loop upon reducing particle size from massive samples to about 20 nm, but then the hysteresis properties remained essentially constant down to a crystallite size of 7 nm (397). Vert, et al (362) have also observed no change in this hysteresis pattern between massive Pd foils and finely divided Pd blacks. In contrast, Moraweck, et al (363) found that on small Pd clusters (10Å), the stoichiometry of the β-phase decreases to PdH0.4 due to a decrease in the number of available interstitial sites. Mazzolai, et al (364), Lewis, et al (365), and Feenstra, et al (366) have investigated the macroscopic dimensional changes during cycles of the Pd-hydride phase transformations, and concluded that the hysteresis effect probably corresponds to differences in the overall dimensions arising from changes in hydrogen content and lattice dimensions in the two phases. Lewis (367) observed a regular decrease in the hydrogen solubility of alloys formed from Pd and other transition metals (Ag,Pb,Bi, Ce,Rh,Pt) as well as a general decrease in the hydrogen diffusion coefficient with increasing per cent alloying metal, while Vert, et al (362) observed an
absence of the horizontal two-phase plateau in the solubility isotherm of a 10% Cu/90% Pd alloy. Feenstra, et al (368) reported a decrease in hydrogen solubility in both the Pd-Co and Pd-U alloy systems (90-95% Pd). The decrease in solubility was more pronounced in the Pd-U alloys, in spite of the fact that U readily absorbs hydrogen and Co does not. Kirchheim and McLellan (369) observed a decrease in hydrogen diffusivity in Pd upon the addition of up to 10% Cu or Nb. The decrease was much larger for Nb addition. Zakumbaeva, et al (370) found that the addition of Cd decreased the amount of hydrogen dissolved in Pd-black hydrogenation catalysts. Wagner, et al (371) observed that Co, Ru, Rh, Sn, Os, Ir, Pt, or Au (~1%) in Pd had a large repulsive interaction with hydrogen, particularly in nearest neighbor sites. Phutela and Kleppa (372) reported an increasingly negative enthalpy of hydrogen solution and a corresponding large increase in the excess entropy of hydrogen with increasing Mn content in a series of Pd-Mn alloys. In addition, Chang, et al (234) have recently found that the existence of strong metal support interaction (SMSI) suppressed the absorption of hydrogen into bulk Pd.

Sakamoto, et al (373,374), on the other hand, observed a decrease in hydrogen diffusivities, but an increase in hydrogen solubility, with increasing alloying concentration in the PdFe, PdV (373), PdAg, and PdAu (374) systems. Chou (375) found a decrease in the rate of hydrogen permeation and an increase in its activation energy upon decreasing the Pd content of Pd-Ag alloys from 30 and 20%. Bowman, et al (376), Spada, et al (377) and Anisochkina, et al (378) have all reported ternary hydride phases of the composition Zr$_2$PdH$_x$ with x as high as 2.7 to 2.9.
Yoshihara and McLellan (379) observed a distinct maximum in hydrogen solubility in Pd–Cu solid solutions at 6% Cu, falling off sharply as the Cu content increased further to 20%. The maximum was more pronounced at lower temperatures.

The mechanism of the β-phase decomposition and the nature of the desorbing hydrogen species have been investigated by Dus and Nowicka (380) Lisowski, et al (381), and Stern, et al (382).

Early results of hydrogen effects on Pd and Ni, which may also form similar hydride phases, have been reviewed by Sheridan and Campbell (383) and by Eley (384), who reported the poisoning of the para-ortho hydrogen conversion on Pd by dissolved hydrogen. In contrast, Dobytschin and Frost (385) found that dissolved hydrogen was more effective for ethylene hydrogenation than gas phase hydrogen. Wagner and Hauffe (386) observed that ethylene admission to a Pd–H system, and the hydrogenation of that ethylene, caused a decrease in the concentration of hydrogen dissolved in the Pd. Couper and Eley (387) also found that pre-exposure of pure Pd to hydrogen markedly reduced its catalytic activity, while Kowaka (388) observed that hydrogen pretreatment promoted the activity of Pd-Ag alloys, but reduced the activity of nonalloyed Pd, for olefin hydrogenation. Karpinski, et al (389) and Jablonski and Palczewska (390) observed the poisoning of atomic H recombination on Ni–Cu by the formation of a β-phase hydride. Bond, et al (77) also reported a similar poisoning effect of hydrogen pretreatment on both acetylene and ethylene hydrogenation on Pd, but in a discussion of a later paper (391), one of the authors inexplicably
reported that they had no evidence of hydrogen poisoning the acetylene hydrogenation activity of Pd.

Munoz and Rouco (392) observed a significant poisoning of hydrogen chemisorption capacity following high temperature hydrogen treatment (which was reversible by simply evacuating the sample, so sintering could not be invoked) of not only Pd (26% decrease in capacity), but also Pt (21%), on both silica and alumina supports. Co, Ni, Rh, Os, and Ir showed smaller (4-11.2%), though perhaps still significant decreases, while treatment had no effect on Ru and increased the capacity of Fe by 176%. If the cause of this decreased capacity is the same over each metal, it would appear that this was not a hydride phase effect, as most of these metals have very low capacities for hydrogen absorption.

Menon and Froment (393) have recently discussed the effects of residual hydrogen on H-chemisorption capacity, hydrogen TPD peak shifts and changes in catalyst activity and/or selectivity.

Rennard and Kokes (394) studied the hydrogenation of ethylene over both Pd hydride phases. They observed a first order dependence on hydride concentration and a zero order dependence on both ethylene and hydrogen pressures. They also reported that the first order rate constant decreased with hydride concentration, although the reaction rate increased with the same due to its first order dependence on hydride concentration. These results are discussed in greater detail by Kokes (395).

Palczewska and co-workers (117,147,396-399) studied the effects of the B-phase hydride on various reactions over Pd, Ni, and NiCu catalysts. They observed a substantial decrease in catalyst activity
for the heterogeneous recombination of hydrogen atoms, para-ortho hydrogen conversion, and ethylene hydrogenation upon passing from hydrogen free NiCu films (3 wt% Cu) to the β-NiCu-H phase (396). This behavior was explained in terms of the hydride directly influencing the electronic states at the metal surface, although no data were available to determine what those states were. Identical results were found over pure Ni evaporated films (397).

Palczewska (117) summarized most of their earlier work on Pd and Ni hydrides. Here, she reported that large metal crystals transform into hydrides slowly, while small crystallites form hydrides instantly. The relations are similar for decomposition; the larger the metal crystals, the slower the hydride decomposes.

In a study of the role of Pd hydrides in the activity and selectivity of Pd catalysts in acetylene hydrogenation, Borodzinski, et al (398) found that the β-phase was less ethylene selective, though more active, than the α-phase (table 11). They also reported that catalysts with a high degree of metal dispersion were unable to form the β-phase hydride, as observed by Boudart and Hwang (356), and Nandi, et al (357,358). They observed that temperature, feed ratio, hydrogen partial pressure, and the degree of Pd dispersion have both independent and conjugated effects on the α-β phase transition. Thus, hydrogen pressures which were sufficient to form the β-phase in the absence of acetylene were too low to do the same in a 2:1 hydrogen/acetylene mixture. Acetylene admitted to a Pd-β-phase hydride catalyst could cause a decomposition of the β-phase, apparently through the consumption of the hydride hydrogen by acetylene hydrogenation. However, feed
ratios and reaction temperatures within an appropriate range (table 11, part "8:1", 309 < T < 331, and part "12:1") allowed the β-phase to be renewed continuously in many Pd particles. At lower hydrogen/acetylene feed ratios and/or lower temperatures, which favor acetylene adsorption and sufficiently decrease the rate of hydrogen reabsorption, the hydride decomposed and the reaction proceeded over the α-phase.

Table 11. The Relationship Between the Course of Acetylene Hydrogenation and the Phase Change in the Pd-hydrogen System (398).

<table>
<thead>
<tr>
<th>Feed Ratio</th>
<th>Partial Pressure (kN/m²)</th>
<th>T/K</th>
<th>observed (111) diffraction peak</th>
<th>hydrocarbons in products (%)</th>
<th>C₂H₆</th>
<th>C₂H₄</th>
<th>C₂H₂</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:1</td>
<td>25.3</td>
<td>331</td>
<td>Pd+(Pd-H)</td>
<td>14.7 5.5 79.6 27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>319</td>
<td>Pd+(Pd-H)</td>
<td>10.3 6.2 83.5 37.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>316</td>
<td>Pd+(Pd-H)</td>
<td>8.7  6.5 84.8 42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>309</td>
<td>Pd+traces (Pd-H)</td>
<td>0.27 4.4 95.2 94</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>305</td>
<td>Pd+traces (Pd-H)</td>
<td>0.27 3.3 96.4 93</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>301</td>
<td>Pd+traces (Pd-H)</td>
<td>0.28 2.9 96.9 91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>25.3</td>
<td>317</td>
<td>Pd</td>
<td>0.12 0.60 99.3 84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>311</td>
<td>Pd</td>
<td>0.08 0.36 99.6 81</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>307</td>
<td>Pd</td>
<td>0.06 0.26 99.7 79</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>303</td>
<td>Pd</td>
<td>0.06 0.21 99.7 78</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>314</td>
<td>Pd</td>
<td>0.07 0.33 99.6 82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>303</td>
<td>Pd</td>
<td>0.05 0.16 99.8 78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12:1</td>
<td>25.3</td>
<td>325</td>
<td>(Pd-H)+ traces Pd</td>
<td>11.8 4.2 84.0 26.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>318</td>
<td>(Pd-H)+ traces Pd</td>
<td>10.0 5.1 83.6 34</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>313</td>
<td>(Pd-H)+ traces Pd</td>
<td>6.8  5.2 88.0 43</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>308</td>
<td>(Pd-H)+ traces Pd</td>
<td>6.2  5.5 88.3 47</td>
<td></td>
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</tr>
</tbody>
</table>

Pd represents α-Pd-H; (Pd-H) represents β-Pd-H phase.

\[
S = \frac{C_2H_4}{C_2H_6 + \text{C}_2H_4}
\]
In a further study of the same reaction over Pd, Palczewska (399) found that in the regions where both hydride phases co-exist, the selectivity for ethylene production was a combination of the low value of the reaction over the β-phase and the high value over the α-phase. Thus intermediate values could be obtained. She again observed that the hydrogen pressure at which the β-phase hydride decomposed increased with decreasing Pd crystallite size.

In all of these studies of acetylene hydrogenation on Pd-hydride catalysts, the formation of C4 and higher hydrocarbons has not been reported. This does not necessarily mean that such compounds were not formed, only that suitable analyses were not performed. Therefore, we have no information about the effects of the β-phase hydride on the amount of oligomeric products formed during this reaction and it is possible that the ethylene selectivities calculated while ignoring oligomer formation are incorrect.

In addition, 14C labeling was not used in any of the studies of Palczewska and co-workers (117,147,396-399) where the selectivity for ethylene was observed to decrease with the formation of the β-phase hydride. Thus, it is not known if this decrease in observed selectivity is a result of an increase in the fraction of acetylene converted to ethane, or an increase in the rate of ethylene hydrogenation in the presence of acetylene. Experiments were conducted at constant gas flow rates in a flow reactor, and because the activity of the β-phase was higher than that of the α-phase, the acetylene conversion was high enough to allow for the undetected adsorption and hydrogenation of ethylene previously formed from acetylene.
From the evidence presented above, it would seem unlikely that the Pd-β-phase hydride would form on typical industrial acetylene hydrogenation catalysts, on which the metal loadings are very low (0.02 to 0.05 wt%) and the metal dispersions very high, particularly for tail-end hydrogenation mixtures with hydrogen/acetylene ratios of 1.2-1.5. However, Scholten and Konvalinka (340) reported that they observed a β-phase hydride of the composition PdH₂ on a 0.5 wt% Pd on alumina catalyst with a mean Pd crystallite size of 15 Å. Unfortunately, the temperature and hydrogen pressure used to achieve this hydride composition were not reported. They report analogous results by Suhrmann, et al (400) for crystallites of 85 Å, and by Turkevich (401). It appears that they have seriously misinterpreted Turkevich. He reported a hydrogen uptake on alumina supported Pd that would correspond to a composition of PdH₂, but he concluded this was due to hydrogen spillover to the alumina support. Hence this type of hydrogen uptake measurement was wrong, as the actual hydrogen/Pd ratio was much smaller (401).

The behavior of the α-β-phase hydrides under typical front-end hydrogenation conditions, with hydrogen/acetylene ratios of 15:1, or more, and in the presence of gas phase CO has not yet been investigated. From the results of Borodzinski, et al (398) (table 11), we might conclude that the β-phase does in fact exist on Pd catalysts under these conditions. However, the effect of CO (which is usually present in amounts of 500 to 1000 ppm in such mixtures) on the Pd-hydride system is currently unknown. The observations of Al-Ammar and Webb (112), LeViness, et al (138), and Weiss, et al (139) strongly suggest that CO
may reduce the surface hydrogen concentration by competition with hydrogen for surface sites. If this is indeed the case, then perhaps the β-phase cannot form under such conditions, as we might expect from the fact that in the presence of CO ethylene selectivities are uniformly high (138,139,142).

The effects of carbonaceous deposits, whether formed in the presence or absence of CO, on the Pd-hydride system are also currently unknown. Boudart, et al (148) have shown that the presence of such deposits enhances the hydrogen uptake of the Pt-C system, and Davis, et al (295) have shown that they may store and exchange hydrogen with reactant surface species on Pt single crystals. If a similar effect occurs here in the Pd-alumina system, as envisioned by Moses, et al (136), the resulting higher surface hydrogen concentration may contribute to the formation of a β-phase hydride under conditions (hydrogen/ethylene ratio, hydrogen pressure) in which it would not otherwise form.

Jenko, et al (147) found that the repeated process of formation-decomposition-formation of the β-phase leads to a low temperature rearrangement of Pd crystallites, and to the formation of the (111) texture without visible particle growth. Catalysts treated in this way showed enhanced activity in subsequent acetylene hydrogenation reactions. Sermon (402) found a similar rearrangement during ambient temperature hydrogen treatment of Pd-blacks. Blume and Munzing (403) found an increase in the activity of commercial Pd catalysts after special hydrogen treatments. Similar effects were suggested by Benedetti, et al (404) to explain the increase in turnover number
observed with decreasing Pd particle size during benzene hydrogenation over Pd/charcoal catalysts.

In contrast, Massardier, et al (285) have recently reported that the formation of Pd hydrides had no effect on the activity of Pd/SiO₂ catalysts in butadiene hydrogenation.

Flanagan and Kishimoto (405) observed that for cold worked Pd and Pd which has been passed through the α-β phase transitions the solubility of hydrogen is increased by interaction with the elastic stress fields of dislocations and by trapping sites. The nature of the latter was not determined, but they were destroyed during annealing at 447 K. Lynch, et al (406) observed enhanced hydrogen solubility following the formation and decomposition of the β-phase, as did Wyrzykowski and Baranowski (407). Similarly, Paal and Thomson (408) observed the existence of at least two different types of hydrogen retained on Pt-black catalysts following adsorption at 360°C, one of which was inaccessible to both hydrocarbons and hydrogen.

Heinemann and Poppa (409) observed an increase of 2.9% in the lattice parameter of Pd particles in the 1-2 nm size range compared to particles of 5 nm mean size. The samples were annealed at up to 250°C, and treated with low pressures of H₂ and CO at 250°C for 10 minutes, but these treatments had no effect on any of the particles characteristics. The authors concluded that this lattice expansion was due to the formation of a bulk face centered cubic (fcc) crystal structure during local e-beam annealing of as deposited icosahedral composite particles.

Gryaznov, et al (410,411) studied the use of membrane catalysts, whereby hydrogen could be introduced in the gas phase during reaction
with hydrocarbons, by diffusion through the membrane, or by both methods simultaneously. They observed an increase in activity for the vapor phase hydrogenations of piperylene, isoprene, and cyclopentene of 1.3–4 times when hydrogen was supplied by transfer through the membrane versus introduction in the reaction gas. During liquid phase hydrogenations, an increase in activity of 100 times was observed, due to the large differences in hydrogen solubility and diffusivity between Pd and either water or organic liquids (410). During similar experiments on CO hydrogenation, both the overall reaction rate and the product composition were strongly affected by the method of hydrogen introduction (411).

Wells (116) has reported the effect of hydrogen occlusion in cavities formed by slow atomic diffusion in powdered Ru, Rh, Os, Ir, Pt, and Au catalysts, and observed that the butane yield during butadiene hydrogenation paralleled the capacity of each metal to occlude hydrogen.

The behavior of the Pd-hydrogen system in the absence of distinct hydride phases has been the subject of a great deal of recent research (412–420). Various investigators have reported evidence of as many as four distinct types of hydrogen held on the surface. Kubas (421) reviewed the formation of molecular hydrogen complexes with transition metals, while Christmann (422) reviewed the general interactions of hydrogen with solid surfaces.

Several recent investigations have suggested that the behavior of hydrocarbon reactions over Pd may be further complicated by the existence of a surface Pd-carbide phase. Early IR spectroscopic
investigations found evidence for the formation of a surface carbide phase upon adsorption of acetylene and ethylene on Ni and Pt (258, 260, 261), but we have been unable to find many other investigations even mentioning the existence of such carbide phases since that time (1969).

The formation of iron carbides during reactions of CO and hydrogen (particularly in Fischer-Tropsch synthesis) and their subsequent effects on the activity and selectivity of Fe(110) (423), iron oxide (424), and alumina supported iron (425) have been investigated. However the role of this iron carbide in the subsequent reaction is not clear. Bonzel and Krebs (423) concluded that the carbide was active towards CO hydrogenation, while the formation of a surface graphitic phase was not. Bianchi, et al (424) concluded that the carbide was a product of the desired reaction and had little effect on the catalyst activity but that a surface graphite caused deactivation. Reymond, et al (425), on the other hand, have concluded that the formation of iron carbide was detrimental to the catalyst activity.

The formation of carbon during the adsorption of light hydrocarbons, particularly acetylene, on Ni at 300-800°C has been reported in a number of cases (426-431), and in several cases a Ni-carbide was suggested or observed (429, 430, 431). However, the same authors found that of the other group VIII and IB metals, only Fe and Co were active for carbon formation, and the rates on these metals were 10-100 times lower than on Ni (429).

The electronic structure of Pd monocarbide has been determined by Shim and Gingerich (432) from all-electron ab initio Hartree-Fock and configuration-interaction calculations. They calculated significant
differences between PdC on one hand and RhC and RuC on the other, particularly that the π-orbitals in the PdC molecule localize and become nonbonding leaving only a σ-bond.

Ratajczykowa (433) studied the reactivity of surface carbon on Pd(111), (mean bulk C/Pd atomic ratio 1.7-4 X 10^{-5}) towards acetylene, ethylene, hydrogen, and CO. She found that carbon segregated to the surface from the bulk carbide was highly reactive towards all of the gases employed, and was easily hydrogenated to the same surface species observed after acetylene adsorption, which she identified as C-CH₂. The activation energy for CO desorption increased from 33 kcal/mole on clean Pd(111) to 40 kcal/mole on the Pd(111)-C surface, while the rate of the transformation of weakly bound ethylene to C-CH₂ was almost an order of magnitude faster over Pd(111)-C. In contrast, Zaidi (434) found that the formation of Pd-C solutions caused a decrease in propylene adsorption compared with pure Pd used in the reaction of oxygen, propylene, and acetic acid to form allyl acetate and carbon dioxide.

Stachurski and Frackiewicz (435) have recently investigated the composition and role of the bulk Pd-carbon system during acetylene hydrogenation. Although their extrapolation of high temperature Pd-carbide thermodynamics suggested a composition of 10^{-3} -10^{-2} atom% C (436, 437), they felt that other investigations implied that much larger concentrations of carbon could dissolve in Pd (438-441).

Anderson and Avery (438) reported carbon corresponding to 12 monolayers coverage present on unoriented Pd films during the isomerization of aliphatic hydrocarbons in hydrogen deficient conditions at T = 200-350°C. As these samples were still active for isomerization,
they concluded that this carbon was most likely dissolved in the metal. Anderson and Clarke (439) observed a total carbon loss of 27% during the reaction of methyamine and hydrogen over evaporated Pd films at 480 K, corresponding to one carbon per 5 Pd atoms, or 16% carbon. However, electron diffraction examination of such Pd samples gave no evidence for the existence of a separate carbide phase.

In addition, Stachurski and Frackiewicz (435) have questioned the assignments of X-ray diffraction peak deformations and displacements as representing the formation of the β-phase Pd-hydride (398). Beginning with a Pd catalyst (foil, black, carbon supported, or silica supported) on which the β-phase hydride had been decomposed, acetylene and hydrogen were reacted and a supersaturated solution of carbon in Pd was observed, which the authors concluded was non-carbidic in nature. The calculated composition of this new phase was PdC₀.₁₃. Even though this phase was thermodynamically unstable, at temperatures below 610 K (460 K in the presence of hydrogen) it decomposed very slowly. At room temperature no change in the X-ray diffraction pattern could be observed even after several months.

Stachurski (441) subsequently investigated the differences in hydrogen sorption between this new phase and Pd. With increasing carbon content, the hysteresis effect characteristic of the formation and decomposition of the β-phase hydride gradually disappeared, until at PdC₀.₁₃, the catalyst samples showed no ability to form the β-phase hydride at all. The small amount of hydrogen which could absorb in this Pd-C phase resembled the α-phase Pd-hydride. Ziemecki, et al (442,443) observed that the β-phase disappears at a composition of PdC₀.₁₅. They
also found that at lesser carbon concentrations, a continuous series of ternary \( \text{PdC}_x\text{H}_y \) \((0<x<0.15, \ 0<y<0.65)\) could be obtained. The quantity of hydrogen in such systems depended only on the carbon concentration. A ternary hydride of the composition \( \text{Na}_x\text{PdH}_y \) which was characterized by a linear \([\text{PdH}_2]\) complex has recently been reported by Noreus, et al (655).

Lalauze, et al (444) investigated the effects of surface carbon, oxygen, and sulfur impurities on the permeation of hydrogen in Pd. They observed that while sulfur was a very active poison, results with carbon were inconclusive. This led the authors to question the role of carbon as the most active element in surface phenomena in the Pd hydrogen system.

These results may explain the apparent lack of Pd-\(\beta\)-phase hydrides during acetylene hydrogenation at conditions where we might otherwise expect them to exist, as evidenced by constant acetylene hydrogenation activity observed as ethylene selectivity decreases \((109,132,136,137-139)\). If the \(\beta\)-phase hydride were responsible for the observed selectivity decline, we would also expect that the acetylene activity would increase \((147,398)\). However, it is not at all clear under what particular acetylene hydrogenation conditions this supersaturated carbon phase will form. Therefore we cannot determine what effects the formation of this phase might have on catalyst activity and/or selectivity, if indeed it has any at all. The possibility that a phase of this type exists under all acetylene hydrogenation conditions cannot be ruled out, in which case it, rather than Pd, would be the active catalyst. This area certainly deserves detailed investigation in the future.
E. Hydrogen Spillover - Ethylene Hydrogenation on Alumina

While the catalytic activity of alumina, and to a lesser degree silica, is well known (445-447), their role in catalytic reactions in which they are used as a support is much less well defined. As long ago as 1963, Sinfelt and Lucchesi (448) and Carter, et al (449) observed that Al₂O₃ mixed with Pt/SiO₂ catalysts increased the rate of ethylene hydrogenation per unit weight Pt (table 12), and suggested that this was due to hydrogen migration - spillover - from Pt sites, where it was dissociatively adsorbed, to the diluent alumina, where it reacted with chemisorbed ethylene. This suggestion was not well received at its presentation, as shown by the discussion following (449), and by the subsequent refutations of Schlatter and Boudart (450) and Briggs, et al (451,452), and we have found no further reference to it until recently.

Table 12. Results on C₂H₄ Hydrogenation over Catalyst Mixtures (449).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Pt-SiO₂ + SiO₂</td>
<td>0.10</td>
</tr>
<tr>
<td>Pt-SiO₂ + Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>(1) ground together</td>
<td>2.1</td>
</tr>
<tr>
<td>(2) simple mixture</td>
<td>0.50</td>
</tr>
</tbody>
</table>

0.050 g of 0.050 wt% Pt-SiO₂ + 0.45 g of diluent.
Hydrogen migration, or "spillover" was first observed by Khoobiar (453) in the action of added 0.5 wt% Pt/Al₂O₃ catalyst to WO₃. During room temperature treatment with hydrogen, WO₃, which has a yellow color, was reduced first to blue W₄O₁₁, and then to brown WO₂. Hydrogen molecules accomplished this reduction at temperatures higher than 200°C, but not at room temperature. The effectiveness of Pt/Al₂O₃ in bringing about this color change, and hence reduction, was attributed to hydrogen dissociation on Pt, followed by migration of H atoms to the WO₂. Since that time, the action of small amounts of added transition metal, usually Pd, Pt, or Ni, in greatly decreasing both the time and temperature necessary for reduction of metal oxides (454-462) and metal sulfides (463,464) has been frequently observed. Early studies of these hydrogen spillover effects have been extensively reviewed by Sermon and Bond (465) and by Charcosett and Delmon (466). Typical results appear in table 13.

Bond, Sermon, Mallet, and Tripathi have continued investigations of various spillover effects (467-471). Among their most important results are the observations that two types of spillover exist. The first, which was called primary spillover, is very fast and occurs only between phases in close physical contact with one another. The second, called secondary spillover, is slow and may occur between phases not in immediate contact (470), but in some systems, in this case Pt-C, occurs only between phases in immediate contact at room temperature (471).

Levy and Boudart (458), Boudart, et al (459), Ambs and Mitchell (472), and Keren and Soffer (473) have observed a large promoting effect of water on the rate of hydrogen spillover, while as previously
discussed, Boudart, et al (148) have reported a large increase in hydrogen uptake by Pt-C catalysts when surface carbon contaminants are present. Neikam and Vannice (474) have observed the promotion of hydrogen spillover from Pt-black to Y zeolites by a variety of

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Catalyst Type</th>
<th>Technique</th>
<th>Lowering of temperature for start of reduction of oxide, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>Pd/WO₃</td>
<td>TGA</td>
<td>30 (210)</td>
</tr>
<tr>
<td>WO₃</td>
<td>Metal/WO₃</td>
<td>TGA</td>
<td>146 140 135 80 100</td>
</tr>
<tr>
<td>WO₃</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>300 76</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Metal/MoO₃</td>
<td>TGA</td>
<td>325 250 235 102</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Pd/MoO₃</td>
<td>TGA</td>
<td>400 99</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>175 76</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Pd/MoO₃</td>
<td>DTA</td>
<td>250 103</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Pd/Fe₂O₃</td>
<td>TGA</td>
<td>270 100</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>Pt/V₂O₅</td>
<td>DTA</td>
<td>200 101</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>250 76</td>
</tr>
<tr>
<td>UO₂</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>310 76</td>
</tr>
<tr>
<td>Co₂O₄</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>170 76</td>
</tr>
<tr>
<td>CrO₃</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>140 76</td>
</tr>
<tr>
<td>CuO</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>115 20</td>
</tr>
<tr>
<td>CdO</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>12 76</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Pd/SiO₂+oxide</td>
<td>DTA</td>
<td>390 20</td>
</tr>
</tbody>
</table>

*References numbered as in (465).*

aromatic and saturated hydrocarbons (perylene, anthracene, n-octadecanol, perhydrophenanthrene, carbon tetrachloride, and Apiezon N stopcock grease). Robell and Ballou (475) have observed the spillover of hydrogen on uncontaminated Pt-C catalysts, although higher temperatures (>300°C) were used in this work.
Using Electron Spin Resonance (ESR), both Sancier and Inami (457) and Vannice and Neikam (476) have concluded that the species in question is atomic, and not molecular, hydrogen. Similar conclusions were reached by Robell, et al (454), Conesa and Sorla (461), Fleisch and Abermann (464), Sheng and Gay (477), Beck and White (478), and Ambs and Mitchell (472), although Levy and Boudart (458) concluded that the spillover species are actually solvated protons, and Keren and Soffer (473) concluded they are a proton-electron pair.

Using Fourier Transform Infrared Spectroscopy, Conner, et al (479) and Cevallos-Candau and Conner (480) have measured the concentration of deuterium on an IR transparent silica wafer during spillover from a Pt point source. Spillover itself (the breaking of the Pt-D bond) was the rate controlling step, and they estimated a surface diffusion coefficient of $10^{-5} - 10^{-4}$ cm$^2$/sec. Identical results have been reported by Bianchi, et al (481). In a similar IR study of hydrogen spillover from Rh to Al$_2$O$_3$, Cavanagh and Yates (482) found that the rate controlling step was the slow migration across the alumina surface, while hydrogen dissociation on the metal and spillover to the alumina occurred much faster.

Although Sancier (483) and Antonucci, et al (484) have observed that the maximum distances that spillover hydrogen can migrate were in the range 500 to 20,000 Å (0.002 mm), and Gadgil and Gonzalez (485) have argued against spillover outside of the metal-support interfacial region of insulating support oxides, Dmitriev, et al (486) have observed room temperature spillover between 0.5% Pt/NaY zeolite and HNaY zeolite
separated on various transport media by distances of 2 to 8 mm. When various oxides (SiO$_2$, ZnO, Fe$_2$O$_3$) were used as the transport medium, the rate of spillover was independent of the chemical nature of the oxide, while the rate of spillover was greatly reduced over stainless steel. The authors concluded that the surface diffusion of hydrogen must involve the participation of surface groups existing only on metal oxides, not on a metal surface. In addition, these species could not be surface hydroxyl groups, as the various oxides differed strongly in their specific -OH group concentrations, and the diffusion must use only a small fraction of the surface species because the specific surface areas of the oxides employed differed greatly. They concluded that this spillover and surface diffusion occurs with the participation of a small amount of the surface lattice oxygen. In contrast, Chang, et al (487) observed a large support effect on the rate and amount of hydrogen spillover during TPR studies of supported Pd catalysts. The extent of spillover was of the order TiO$_2$ > Al$_2$O$_3$ > SiO$_2$.

Recent reviews by Dowden (488), Bond (489), Teichner, et al (490), Khoobiar (491), and Conner, et al (492) present state of the art knowledge of hydrogen spillover and discuss those areas in which important unanswered questions lie.

Gardes, et al (493), Bianchi, et al (494,495), Teichner, et al (496), Sermon and Lau (497), Saltsburg and Mullins (498), Lenz and Conner (499), Lacroix, et al (500), and Marcq, et al (501) have observed ethylene hydrogenation over silica (494,495,499,500), alumina (493,494,496,497,498), silica-alumina mixtures (497), and hydrogen molybdenum oxide bronzes (501), while El Tanany, et al (502) have
observed n-heptane hydroconversion over H-erionite zeolites, after
contacting with Pt or Ni on alumina and silica supported catalysts in
the presence of gas phase hydrogen. Gadgil and Gonzalez (485) argue
that the amounts of hydrogen spilling over to such oxides is
insufficient to account for the hydrogenation activity observed in the
reports above. In contrast, Baumgarten, et al (503) found that although
HD exchange with support -OH groups through hydrogen spillover took
place, unsaturated carboxylic acids adsorbed on Al₂O₃ in the presence of
a Pt/Al₂O₃ catalyst were not hydrogenated to any detectable degree.

Sancier (483), Antonucci, et al (484) and Ceckiewicz and Delmon
(504) have observed an increase in the rate of benzene hydrogenation to
cyclohexane over alumina supported Pd and Pt catalysts upon dilution
with alumina. It should be noted, however, that the results of Sancier
(483) have been challenged by Vannice and Neikam (505), and refuted by
Sancier (506). Table 14 and figure 17 (483) and table 15 (484) clearly
show this effect, which all three groups proposed was due to atomic
hydrogen spillover to the added alumina, where additional hydrogenation
reactions could take place.

Alternatively, Chou and Vannice (507-509) have concluded that a
modified Langmuir-Hinshelwood model satisfactorily describes the benzene
hydrogenation reaction kinetics over supported and unsupported Pd
catalysts. The enhanced activity they observed over SiO₂-Al₂O₃ and TiO₂
catalysts was attributed to additional benzene adsorption sites located
at the metal-support interfacial regions of these two catalysts.
Subsequently Vannice and Chou (510) concluded that enhanced activity
displayed by titania and silica-alumina supported Pd benzene
Table 14. Hydrogenation of Benzene to Cyclohexane Over the Mixed Catalyst Pd/Al₂O₃ and Al₂O₃ at 150°C (483).

<table>
<thead>
<tr>
<th>Catalysta</th>
<th>Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (mg)</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>55</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>900</td>
</tr>
<tr>
<td>50</td>
<td>950</td>
</tr>
<tr>
<td>25</td>
<td>475</td>
</tr>
<tr>
<td>25</td>
<td>975</td>
</tr>
<tr>
<td>5</td>
<td>995</td>
</tr>
<tr>
<td>1.5</td>
<td>1000</td>
</tr>
<tr>
<td>0</td>
<td>1000</td>
</tr>
</tbody>
</table>

aPd/Al₂O₃ and Al₂O₃ were added separately, mixed, and pretreated at 200°C in H₂ for 2 hrs.

Figure 17. Effect of Diluting Pd-Alumina with Alumina on the Percentage Hydrogenation of Benzene at 150°C (483).
Table 15. 0.31 wt% Pt on \( \gamma \)-\( \text{Al}_2\text{O}_3 \) Variously Diluted with \( \gamma \)-\( \text{Al}_2\text{O}_3 \) (484).

<table>
<thead>
<tr>
<th>Catalyst (g)</th>
<th>( \gamma )-( \text{Al}_2\text{O}_3 ) mg Pt</th>
<th>Conversion (%)</th>
<th>( \text{mol} \text{C}_6\text{H}_6 \times 10^3 ) hr/mg Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/( \text{Al}_2\text{O}_3 )</td>
<td>Al(_2\text{O}_3 ) total per mg Pt</td>
<td>Pt/Al(_2\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>0</td>
<td>6.54</td>
<td>40.0</td>
</tr>
<tr>
<td>0.53</td>
<td>1.58</td>
<td>1.64</td>
<td>26.5</td>
</tr>
<tr>
<td>0.211</td>
<td>1.82</td>
<td>0.65</td>
<td>15.0</td>
</tr>
<tr>
<td>0.100</td>
<td>2.01</td>
<td>0.31</td>
<td>8.0</td>
</tr>
<tr>
<td>0.042</td>
<td>2.07</td>
<td>0.13</td>
<td>5.0</td>
</tr>
<tr>
<td>0.021</td>
<td>2.09</td>
<td>0.06</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Hydrogenation catalysts may be due to hydrogen spillover from the Pd sites to support acidic sites, where reaction with adsorbed benzene could take place. However, the distance that such spillover hydrogen could migrate was assumed small, so that all active support sites were located near the Pd-support interface. It should be noted, however, that these four reports neither cite nor discuss the results and conclusions of the three groups discussed above (483,484,504).

Anderson, et al (511) proposed a model involving the activation of Ti species at the metal support interface on titania supported Ni, Pd, and Ir CO hydrogenation catalysts. Stadler, et al (512) also found enhanced 1,5-hexadiene hydrogenation activity on Pd/TiO\(_2\) catalysts, and concluded it was due to additional reaction occurring at Ti\(^{3+}\) support sites generated by hydrogen spillover from the Pd. Glugla, et al (513) proposed a two site mechanism for CO hydrogenation on Ni/Al\(_2\text{O}_3\) catalysts involving the migration of CO from the Ni to the support.

Sermon, Bond, and Webb (514) have proposed a similar two site mechanism for the hydrogenation of 1-pentene and 1,3-butadiene over
boehmite (AlOOH)/Al₂O₃ catalysts; one site dissociatively adsorbs hydrogen and initiates spillover to the second site, where hydrocarbon adsorption and hydrogenation occurs. Sachtler and Bostelaar (515) proposed an identical mechanism for the hydrogenation of methyl acetoacetate on Ni catalysts, while Gustafson and Kapner (516) observed trichlorosilane adsorption on alumina followed by surface migration to group VIII metal sites where reaction with acetylene took place.

A somewhat analogous case has been reported by Wood and Wise (517), who observed that hydrogen atoms supplied to a gold film by adsorption on and diffusion through a Pd-Ag alloy thimble was active in the hydrogenation of cyclohexane, even though the chemisorption of gaseous hydrogen on gold was negligible at identical conditions.

Frusteri, et al (256) have observed the self-regeneration of deactivated Pt/Al₂O₃ reforming catalysts by reverse spillover of hydrogen from the support, which hydrogenates and removes surface carbonaceous deposits, provided Cl is present on the support also. Fujimoto and Toyoshi (518) reported an increase in the dehydrogenation of cyclohexane and isopentane over metal promoted carbon catalysts due to reverse hydrogen spillover, which promotes the transfer of hydrogen away from the carbon catalyst to the metal where desorption to the gas phase may occur. Lacroix, et al (500) observed the activation of silica aerogel by hydrogen spilled-over from Pt, converting it into a catalyst active in hydrogenolysis, cyclization and cracking at moderate temperatures (170 to 270°C).

Campbell and Mooney (519) observed that support hydrogen participated in ethylene hydrogenation, and that hydrogen from
previously accumulated surface residues is incorporated into ethylene and ethane over Ni/Al₂O₃ and Ni/SiO₂ catalysts at temperatures greater than 423 K. Somorjai and Davis (520) found that carbonaceous residues formed during reforming on Pt single crystal catalysts provide sites on which reaction products are only weakly bound, thereby facilitating desorption, and are capable of storing about 10 times more hydrogen than the clean metal surface. Neikam and Vannice (474, 520) observed that perylene ion radicals act as sinks for migrating hydrogen and serve as bridges permitting hydrogen spillover from Pt black to CeY zeolite catalysts, as do other aromatic and saturated hydrocarbons, including Apiezon N stopcock grease.

Kramer and Andre (521) studied the behavior of atomic hydrogen, produced by both high frequency discharge and spillover from Pt and Ni catalysts, on alumina. They calculated the saturation coverage, coefficient of surface diffusion, and activation energy of this spillover hydrogen. In addition, they found that all of this surface atomic hydrogen was not desorbed by TPD until T = 480°C, which is very close to the temperature of 450°C found necessary by Moses, et al (136) to remove hydrogen which otherwise caused a decrease in ethylene selectivity during the initial period of acetylene hydrogenation. In batch experiments using ¹⁴C labeled ethylene, LeViness (89) found that although this retained hydrogen had no effect on the rate of acetylene consumption (compared to catalysts with no retained hydrogen) some 11 times as much of the observed increase in ethane production came from ethylene hydrogenation as from direct hydrogenation of acetylene. He therefore concluded that this hydrogen was retained on the alumina
support, and that the observed decrease in ethylene selectivity was due primarily to ethylene hydrogenation taking place there.

Similarly, Weiss, Guzzi, and various coworkers (138-142) have recently proposed that the decrease in total ethylene selectivity observed during continuous operation of Pd on alumina acetylene hydrogenation catalysts is the result of surface polymer assisted hydrogen migration, rather than spillover which connotates hydrogen saturation on the source, to the alumina support where sites for ethylene hydrogenation may be generated. The possible roles of spillover species, particularly hydrogen, during hydrogenation reactions has been reviewed and discussed in great detail by Hodnett and Delmon (522).

Accepting that ethylene hydrogenation may occur on alumina and/or silica supports in the presence of hydrogen spillover under conditions where it would not otherwise occur, the question that remains is the actual nature of the active sites on the support surface.

Numerous authors have reported two distinct forms of adsorbed ethylene on alumina, which are characterized by the strength of adsorption in each case, and together cover 2-3% of the alumina surface (532-529). Yates and Lucchesi (530) also observed two types of adsorbed acetylene, which they proposed were associated with surface hydroxyl groups (-OH). The adsorption capacities of both acetylene and ethylene were unaffected by the presence or absence of the other, suggesting that independent sites are involved. In addition, no evidence of surface mobility of either compound on alumina was observed under any conditions, suggesting that acetylene-ethylene surface diffusion effects
on alumina supported catalysts are insignificant, contrary to the conclusions of Weiss and Bell (531).

The presence or absence of surface hydroxyl groups was observed to have no effect on ethylene adsorption by Hinden and Weller (523,524), Yates and Lucchesi (530), Weller and Montagna (532), and Knozinger and Ratnasamy (445), all of whom concluded that sites for ethylene adsorption and reaction are surface defects, perhaps formed by dehydroxylation (523,524). In contrast, Peri (533) concluded that Lewis acid sites, formed during removal of the last 30 to 40% of surface hydroxyl groups, are responsible for the strong adsorption and isomerization activity of 1-butene. Similar conclusions were reached by Webb (534) during studies of 1-diphenylethylene, 2-butene, and ethylene adsorption on silica-alumina cracking catalysts.

Although acetylene hydrogenation over alumina has not been reported, Heaviside, et al (219) reported the room temperature polymerization of acetylene over alumina. Bhasin, et al (535) found a slow self-hydrogenation and polymerization reaction during acetylene adsorption on Al₂O₃, which they felt occurred on Lewis and/or Bronsted acid sites. Galuszka and Amenomiya (327) observed a strong perturbation in the IR characteristics of alumina hydroxyls during acetylene adsorption on Ni/Al₂O₃ catalysts.

Ethylene hydrogenation is known to occur at temperatures greater than about 200°C (445,523,526,528,536), and Amenomiya, et al (527) observed room temperature hydrogenation if ethylene was preadsorbed. Experiments in the presence and absence of added transition metal and
halogen impurities showed that this was not an artifact, but an intrinsic property of the alumina used.

Amenomiya, et al (524,525,527,528,536) have also shown that of the two types of sites for ethylene adsorption on alumina; type 1 account for 60% of the total number, are less active than type 2 sites, and are active in ethylene hydrogenation. Type 2 sites account for the remaining 40% of the surface sites, are more active than type 1 sites, and are active in the room temperature polymerization of ethylene, the rate of which they found proportional to the gas phase ethylene pressure, and not the amount adsorbed. It should be noted that no polymerization products were observed in the gas phase during reaction or catalyst evacuation, but only after flash desorption to temperatures greater than 250°C (254).

Rosynk and Hightower (537) found evidence for at least two types of active sites on gamma alumina, the first of which were active for hydrogen exchange with olefins and aromatics and could be totally poisoned by CO₂. The second type were active for olefin isomerization and were not affected by CO₂. In addition, TPD studies indicated the existence of two types of adsorption sites which were not responsible for the observed isomerization and exchange activity.

IR spectra conducted be Lucchesi, et al (538) have shown the existence of both $\text{H}_2\text{C}=\text{CH}_2$ and $\text{H}_3\text{C}=\text{CH}_3$ upon ethylene adsorption on alumina, indicating some degree of self-hydrogenation, and concluded that hydrogenation takes place through half hydrogenated species formed by atomic hydrogen addition, in agreement with the conclusions of Yates and Lucchesi (530) and Amenomiya, et al (527). Asmolov and Krylov
(539), however, have ascribed the primary UV absorption band formed upon ethylene, propylene, and 1-butene adsorption on alumina to an alkenylcarbonium ion.

Because trans-2-butene (540) and propylene (541) adsorption measurements on alumina showed identical capacities as ethylene adsorption (524), Amenomiya, et al (524,540,541) concluded that these sites are physically separated, rather than existing in clusters, as no steric effects were observed with increasing molecular size. In agreement with this result, they found evidence suggesting that ethylene polymerization occurs by a Twigg-Rideal mechanism between adsorbed and weakly physisorbed or gas phase ethylene (489,483).

Based upon the results discussed above, we must accept the possibility that the decrease in ethylene selectivity observed during acetylene hydrogenation over alumina and/or silica supported Pd catalysts may be at least partly due to a hydrogen spillover induced activity of the alumina support for ethylene hydrogenation.
F. **Bimetallic/Alloy Catalysts for Acetylene Hydrogenation**

It is possible to modify the Pd atoms in the typical Pd on alumina catalysts both electronically and geometrically by the addition of a second metal. This effect has been observed in many different alloy catalyst systems and for several different hydrocarbon reactions ([48, 370, 542–559]). Figure 18 shows this effect on acetylene hydrogenation activity and activation energy for various Pd-Au alloys, while tables 16 and 17, and figures 19 and 20, show this effect on the rate of ethylene hydrogenation over Pd-Sn, Pt-Sn, Pd-Pt, and Pd-Ag alloys, respectively. Campbell and Emmett ([561]) found similar results for ethylene hydrogenation activity of Pd-Ag alloys, and in addition variations in both the activation energy and reaction order in ethylene.

The presence of a second metal in the Pd crystal structures, yielding Pd-X ensembles, would result in a decrease in the Pd site
Table 16. Conversion of Hydrogenation of Ethylene (Pd-Sn-Silica) and Benzene (Ni-Sn-Silica) (562).

<table>
<thead>
<tr>
<th>Pd/Sn</th>
<th>C₂H₄ to C₂H₆</th>
<th>Ni/Sn</th>
<th>C₆H₆ to cyclo-C₆H₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>∞</td>
<td>100</td>
<td>∞</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>0.3</td>
<td>28</td>
<td>2.5</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 17. Relative Activity of Pt-Alumina and Pt-Sn-Alumina Catalysts (563).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt-Alumina</th>
<th>Pt-Sn-Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenolysis of ethane</td>
<td>4.66</td>
<td>1.0</td>
</tr>
<tr>
<td>Activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dehydrogenation of cyclohexane</td>
<td>36.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogenation of ethylene</td>
<td>14.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 19. Ethylene Hydrogenation Activity per Site vs. Pd in Pd/Pt Alloys (564).
density, and thus a decrease in those reactions requiring multiple metal sites (543, 566, 567). Clarke (567) predicted that such alloying should decrease the relative rate of acetylene polymerization, if, as assumed, this reaction requires the presence of two acetylene molecules adsorbed on neighboring sites. We would also expect that other reactions requiring multiple surface sites, such as the formation of ethylidyne (which requires three) would be suppressed.

Palczewska, et al (568, 569) observed that the addition of Pb to Pd(111) surfaces results in the formation of bidimensional ordered surface clusters of a Pd₃Pb phase presursor or compound which exhibits a high and very stable ethylene selectivity. On this type of catalytic surface, acetylene adsorbed in a weakly bound molecular form, while its dissociative adsorption and the adsorption of both hydrogen and molecular ethylene were strongly suppressed. Zakumbaeva, et al (370)
found that the addition of Cd to Pd black catalysts increased the selectivity of acetylenic alcohol hydrogenation (propargyl alcohol, 1-butyn-3-ol, 2-butyne-1,4-diol, tetramethyl butynediol) to the olefinic species and suppressed the subsequent hydrogenation to paraffinic ones.

Dowden, et al (570) studied the effects of added Re on hydrogen spillover over Pt/Al₂O₃ catalysts. They observed a critical Re/Pt ratio, somewhere between 60:40 and 80:20, where the amount of Re was sufficient to prevent spillover to the alumina. The authors concluded that this critical ratio was that at which each metal particle consisted of either Pt completely surrounded by Re, or Pt ensembles isolated in a continuous Re matrix, thus blocking spillover from the Pt to the support. This interpretation is consistent with the observations of Dmitriev, et al (486), that rapid spillover occurs only on oxide species and is very slow over stainless steel.

Electronic effects of a second, added metal on Pd are much more difficult to predict. Abon, et al (571) have observed that acetylene is much more strongly adsorbed than ethylene over Pt₅₀Ni₅₀(111) surfaces, while the difference was much less marked on Pt(111). The acetylene hydrogenation rate was enhanced by the presence of Ni, which the authors believed consistent with a decrease in adsorption strength. Curiously, the selectivity for ethylene was not enhanced over the alloy catalyst; the authors expected it would be if the selectivity were controlled by the energetics of competitive acetylene-ethylene adsorption. They therefore concluded that the thermodynamic factor of Bond and Wells (78,79,85) was not operative here. However, in light of the fact that ethane may be formed directly from acetylene (the mechanistic factor
(78,79,85)), we might instead conclude that the thermodynamic factor (complete monopolization of the surface by acetylene) was indeed active over both catalysts, preventing ethylene hydrogenation to ethane at all times, while the percentage of acetylene forming ethane was unaffected by alloying.

Palczewska, et al (572) have investigated the addition of boron to Pd-black 2-butyne and phenylacetylene hydrogenation catalysts and reported a well pronounced increase in (Z)-2-butene selectivity from 2-butyne upon hydrogen pretreatment or heat treatment. These treatments induced a distinct boron surface segregation into two surface boron states, dubbed an "oxide" and a "boride" by the authors. Tamaki, et al (180) observed a similar increase in ethylene selectivity upon the addition of both boron and phosphorus to Pd-film acetylene hydrogenation catalysts, particularly after heat treating samples with high B or P concentrations. This selectivity enhancement was explained by the low electron density of Pd, the small ensemble size, and the appearance of Pd₃B, Pd₄,P or Pd₅P₂ phases upon heat treatment.

A similar unequal effect of alloying on metal-hydrocarbon bond strengths for alkynes and olefins has been observed on other alloy systems (566,567). Because data are lacking on many alloy systems in different hydrocarbon reactions, it is usually not possible to predict the nature and effects of such interactions prior to experimental observations.

Palazov, et al (573) have recently observed the effects of both electronic and geometric alterations by Sn addition to Pt/Al₂O₃ catalysts in the adsorption and hydrogenation of ethylene, 1-hexene, and benzene.
Similar effects have been reported by Briggs, et al (574) during ethylene hydrogenation over unalloyed Pt catalysts, caused by the nature of the different oxide supports used. Changes in the chemical state and local environment of Pd and Ir catalysts dependent upon metal concentration, nature of the support, drying temperature, and reduction conditions have been reported by Bozon-Verduraz, et al (575).

Although not usually treated as a topic in alloy or bimetallic catalysis, it appears that the major effects of strong metal support interaction (SMSI) are indeed due to some degree of bimetallic interaction between platinum metals and various support species, particularly TiO₂, which may form an overlayer during moderate or high temperature H₂ treatment (576). Juszczyk, et al (577) reported that high temperature (723-873 K) reduction of Pd/SiO₂ catalysts resulted in the formation of Pd silicide species, which caused an increase in the isomerization selectivity of neopentane. High temperature reduction of titania and ceria supported Pd showed similar changes; alumina, magnesia and lanthana supported Pd underwent only minor modifications.

Zakumbaeva, et al (578) and Sokolskii, et al (579) found that the formation of PdZn and Pd₂Zn₃ intermetallic compounds on Pd/ZnO catalysts rendered them inactive for isoprene hydrogenation. Babenkova, et al (580) related changes in hydrogen chemisorption behavior to SMSI on Ce, Pd, and Ce-Pd on Al₂O₃ catalysts.

Demmin, et al (581) deposited a titania overlayer on Pt, Rh, and Pd foils and a niobia layer on Pt. The rate of CO methanation over the titania and niobia covered Pt was identical to that observed over a conventional Pt/TiO₂ catalyst, suggesting the presence of such an
overlayer on the latter. More complicated interactions between supports, including titania, and Ni, Pd, and Ir have been reported by Anderson, et al (582).

The general effects of adding a second metal to a supported metal catalyst of low metal loading has been discussed in detail by Gucci (583), Sinfelt (157,582), and Gucci and Schay (547).

A very serious problem is the almost complete lack of understanding of the behavior of supported bimetallic catalyst systems in which the metal contents are very low. The actual alloy composition may not be even close to the nominal Pd/X (X is the second metal) ratio, due to incomplete contact (mixing) between the two metals during impregnation, and/or surface enrichment (segregation) effects, particularly during elevated temperature catalyst activation (278,599).

Margitfalvi, et al (549) have recently reviewed the preparation of supported bimetallic catalysts prepared by controlled surface reactions, and their catalytic properties in a number of hydrocarbon reactions, including benzene hydrogenation. Their results promise much greater control of the actual surface alloy composition, and may in the future overcome the problems discussed above. However since they have not yet been applied to acetylene hydrogenation catalysis, no conclusions can be made.

Another serious problem is that methods for characterizing the degree of alloying and the degree of metal dispersion of bimetallic acetylene hydrogenation catalysts, where the total Pd metal loading is usually much less than 0.1 wt%, are completely lacking. Thus, any change in reaction behavior observed upon the addition of a second metal
may not be directly related to changes in the catalyst surface structure. The previously discussed investigations of Weiss, Guzzi, and various co-workers (89,137-143), and the more recent review of this and other work by Guzzi and Schay (547) clearly illustrate this problem. They observed that the addition of Cu, and to a lesser degree Sn, to conventional 0.04 wt% Pd/Al₂O₃ hydrogenation catalysts caused a significant decrease in the overall rate of ethane formation, a decrease in the catalyst activity, and a marginal decrease in selectivity for oligomer formation. The authors have interpreted these results as the effects of Cu covering part of the Pd surface, thereby decreasing catalyst activity and the dissociative adsorption of acetylene, in agreement with the observations of Palczewska, et al (568,569) on Pd-Pb catalysts. In addition, they concluded that the copper may block the spillover of hydrogen to the support where it could react with adsorbed ethylene, in agreement with the results of Dowden, et al (570), and may hinder the formation of surface oligomeric species, thought to facilitate hydrogen transport to the support.

All of these conclusions appear very reasonable in light of previous investigations. Yet, it must be stressed that apart from the changes in reaction activity and selectivity values, there is no independent evidence for any degree of interaction between the Pd and added Cu and Sn. From the reported changes in the reaction behavior, it seems correct to assume some degree of bimetallic interaction, but the extent of this interaction has not be quantified in any way.

It is clear that the use of bimetallic catalysts represents perhaps the best method of improving catalyst stability and selectivity
to the desired product, ethylene, during acetylene hydrogenation. However, until methods for characterizing the degree and the type of interaction present between the two metals are established, the scientific (though not industrial) usefulness of reaction data gathered on these catalysts will remain limited. Recent results from at least one research laboratory (584) suggest that the solution to this problem may be shortly attained.
G. The Role of Added Carbon Monoxide.

Carbon monoxide is commonly added to acetylene selective hydrogenation feedstocks in amounts near 1000 ppm, particularly those with high hydrogen to acetylene ratios (front-end mixtures), where the ethylene selectivity would be very poor in its absence (31, 89). Investigations on the effects of added CO have consistently shown uniformly high ethylene selectivities, particularly when added to catalysts exhibiting very low or negative values (net ethylene consumption) prior to its addition (37, 108-112, 138, 139, 142, 568). The rate of acetylene consumption may be decreased by only a small amount (37, 108-112, 142, 568), or by as much as 100 times (138, 139), apparently depending on the gas phase hydrogen pressure. In addition, the deactivation of catalysts used during operation with CO has been reported under conditions where no deactivation was observed in its absence (138, 139, 142). A number of different proposals have been made to explain this behavior.

McGown, et al (108, 109) found that amounts of CO less than about 578 ppm had little effect on the rate of acetylene hydrogenation, but sharply reduced the rate of ethane production; amounts greater than 1155 ppm resulted in a very slow rate of ethylene hydrogenation after all acetylene had been consumed (in batch reactions). They concluded that 2 distinct types of Pd sites existed on the catalysts they used, one on which either acetylene or ethylene could adsorb and react on, but on which acetylene was adsorbed 2200 times more strongly than ethylene, and one on which only ethylene could adsorb and react. They interpreted the
results of CO addition as caused by CO blocking these second, ethylene only, sites.

Al-Ammar and Webb (110-112) also observed a decrease in the rate of ethane production upon CO addition. Upon investigating the simultaneous adsorption of $^{14}$CO, $^{14}$C$_2$H$_2$, and $^{14}$C$_2$H$_4$, they found that all 3 compounds adsorbed in approximately the same amounts, regardless of the presence or absence of either, or both, of the others. Hydrogen adsorption, however, was drastically reduced by prior CO adsorption, and resulted in the displacement of a small amount of the preadsorbed CO. These authors had earlier postulated the existence of three distinct types of Pd sites on their catalysts, one on which acetylene reacted to form ethylene, the second to form ethane, and the third ethylene to form ethane. They therefore concluded that the effects of CO were caused by its competition with hydrogen, resulting in a reduced surface hydrogen concentration and thus higher ethylene selectivities. They also postulated almost complete hydrogen occlusion between the acetylene only and ethylene only sites to explain the usually high ethylene selectivity values observed. It is unclear how CO could prevent ethylene hydrogenation so exclusively, as acetylene consumption was affected much less severely, by simply blocking the adsorption of hydrogen.

Palczewska, et al (568) studied the thermal desorption spectra of hydrogen, acetylene, ethylene, and CO from a number of different Pd single crystal surfaces. They observed that CO blocked the surface for both hydrogen and ethylene, although acetylene could displace it and react. Similarly, Ratajczykowa and Szymerska (585) observed that adsorbed CO blocks the part of a Pd(111) surface that is not covered by
acetylenic residues and which would otherwise be active for ethylene adsorption and hydrogenation, and decreases the accessibility of hydrogen on the surface. Pope, et al (586) found that CO concentrations as low as 0.5 to 2.5 ppm could completely poison Pd-charcoal catalysts in the low temperature hydrogenation of ethylene.

LeViness, et al (138) observed that the addition of 60 ppm CO to tail-end (low hydrogen/acetylene) mixtures sharply decreased the rate of ethylene hydrogenation to ethane, and amounts > 500 ppm completely terminated it. Under the same conditions the rate of acetylene consumption was only marginally lowered (table 18). Weiss, et al (139)

<table>
<thead>
<tr>
<th>CO (ppm)</th>
<th>Rate C₂H₂ (mole/gcat/s)</th>
<th>C₂H₂ Conversion (%)</th>
<th>Selectivity (%) C₃H₄ C₂H₆ C₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.30 x 10⁻⁸</td>
<td>72.3</td>
<td>-4.2 76.6 26.8</td>
</tr>
<tr>
<td>58</td>
<td>3.18 x 10⁻⁸</td>
<td>69.5</td>
<td>38.7 27.8 33.3</td>
</tr>
<tr>
<td>114</td>
<td>3.14 x 10⁻⁸</td>
<td>68.7</td>
<td>43.0 23.5 33.4</td>
</tr>
<tr>
<td>224</td>
<td>2.98 x 10⁻⁸</td>
<td>65.2</td>
<td>52.0 15.9 31.9</td>
</tr>
<tr>
<td>439</td>
<td>2.62 x 10⁻⁸</td>
<td>57.4</td>
<td>60.7 8.5 30.9</td>
</tr>
<tr>
<td>843</td>
<td>2.38 x 10⁻⁸</td>
<td>52.0</td>
<td>65.5 5.3 28.9</td>
</tr>
<tr>
<td>1650</td>
<td>1.76 x 10⁻⁸</td>
<td>38.5</td>
<td>64.8 2.0 33.1</td>
</tr>
<tr>
<td>3240</td>
<td>1.50 x 10⁻⁸</td>
<td>32.8</td>
<td>70.0 1.3 28.0</td>
</tr>
<tr>
<td>6340</td>
<td>1.27 x 10⁻⁸</td>
<td>27.8</td>
<td>74.1 0.9 25.0</td>
</tr>
<tr>
<td>12500</td>
<td>9.82 x 10⁻⁹</td>
<td>21.5</td>
<td>75.2 0.5 24.3</td>
</tr>
</tbody>
</table>

and LeViness (89) studied the effects of 800 ppm added CO on both front and tail end hydrogenation mixtures. While this CO addition reduced the rate of acetylene consumption by a factor of about 3 in a tail end mixture (hydrogen/acetylene = 1.5), it reduced the rate by almost 2 orders of magnitude when added to a front end mixture.
(hydrogen/acetylene > 15). As the selectivity to C₄ and higher hydrocarbons was only marginally affected, the authors concluded that this reduction in rate was due to competition between CO and hydrogen. Thus the surface hydrogen concentrations were assumed to be nearly the same in the presence of 800 ppm CO, while in its absence, the surface hydrogen concentration of the catalyst used with the front end mixture would be much higher. In addition, these authors concluded that the decrease in the rate of ethylene hydrogenation to ethane observed at very low CO concentrations, where no decrease in the rate of acetylene consumption was observed, was due to CO preventing hydrogen spillover to the support, where it could react with adsorbed ethylene. LeViness (89) has also suggested that CO may compete with ethylene for adsorption sites on the alumina support.

Because many of the conclusions about the role of added CO reported above are inferred from overall reaction rate measurements, and not supported by any direct observations of catalyst – CO interactions, it would seem important to review the related literature on the behavior of CO in catalytic hydrocarbon reactions to try to gather evidence supporting or contradicting these inferences.

The reaction of carbon monoxide and hydrogen to form higher hydrocarbons over platinum group metals is well known (587-592). Chemisorption on Pd(110) at 110 and 300 K (593) showed only associatively adsorbed CO predominantly in two-fold bridged sites along the rows of metal atoms. Studies of this reaction over supported Pd catalysts have shown that at temperatures up to 300°C, CO adsorption is substantially nondissociative (594). Benziger (595) estimated the
dissociative heat of adsorption of CO on Pd as > 25 KJ/mole, and the 
heat of molecular adsorption as -130 to -142 KJ/mole. Extended Hückel 
Molecular Orbital calculations of Rong, et al (596) were in general 
agreement with these observations. Rieck and Bell (597) recently 
concluded that the dissociation of CO is the rate limiting step on Pd, 
and that the hydrocarbon product is essentially all methane, regardless 
of the H₂/CO ratio.

In contrast, Lunsford (598) observed the selective formation of 
methanol, as did Poels, et al (599) and Kikuzono, et al (600), who also 
observed small amounts of methane, over supported Pd catalysts prepared 
from M₂PdCl₄ complexes (M = Li, Na, K, Rb, Cs). The catalyst activity and 
selectivity were very dependent on the type of alkali metal cation 
present on each sample. Different behavior for methanol and methane 
formation led them to conclude that different sites were operating in 
each case. Thermal desorption spectra showing more than one distinct 
peak led Efromov, et al (601) to conclude the existence of at least two, 
and probably more, energetically different adsorption forms of CO on Pd.

Berube, et al (602) recently studied the Pd catalyzed CO 
hydrogenation to methanol. They too found evidence for more than one 
type of active site. They, however, concluded that the second type was 
a unique site located at the Pd-support interface, and the number and 
characteristics of this type of site was extremely dependent on the 
nature of the support. The total number of these sites was always 
small, as those supports sites at large distances from Pd crystallites 
did not participate in the reaction. Anderson, et al (511) also 
concluded that Ti species near the metal support interface on titania
supported Ni, Pd, and Ir were responsible for the enhanced CO hydrogenation activity of these catalysts. Bailey, et al (603) and Glugla, et al (513) found similar evidence for the existence of two types of sites during CO hydrogenation on Ni/Al₂O₃ catalysts. Kramer, et al (604) made a similar proposal for the reaction on Pt/silica, as did Sen and Falconer (605) over Ru/Al₂O₃.

Fajula, et al (606) studied the hydrogenation of CO over Pd supported on different silicas and on HY and NaY zeolites. Methanol was produced on catalysts exhibiting small Pd crystallites, on which CO was only weakly adsorbed, while the formation of methane was related to the acidic site density of the support. Thomson and Wolf (607) concluded that hydrocarbon synthesis from CO and hydrogen over Pd/ZSM-5 catalysts occurs via a bifunctional route, with methanol formation on Pd followed by conversion of this methanol to higher hydrocarbons on zeolite Bronsted acid sites.

Mitchell and Vannice (608) reported the formation of methanol and dimethyl ether over a series of rare earth oxide supported Pd catalysts. The results showed a large support effect on both activity and selectivity, and indicated that large fractions of the Pd surface were blocked by the oxide support. Ilinich, et al (609) observed that the addition of acidic (H₃PO₄) promoters to silica supported Pd and Rh catalysts improved the yield of CO hydrogenation to methanol, while the addition of alkaline (NaOH) promoters improved the yield of ethanol. Hinderman, et al (610) correlated the methanol activity of Pd-MgO-SiO₂ catalysts with the concentration of surface formyl species, and proposed
that the reaction between CO and hydrogenation takes place on oxidized Pd in the vicinity of the support or promotor.

The structure of dense CO overlayers on a number of surfaces, including Pd(100) has been investigated by Uvdal, et al (611).

Unfortunately, because Pd is not a particularly active methanation catalyst, the number of investigations on its role in this reaction are limited. Still, Vannice and Garten (612) have found that the activity of certain Pd-Al₂O₃ catalysts may be only a factor of 3 less than those for typical Ni methanation catalysts, and argued that the use of Pd may be justified by other physical and chemical considerations (particularly that Ni catalysts may form the volatile and toxic Ni(CO)₄), but it does not appear that many have accepted this suggestion.

However, hydroformylation reactions between CO and olefins are well known (613,614). Tsuji and co-workers (615-619) observed the Pd catalyzed homogeneous carbonylation of acetylene to form muconyl chloride, fumaryl chloride, maleyl chloride, and ultimately methyl muconate (615), the carbonylation of ethylene to form ethyl propionate and ethyl β-ethoxypropionate (616) and various other reaction of propargyl chlorides, acetylenic alcohols, and vinyl and allyl chlorides (616-619). More recently, Tsuji, et al (620) reported the homogeneous Pd catalyzed carbonylation of 1-octyne to methyl 2-methyleneoctaneote, and of diphenylacetylene and 4-octyne to various monoesters. Lapidus and Pirozhkov (621) observed the carboxylation of olefins by CO₂ in the presence of Pd and Rh complexed catalysts. Ethylene carboxylation produced propionic acid, ethanol, and various hydration products.

Bhattacharvya and Sen (622) observed the formation of acrylic acid and
ethyl acrylate from acetylene, CO, and water or ethanol over Ni and Fe salts.

Watson and Somorjai (623) studied the hydrogenation of CO over rhodium oxide catalysts and found that the addition of ethylene to the reaction mixture resulted in its conversion to propionaldehyde. Morris, et al (624) observed the incorporation of both ethylene and propylene added to H₂/CO mixtures over supported ruthenium catalysts. Jordan and Bell (625–627) studied the effects of adding ethylene, propylene, and 1-butene to H₂/CO mixtures, also over supported ruthenium. The efficiency of the olefins in producing monomers active in chain growth were in the order C₂H₄ > C₃H₆ > C₄H₈. With increasing olefin pressure, hydrocarbon formation from CO was suppressed. As the rate of olefin homologation increased with olefin pressure, the overall rate of higher molecular weight hydrocarbons was enhanced. Hydroformylation of ethylene to propanal and 1-propanol (625), propylene to butanal and butanol (626), and 1-butene to pentanal and pentanol (627) was also observed.

Over similar Ru catalysts, however, Kobori, et al (628) observed that most added olefin is hydrogenated to the corresponding parrafin, and only a small fraction is incorporated into the higher molecular weight products. Kellner, et al (629) added ethylene in amounts corresponding to those usually found in the exit streams of CO hydrogenation reactors, and observed no subsequent effects. Increasing the ethylene concentration by 20 to 40 times did result in an increase in the production rates of C₃ and C₄ species, but those of C₆ and higher species decreased to a greater extent.
Hall, et al (630), Dwyer and Somorjai (631), and Barrault, et al (632) all observed the incorporation of added ethylene into C₃ and higher hydrocarbons during CO hydrogenation over Fe catalysts, although Hall, et al (630) found the percentage incorporated during addition of propanol and propionaldehyde much higher than ethylene. Bonzel, et al (633) found that although CO insertion did occur during polymerization of acetylene over Fe foil, it was not necessary for hydrocarbon chain growth, which could be initiated and propagated by acetylene alone. Eidus (634) has reported hydrocondensation reactions of CO and various light olefins over Co catalysts at 190 to 200°C.

Lin and Knifton (635) have recently investigated the oxidative carbonylation of 1,3-butadiene and propylene, and the hydrodimerization of 1,3-butadiene over Pd catalysts. Carbonylation of 1,3-butadiene yielded predominantly dimethyl hex-3-ene-1,6-dioate and methyl 5-methoxy-3-pentenoate; propylene gave predominantly dimethyl α-methylsuccinate. The hydrodimerization of 1,3-butadiene yielded mostly 1,6-octadiene and 4-vynylcyclohexene, with a small amount of 1,7-octadiene. Lines and Long (636) investigated the carbonylation of acetylene by palladium iodide/sodium iodide in n-butanol mixtures. A number of n-butyl esters, mostly the succinate and acrylate, with decreasing amounts of the fumarate, propionate and maleate, were observed during the reactions of CO/C₂H₂ = 1.60 mixtures at 75°C. Medema and Van Helden (637) reported the formation of n-dodeca-1,3,6,10-tetraene and 1,3,7-octatriene from the reaction of butadiene and CO in benzene in the presence of a π-allyl Pd acetate catalyst. Kaneda, et al (638) observed
the formation of C₅ alcohols from the reaction between CO and 1-octene over homogeneous Rh complexes.

Sakai, et al (639) found that CO poisoned the desorption of hydrogen from Pd wires, which they concluded was caused by CO blocking the surface sites where H atoms recombine, while Conrad, et al (640) observed the complete displacement of hydrogen from Pd surfaces during co-adsorption with CO. Noordermeer, et al (641-643) found that CO adsorption hampers hydrogen adsorption, displaces previously adsorbed hydrogen to the bulk, and is unaffected by pre or post hydrogen treatment, on Pd(111), Pd₀.₇Cu₀.₃(111), and Pd₅₀Ag₅₀(111). The adsorption capacities of both CO and hydrogen on the alloys were always smaller than the pure Pd sample. Kiskinova, et al (644) also observed that the presence of CO favored mainly hydrogen penetration into the bulk rather than its desorption. Guo, et al (645) report a similar effect during CN adsorption on Pd(111).

Apple and Dybowsk (646) observed that preadsorption of CO inhibited the formation of spillover hydrogen on Rh/TiO₂ catalysts, even while the total hydrogen uptake increased by forming a new species observed by NMR. They proposed that the presence of bidentate carbonyl species at points where the dissociative adsorption of hydrogen occurs inhibited the formation of the spillover species. Cavanagh and Yates (482) found that CO chemisorption on alumina supported Rh caused a marked reduction in the rate of hydrogen spillover to the support due to site blockage on the Rh.

In recent studies of the adsorption heats of hydrogen and CO on silica, alumina, and titania supported Pd, Chou and Vannice (647-649)
and Vannice (650) observed that although the values of $Q_{ads}$ were not affected by the nature of the support or by the Pd crystallite size in the range of 3 to 1000 nm, they increased sharply as the crystallite size dropped below 3 nm. The value of $Q_{ads}$ for hydrogen in the range 3 to 1000 nm was 15 kcal/mole, and for CO it was 22; on crystallites smaller than 3 nm, maximum values of 24 and 35 kcal/mole, respectively, were obtained. For all crystallite sizes CO was more strongly adsorbed than hydrogen. In contrast Chen, et al (651) observed a hydrogen adsorption heat of only 13.7 KJ/mole (3.3 Kcal/mole) on Pd/Al$_2$O$_3$ catalysts. Christmann (422) reported a hydrogenation adsorption heat of 24 Kcal/mole on the Pd(100) surface, and 21 Kcal/mole on Pd(111).

Although we could find no information on the relative strengths of CO and ethylene adsorption on alumina, Khodakov, et al (529) have observed the displacement of both ethylene and hydrogen by CO on lanthanum oxide catalysts, which suggests that similar behavior might be expected on alumina.

The data presented above clearly show that we would expect CO to compete successfully with hydrogen for adsorption sites, thereby reducing the surface hydrogen concentration, increasing the selectivity and decreasing the reaction rate. If the hydrogenation of ethylene takes place on the support due to activation by hydrogen spillover, then CO could conceivably decrease the rate of this reaction by blocking the spillover hydrogen and perhaps by blocking ethylene adsorption on the support. The incorporation of CO into the surface polymers would also be expected, as might the production of methane from CO, which was suspected, though not detected, by Battison, et al (652) during studies
of selective acetylene hydrogenation in the presence of added CO. The only examples of CO displacement of ethylene (568, 585) were conducted on Pd single crystals, and the results may not apply to highly disperse supported samples. At the present time, there is simply not enough evidence to support either conclusion.

Perhaps the most important effect of added CO has not yet been covered. This is the decrease in the rate of acetylene consumption upon CO addition, particularly in mixtures with high hydrogen concentrations. Although the reasons may not be readily apparent, it is not desirable to have a very active catalyst for selective acetylene hydrogenation (4). Because of the very low outlet acetylene concentration specifications for polyethylene production (< 10 ppm (22, 30-38)), every commercial reactor will reach conditions where the reaction rate of acetylene becomes acetylene pore diffusion controlled at some point before the end of the catalyst bed. In batch reactions with very high hydrogen to acetylene ratios, LeViness (89) and LeViness, et al (138) have observed that the rate of ethylene hydrogenation after complete acetylene consumption is some 10 times faster than the prior rate of acetylene hydrogenation. Thus, if even a small number of surface sites become available for ethylene hydrogenation, the observed selectivity for ethylene production may quickly become negative (net ethylene consumption), and because of the exothermic nature of both reactions, temperature runaway is a real possibility (and became a real reality in one laboratory experiment (89)).

Therefore, although commercial reactors are operated at the lowest temperatures feasible with water cooling, the activity of Pd catalysts
is still commonly too high (33). The addition of Pb (Lindlar type catalysts) and CO are used to decrease the surface reaction rate even more, as well as poison the catalyst activity for ethylene hydrogenation even in the absence of acetylene (33). Low metal loadings and eggshell type impregnation profiles contribute further to reduce the acetylene pressure at which pore diffusion control begins (33).

The addition of CO is also not without its problems. Both McGown, et al (110) and Sarkany, et al (141) have observed that the selectivity to gas phase oligomers passes through a broad maximum as CO concentration increases, and although there is no experimental evidence at the present time, we might expect that the selectivity to surface oligomers behaves similarly. Thus, while catalysts operated in the presence of CO deactivate under conditions were they would not in its absence (89,142), we might also expect that the operational lifetime of catalysts used in the presence of CO would be decreased, necessitating more frequent regeneration cycles. The increase in gas phase oligomer concentration may also contribute to the real problems of reactor fouling and plugging (33).

Huang (51) studied the effects of small changes in process variables on the optimization of acetylene hydrogenation in excess ethylene. At optimal conditions, a 1% increase in CO feed concentration resulted in a 15% increase in outlet acetylene and a 6% decrease in ethylene loss, while a 1% decrease in feed CO resulted in a 20% decrease in outlet acetylene and a 6% increase in ethylene loss. As increases in outlet acetylene cannot be tolerated due to downstream product specifications (22,30-38), and ethylene is the desired product, the loss
of which must be minimized, we must agree with Sarkany, et al (142),
that the optimization of the CO concentration is of crucial importance
in the continuous operation of a selective hydrogenation plant.
H. Literature Review Summary

The reaction between acetylene and hydrogen over Pd catalysts takes place on sites associated with Pd. Regardless of the possibility that ethylene hydrogenation takes place on support sites through hydrogen spillover from Pd, there is no evidence of a similar support effect on the reaction of acetylene (table 19). The reported values of K vary widely, perhaps because of differences in metal dispersion, the possible existence of β-phase hydrides in some cases, and/or errors introduced by the kinetic equation used to calculate K (first order hydrogen, zero order acetylene), but no trends indicating substantially higher K values with increasing support/Pd ratios (except perhaps small increases that can be explained by increasing metal dispersion) are apparent.

The active sites which catalyze this reaction are almost certainly not bare Pd. The results of Inoue, et al (103,107), Al-Ammar and Webb (110-112) and Moses, et al (136) show that the behavior of Pd catalysts is very dependent on the nature of the hydrocarbon species to which it is first exposed. This conclusion is consistent with the proposal of Thomson and Webb (102) that some hydrocarbon species associated with surface metal sites acts as an active intermediate in catalyzing the reaction, although we cannot definitely conclude that this species transfers hydrogen to adsorbed hydrocarbons. This conclusion is also consistent with single crystal studies which have shown that the surface of a working hydrocarbon conversion catalyst is composed of disordered
and/or ordered hydrocarbon species over and around the surface of the active metal (291-295,300).

Table 19. First Order (Hydrogen) Rate Constants Reported in the Literature.

<table>
<thead>
<tr>
<th>Catalyst (wt% Pd)</th>
<th>System</th>
<th>T (K)</th>
<th>P_t (torr)</th>
<th>P_H2 (torr)</th>
<th>P_C2H2 (torr)</th>
<th>K (mol/mol<em>torr</em>min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>PFR</td>
<td>273</td>
<td>3 atm</td>
<td>17.3</td>
<td>8.0</td>
<td>3.77</td>
<td>(132)</td>
</tr>
<tr>
<td>0.04</td>
<td>Batch</td>
<td>293</td>
<td>54.9</td>
<td>6.2</td>
<td>3.1</td>
<td>0.0123</td>
<td>(108)</td>
</tr>
<tr>
<td>0.04</td>
<td>Batch</td>
<td>293</td>
<td>100</td>
<td>30.8</td>
<td>15.0</td>
<td>0.0129</td>
<td>(136)</td>
</tr>
<tr>
<td>0.04</td>
<td>FFR</td>
<td>293</td>
<td>760</td>
<td>110</td>
<td>3.9</td>
<td>0.044</td>
<td>(89)</td>
</tr>
<tr>
<td>0.038</td>
<td>CSTR</td>
<td>295</td>
<td>760</td>
<td>1.8</td>
<td>0.73</td>
<td>0.132</td>
<td>(141)</td>
</tr>
<tr>
<td>0.04</td>
<td>Batch</td>
<td>296</td>
<td>670</td>
<td>101</td>
<td>6.9</td>
<td>0.032</td>
<td>(89)</td>
</tr>
<tr>
<td>5.0</td>
<td>Batch</td>
<td>298</td>
<td>50</td>
<td>37.5</td>
<td>12.5</td>
<td>0.0109</td>
<td>(110)</td>
</tr>
<tr>
<td>0.058</td>
<td>Batch</td>
<td>298</td>
<td>15 atm</td>
<td>3420</td>
<td>82</td>
<td>0.0161</td>
<td>(192)</td>
</tr>
<tr>
<td>0.04</td>
<td>CSTR</td>
<td>298</td>
<td>760</td>
<td>1.62</td>
<td>1.37</td>
<td>0.094</td>
<td>(229)</td>
</tr>
<tr>
<td>0.04</td>
<td>CSTR</td>
<td>298</td>
<td>760</td>
<td>1.37</td>
<td>1.16</td>
<td>0.185</td>
<td>(229)</td>
</tr>
<tr>
<td>5.0</td>
<td>Batch</td>
<td>298</td>
<td>50</td>
<td>37.5</td>
<td>12.5</td>
<td>0.364</td>
<td>(110)</td>
</tr>
<tr>
<td>1.0</td>
<td>Batch</td>
<td>303</td>
<td>514</td>
<td>332</td>
<td>182</td>
<td>0.0247</td>
<td>(72)</td>
</tr>
<tr>
<td>0.04</td>
<td>Batch</td>
<td>305</td>
<td>670</td>
<td>101</td>
<td>6.9</td>
<td>0.059</td>
<td>(89)</td>
</tr>
<tr>
<td>10</td>
<td>Batch</td>
<td>309</td>
<td>600</td>
<td>400</td>
<td>200</td>
<td>0.00070</td>
<td>(70)</td>
</tr>
<tr>
<td>0.04</td>
<td>Batch</td>
<td>315</td>
<td>670</td>
<td>101</td>
<td>6.9</td>
<td>0.131</td>
<td>(89)</td>
</tr>
<tr>
<td>0.038</td>
<td>CSTR</td>
<td>328</td>
<td>760</td>
<td>1.60</td>
<td>0.81</td>
<td>1.02</td>
<td>(141)</td>
</tr>
<tr>
<td>0.038</td>
<td>CSTR</td>
<td>351</td>
<td>760</td>
<td>0.74</td>
<td>0.46</td>
<td>8.50</td>
<td>(141)</td>
</tr>
<tr>
<td>0.04</td>
<td>PFR</td>
<td>353</td>
<td>760</td>
<td>106.4</td>
<td>4.9</td>
<td>1.32</td>
<td>(144)</td>
</tr>
<tr>
<td>0.04</td>
<td>PFR</td>
<td>353</td>
<td>760</td>
<td>2.51</td>
<td>1.9</td>
<td>1.32</td>
<td>(144)</td>
</tr>
<tr>
<td>0.04</td>
<td>CSTR</td>
<td>353</td>
<td>760</td>
<td>0.30</td>
<td>0.63</td>
<td>1.73</td>
<td>(139)</td>
</tr>
<tr>
<td>0.038</td>
<td>PFR</td>
<td>353</td>
<td>10 atm</td>
<td>104</td>
<td>82.2</td>
<td>1.98</td>
<td>(4130)</td>
</tr>
<tr>
<td>0.038</td>
<td>CSTR</td>
<td>366</td>
<td>760</td>
<td>0.37</td>
<td>0.22</td>
<td>22.6</td>
<td>(141)</td>
</tr>
</tbody>
</table>

The nature of this surface hydrocarbon species is presently unknown. If it is an ordered structure, as envisioned by Thomson and Webb (102), Al-Ammar and Webb (110-112), and Davis, et al (300), ethylidyne would appear to be a likely candidate, as Davis, et al (300) have proposed. However, the only well defined Pd surface on which
ethyldyne formation has been observed is the Pd(111) surface
(317,320,321,323,324,331), which has three fold symmetry (table 20). The

Table 20. Surface Species Formed Upon Acetylene
and/or Ethylene Adsorption on Pd.

<table>
<thead>
<tr>
<th>Pd Type</th>
<th>T (K)</th>
<th>Method</th>
<th>Adsorbate</th>
<th>Structures Observed</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pd/alumina</td>
<td>298</td>
<td>$^{13}$C NMR</td>
<td>C$_2$H$_4$</td>
<td>H$_2$C=CH$_2$ H=C=CH $\equiv$C=CH$_2$</td>
<td>(325)</td>
</tr>
<tr>
<td>5.8% Pd/silica</td>
<td>290</td>
<td>IR</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH $\equiv$C=CH$_2$</td>
<td>(262)</td>
</tr>
<tr>
<td>5.8% Pd/alumina</td>
<td>290</td>
<td>IR</td>
<td>C$_2$H$_4$</td>
<td>H$_2$C=CH$_2$ $\equiv$C=CH$_3$</td>
<td>(326)</td>
</tr>
<tr>
<td>9% Pd/alumina</td>
<td>195</td>
<td>IR</td>
<td>C$_2$H$_4$</td>
<td>H$_2$C=CH$_2$ $\equiv$C=CH$_3$</td>
<td>(326)</td>
</tr>
<tr>
<td>10% Pd/Alumina</td>
<td>300</td>
<td>IR</td>
<td>C$_2$H$_4$</td>
<td>H$_2$C=CH$_2$ $\equiv$C=CH$_3$</td>
<td>(326)</td>
</tr>
<tr>
<td>Pd Membrane</td>
<td>363</td>
<td></td>
<td>C$_2$H$_4$</td>
<td>H$_2$C=CH$_2$ $\equiv$C=CH$_3$</td>
<td>(326)</td>
</tr>
<tr>
<td>Pd</td>
<td>150</td>
<td>UPS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd</td>
<td>300</td>
<td>UPS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd</td>
<td>140</td>
<td>UPS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd</td>
<td>115</td>
<td>EELS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>80</td>
<td>EELS</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>H$_2$C=CH$_2$ H$_2$C=CH$_2$</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>100-300</td>
<td>EELS</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>H$_2$C=CH$_2$ H$_2$C=CH$_2$</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>110</td>
<td>EELS</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>H$_2$C=CH$_2$ H$_2$C=CH$_2$</td>
</tr>
<tr>
<td>Pd(110)</td>
<td>&lt;180</td>
<td>UPS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>293</td>
<td>UPS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>300</td>
<td>EELS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>300</td>
<td>EELS</td>
<td>C$_2$H$_2$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>310</td>
<td>UPS</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>300</td>
<td>IR</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>175</td>
<td>UPS</td>
<td>C$_2$H$_4$</td>
<td>H=C=CH</td>
<td>C$_4$H$_6$</td>
</tr>
</tbody>
</table>

small number of investigations on the relative hydrogenation activities of different Pd surfaces have found that the activity of Pd(111) is substantially lower than that of Pd(220) for acetylene hydrogenation (150), and some ten times lower than Pd(110) for butadiene hydrogenation (285). Beebe and Yates (305) and Moshin, et al (306) have observed that ethylene hydrogenation over supported Pd and Pt catalysts occurs at identical rates whether or not ethyldyne is present. These results
suggest that even though ethylidyne may be an active species in hydrogenation reactions over Pd(111), other species formed on different Pd surfaces are more active, and hence the Pd(111)-ethylidyne surface may not be a particularly good hydrogenation catalyst (150).

Any definite conclusions on the true nature of the active surface species is hampered by the very limited amount of data available, as few detailed surface investigations have also included catalyst activity measurements. Studies of catalytic hydrogenation reactions have usually been conducted on catalysts that could not be well defined (e.g. low loaded supported Pd). This problem is made more acute by the lack of understanding of how low pressure, single crystal surface observations relate to high pressure reactions over polydisperse catalysts.

The chemical nature of the Pd itself is also not easily defined. At hydrogenation conditions, it is certainly Pd(0), not some higher oxidation state. However, it could also exist as an α- or θ-phase hydride (149,340,398) or as a supersaturated Pd-C phase (435,441-443). If the assignments of XRD peak deformations and displacements made by Borodziński, et al (398) are correct, than the θ-phase hydride is more active, and less ethylene selective than the α-phase. However, if Stachurski and Frackiewicz (435) are correct in concluding that the XRD data represent the formation of a supersaturated Pd-C phase, than it is more active and less ethylene selective that the α-phase hydride and/or bare Pd.

Unfortunately, Stachurski and Frackiewicz (435) did not investigate the relative activity of this Pd-C phase compared to Pd. Ratajczykowa (433), however, did observe that the transformation of weakly bound
ethylene to C-\text{CH}_2\text{ over Pd(111)} - \text{C was almost an order of magnitude faster than over Pd(111). At the present time, the conditions (temperature, hydrogen and acetylene pressures, surface carbon concentration, metal crystallite size, etc.) at which the two hydride phases and/or the supersaturated carbon phase exist, and their effects on the activity and product selectivities of Pd acetylene hydrogenation catalysts, must be considered relatively unknown.}

Regardless of the nature of the actual catalytically active sites, the mechanism of acetylene hydrogenation itself is fairly well understood. Studies of the reaction between acetylene and deuterium (75, 76, 88, 133-135) have shown that the formation of ethylene proceeds through the stepwise addition of hydrogen atoms to an adsorbed acetylene molecule (most likely associatively adsorbed), forming first HC=CH, then adsorbed ethylene, which desorbs. Ethane formation also proceeds through the stepwise addition of hydrogen atoms. Whether this results simply from the addition of hydrogen to adsorbed ethylene, in a continuation of the hydrogenation mechanism described above, or from addition to fundamentally different adsorbed acetylene species (such as ethylidyne (134-136)) is not completely clear.

The mechanism proposed by Wells (116) to explain butane formation during butadiene hydrogenation, whereby butane is formed near pockets of occluded hydrogen, is perhaps applicable to the formation of ethane from acetylene as well. We have no data regarding the ability of Pd to occlude hydrogen, but in light of the very low butane selectivities observed during Pd catalyzed butadiene hydrogenation (125-131), it must be very small if Wells's mechanism is correct. The very small ethane
selectivities over Pd - 1 to 5% of the consumed acetylene as observed by $^{14}$C labeling (108,112,133-135,138-141,143) - are in good agreement with this proposal, and indicate that there is little room for catalyst improvement in this area.

Nakatsuji and Hada (653) and Nakasuji, et al (654) recently conducted theoretical studies of acetylene hydrogenation on Pd. Using ab initio quantum chemical methods with a cluster model, they concluded that a two step Langmuir-Hinshelwood mechanism involving a vinyl radical reaction intermediate is more energetically realistic than a one step Langmuir-Hinshelwood or Eley-Rideal mechanism. Calculations of the energetics of surface species confirmed the higher affinity of acetylene versus ethylene on Pd, and suggested that the observed selectivity also arises from the production of different surface species during adsorption of the two hydrocarbons.

There is good agreement in the literature that the reaction is first order in hydrogen (table 21), although the value of the acetylene order is controversial. A positive order in hydrogen is consistent with the observation that hydrogen addition to adsorbed species is the rate limiting step, although depending on which addition (to $\text{HC}=\text{CH}$ or $\text{HC}=\text{CH}_2$) is rate limiting, orders other than one may be theoretically calculated. A negative order in acetylene, particularly when observed at acetylene pressures lower than those where zero order behavior is observed (89,134,135,138), may represent the formation of a more reactive adsorbed acetylene species, or may be due to higher surface hydrogen concentrations, with either occurring because of less than complete acetylene coverages. At very low acetylene pressures, ethylene may be
Table 21. Reported Kinetic Parameters for Acetylene Hydrogenation

<table>
<thead>
<tr>
<th>Catalyst (wt% Pd/support)</th>
<th>T (°C)</th>
<th>(P_T) (atm)</th>
<th>(E_{act}) (Kcal/mol)</th>
<th>(H_2) (order)</th>
<th>(C_2H_2) (order)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/pumice</td>
<td>36</td>
<td>0.79</td>
<td>12-15</td>
<td>1.0</td>
<td>-0.4</td>
<td>-0.7</td>
</tr>
<tr>
<td>1/γ-alumina</td>
<td>30</td>
<td>0.68</td>
<td>12</td>
<td>1.0</td>
<td>-1.0</td>
<td>(72)</td>
</tr>
<tr>
<td>5/α-alumina</td>
<td>20</td>
<td>0.26</td>
<td>-</td>
<td>1.42</td>
<td>-</td>
<td>(77)</td>
</tr>
<tr>
<td>5/α-alumina</td>
<td>0-30</td>
<td>0.20</td>
<td>11</td>
<td>1.0</td>
<td>-0.55</td>
<td>(86)</td>
</tr>
<tr>
<td>5/silica</td>
<td>25</td>
<td>0.066</td>
<td>-</td>
<td>1.0(^a)</td>
<td>(110-112)</td>
<td></td>
</tr>
<tr>
<td>0.1/γ-alumina</td>
<td>25</td>
<td>3.04</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>(132)</td>
</tr>
<tr>
<td>0.058/α-alumina</td>
<td>25</td>
<td>15</td>
<td>6</td>
<td>1.0</td>
<td>0</td>
<td>(192)</td>
</tr>
<tr>
<td>0.04/γ-alumina</td>
<td>80</td>
<td>1.0</td>
<td>13</td>
<td>1.0</td>
<td>0</td>
<td>(144)</td>
</tr>
<tr>
<td>0.04/γ-alumina</td>
<td>19.5</td>
<td>1.0</td>
<td>10</td>
<td>1.0</td>
<td>-0.4(^b)</td>
<td>(89,138)</td>
</tr>
<tr>
<td>0.04/γ-alumina</td>
<td>25</td>
<td>0.13</td>
<td>10</td>
<td>1.0</td>
<td>0</td>
<td>(136)</td>
</tr>
<tr>
<td>0.04/γ-alumina</td>
<td>20</td>
<td>0.072</td>
<td>11.2</td>
<td>-</td>
<td>-</td>
<td>(108)</td>
</tr>
<tr>
<td>0.038/γ-alumina</td>
<td>22</td>
<td>1.0</td>
<td>15-19</td>
<td>-</td>
<td>-</td>
<td>(141)</td>
</tr>
</tbody>
</table>

\(^a^\)first order in total pressures.  
\(^b^\)complicated behavior including a maximum in rate vs. pressure.

able to compete for surface sites and react to form ethane, or the reaction of acetylene may become diffusion limited. Both drastically lower the observed ethylene selectivity.

The formation of \(C_4\) and higher hydrocarbons is also primarily associated with Pd sites, as \(C_4\) selectivities are remarkably unaffected by large changes in Pd metal loadings (table 8, p. 67). Several authors have reported the room temperature polymerization of acetylene on alumina (219,220), but the extent of reaction is very small. The limited number of investigations of the composition of the \(C_4\) fraction (86,89,138) further supports this conclusion, as the concentration of n-butane (0 to 5%) matches the selectivity to ethane from acetylene only, as observed by \(^{14}\)C labeled species. The extent of gas phase oligomerization products is generally in the range 20-40% (table 8). Most investigations considering the formation of \(C_4\), gas phase and/or
surface polymers have observed it, although it has rarely been quantified (table 22).

<table>
<thead>
<tr>
<th>Catalyst (wt% Pd/support)</th>
<th>T (°C)</th>
<th>Pt (atm)</th>
<th>SC₄</th>
<th>SC₄⁺</th>
<th>Surf.</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/pumice</td>
<td>36</td>
<td>0.79</td>
<td>20</td>
<td>10</td>
<td>yes</td>
<td>(70)</td>
</tr>
<tr>
<td>5/α-alumina</td>
<td>0-30</td>
<td>0.20</td>
<td>37</td>
<td>trace</td>
<td>-</td>
<td>(86)</td>
</tr>
<tr>
<td>1.0/γ-alumina</td>
<td>30</td>
<td>0.68</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>(72)</td>
</tr>
<tr>
<td>Pd</td>
<td>100-200</td>
<td>8-40</td>
<td>5-28</td>
<td>yes</td>
<td>yes</td>
<td>(37)</td>
</tr>
<tr>
<td>0.1/γ -alumina</td>
<td>25</td>
<td>3.04</td>
<td>-</td>
<td>-</td>
<td>no</td>
<td>(132)</td>
</tr>
<tr>
<td>0.058/α-alumina</td>
<td>25</td>
<td>15</td>
<td>no</td>
<td>no</td>
<td>-</td>
<td>(192)</td>
</tr>
<tr>
<td>0.04/γ -alumina</td>
<td>80</td>
<td>1.0</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>(144)</td>
</tr>
<tr>
<td>0.04/γ -alumina</td>
<td>19.5</td>
<td>1.0</td>
<td>20-30</td>
<td>trace</td>
<td>(yes)</td>
<td>(89)</td>
</tr>
<tr>
<td>0.04/α -alumina</td>
<td>25</td>
<td>1.0</td>
<td>25</td>
<td>-</td>
<td>yes</td>
<td>(229)</td>
</tr>
<tr>
<td>0.04/γ -alumina</td>
<td>25</td>
<td>1.0</td>
<td>25</td>
<td>-</td>
<td>yes</td>
<td>(229)</td>
</tr>
<tr>
<td>0.04/γ -alumina</td>
<td>25</td>
<td>0.13</td>
<td>yes</td>
<td>yes</td>
<td>(yes)</td>
<td>(136)</td>
</tr>
<tr>
<td>0.04/γ -alumina</td>
<td>20</td>
<td>0.072</td>
<td>no</td>
<td>no</td>
<td>(no)</td>
<td>(108)</td>
</tr>
<tr>
<td>0.038/γ -alumina</td>
<td>22</td>
<td>1.0</td>
<td>25-35</td>
<td>2.5-3.5</td>
<td>2</td>
<td>(141)</td>
</tr>
<tr>
<td>0.038/α-alumina</td>
<td>80</td>
<td>10</td>
<td>9</td>
<td>1</td>
<td>(yes)</td>
<td>(190)</td>
</tr>
<tr>
<td>0.035/θ-alumina</td>
<td>37.5</td>
<td>5</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>(194)</td>
</tr>
</tbody>
</table>

yes = observed but not quantified. no = investigated and not observed. - = not investigated and/or not reported.
(yes) = presence suspected, though not directly observed.
(no) = presence discounted, though not by direct observation.

The mechanism of polymer formation is also unclear. Sheridan (67) proposed a free radical mechanism for acetylene polymerization during hydrogenation on Ni. It is possible that this mechanism also applies to the reaction catalyzed by Pd, but the free radical species has never been observed. The remarkably similar values of C₄ selectivities...
observed over many different Pd catalysts indicate that polymer formation and hydrogenation are related in some fundamental way. Polymer formation may arise from the production of certain dissociated species formed in the course of acetylene adsorption or from the surface geometry of adsorbed molecules. Polymer formation is almost always observed during acetylene hydrogenation, and any mechanism of hydrogenation must successfully address this condition.

The initial extent of surface oligomer formation is at least 2-5% of the total acetylene consumed, but may be 5 or more times higher (see p. 62). Regardless of its initial value it decreases during subsequent operation (141,194). We would expect this as any catalyst pellet has a finite capacity (the catalyst porosity) for liquid and/or solid polymeric species. However, this behavior has been investigated only rarely, and many questions about the structure, extent, and effects of these species remain.

Ethylene hydrogenation over aged supported catalysts in the presence of acetylene concentrations sufficient to terminate it on unsupported or freshly oxidized and reduced supported Pd catalysts definitely can occur (108,112,138-141). This requires the conclusion that surface sites active only in the adsorption and hydrogenation of ethylene exist. From this information, these sites could be either different Pd sites (108,112) or alumina support sites (138-141). If these sites are Pd, they would most likely represent a different Pd crystal face upon which acetylene cannot adsorb, or one on which the strengths of adsorption of acetylene and ethylene are comparable. Because of the high ethylene/acetylene ratio common in selective
acetylene hydrogenation reactions, the result is the same in either case.

The rate of ethylene hydrogenation is initially very small, and increases during catalyst operation (108,112,132,136-141); these sites must be physically separated and a mechanism for their gradual activation must be found. The observations that surface hydrocarbon species may promote hydrogen spillover (148,295,474,520) fulfill the latter requirement, regardless of the nature of the ethylene only site. The requirement that the different types of sites be physically separated is met if ethylene only sites are on the support. Reconciling Pd ethylene only sites with this requirement is more difficult, and has not been accomplished at this time.

A decrease in the observed ethylene selectivity may also be observed at conditions where the reaction is acetylene pore diffusion limited. In batch reactions, the point at which this occurs is clear because the rate of pressure drop increases sharply as large scale ethylene hydrogenation begins (70,77,89,108,110-112,138). However, under continuous flow conditions -CSTR or PFR - it is possible to envision pseudo steady state conditions where only a small number of Pd sites are available for ethylene hydrogenation and reaction. In the absence of nonisothermal conditions in the catalyst pellet (reactor runaway because of the high rate of ethylene hydrogenation (89)), it may not be readily apparent that the resulting decrease in ethylene selectivity is due to such pore diffusion effects. In addition, $^{14}$C labeling will show that most of the ethane is produced from ethylene, as it does when ethylene reacts on ethylene only sites.
Such conditions may readily occur if the rate of surface polymer formation is as high as it appears it may be (p. 62), for the catalyst pore diameter will decrease as surface species build-up. In this case, however, we should expect that further operation will eventually show a decrease in acetylene hydrogenation activity, as diffusion effects become more pronounced with increasing polymer loadings.

Most investigations on the continuous operation of low loaded Pd catalysts have observed a decline in observed ethylene selectivities, although several have reported a decrease in catalyst activity at higher reactant pressures and/or longer operation times. For similar catalysts, there appears to be a relationship between the total amount of acetylene reacted per gram catalyst and the extent of this deactivation (table 23), but the amount of data is small. Deactivation caused by the build-up of polymeric species on the catalyst surface would certainly explain this apparent trend, as those that did not deactivate did not react enough acetylene to produce polymer sufficient to block the catalyst pores. This may also explain the deactivation always observed over catalysts of high Pd loadings (70,77,110-112).

A decrease in ethylene selectivity during deactivation has been reported (70), but in the other cases, it has remained fairly constant (77,86,110-112). This may be due to a different distribution of Pd crystal faces at high versus low loadings (assuming ethylene only sites are Pd), or the much smaller alumina/Pd ratio at high loadings (assuming ethylene only sites are the alumina). Unfortunately, ethylene selectivities observed during deactivation of low loaded catalysts were not reported (190,194).
Table 23. Selectivity and Activity Changes Reported During Operation Of Pd Selective Acetylene Hydrogenation Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>System Type</th>
<th>$t$</th>
<th>$T$</th>
<th>$\Delta$Sel$^b$</th>
<th>$\Delta$Act$^c$</th>
<th>Moles $\text{C}_2\text{H}_2$ Reacted</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9%/pumice</td>
<td>batch</td>
<td>8</td>
<td>36</td>
<td>dec.</td>
<td>0.05</td>
<td>0.0398</td>
<td>0.442</td>
</tr>
<tr>
<td>5%/α-alumina</td>
<td>batch</td>
<td>-20</td>
<td>inc.</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>(86)</td>
</tr>
<tr>
<td>5%/α-alumina</td>
<td>batch</td>
<td>8</td>
<td>25</td>
<td>const.</td>
<td>0.125</td>
<td>0.0287</td>
<td>0.574</td>
</tr>
<tr>
<td>5%/silica</td>
<td>batch</td>
<td>12</td>
<td>25</td>
<td>const.</td>
<td>0.125</td>
<td>0.0430</td>
<td>0.867</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>batch</td>
<td>4</td>
<td>20</td>
<td>dec. const +</td>
<td>0.00012</td>
<td>0.309</td>
<td>(108)</td>
</tr>
<tr>
<td>0.04%/α-alumina</td>
<td>CSTR</td>
<td>101</td>
<td>25</td>
<td>dec. ±</td>
<td>0.0034</td>
<td>8.64</td>
<td>(229)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>batch</td>
<td>18</td>
<td>25</td>
<td>dec. + -</td>
<td>0.0040</td>
<td>10.16</td>
<td>(136)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>CSTR</td>
<td>105</td>
<td>22</td>
<td>dec const +</td>
<td>0.00525</td>
<td>13.82</td>
<td>(141)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>CSTR</td>
<td>138</td>
<td>25</td>
<td>dec. ±</td>
<td>0.0079</td>
<td>19.75</td>
<td>(229)</td>
</tr>
<tr>
<td>0.1%/γ -alumina</td>
<td>PFR</td>
<td>737</td>
<td>25</td>
<td>dec. const +</td>
<td>0.0176</td>
<td>17.6</td>
<td>(132)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>CSTR</td>
<td>105</td>
<td>55</td>
<td>dec const +</td>
<td>0.0352</td>
<td>92.6</td>
<td>(141)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>CSTR</td>
<td>55</td>
<td>78</td>
<td>dec const +</td>
<td>0.078</td>
<td>194</td>
<td>(141)</td>
</tr>
<tr>
<td>0.04%/γ -alumina</td>
<td>CSTR</td>
<td>103</td>
<td>93</td>
<td>dec. const +</td>
<td>0.186</td>
<td>490</td>
<td>(141)</td>
</tr>
<tr>
<td>0.038%/α-alumina</td>
<td>PFR</td>
<td>120</td>
<td>80</td>
<td>?</td>
<td>0.87</td>
<td>5.08</td>
<td>13400</td>
</tr>
<tr>
<td>0.035%/θ-alumina</td>
<td>PFR</td>
<td>800</td>
<td>37</td>
<td>?</td>
<td>0.50</td>
<td>129</td>
<td>369000</td>
</tr>
</tbody>
</table>

a For batch systems, number shown is number of reactions.
b Selectivity change: dec. = significant decline
   inc. = significant increase
   const = no significant change
   ? = not reported
c Activity change: number = ratio of final over initial K.
   const + = constant conversion, K increases due to $\Delta$Sel.
   $\pm$ = decrease in conversion, K increases due to $\Delta$Sel.
   + - = K increases in first 10, decreases in next 8.

Contrary to the conclusions of Wells (80), the behavior of Pd
cetylene hydrogenation catalysts is better understood in the presence
of CO than in its absence. CO definitely competes with hydrogen,
reducing the surface hydrogen concentration (89,110-112,138,142). This
apparently also reduces the hydrogen supply to ethylene-only sites,
regardless of their actual nature. It may also compete with ethylene for Pd and/or alumina adsorption sites, but the data are inconclusive. At high CO concentrations, the reaction of acetylene is also inhibited (table 18, p. 125), most likely through further reduction in the surface hydrogen concentration.

Catalysts operated in the presence of CO invariably deactivate from the start of reaction (89,109,138,142). Sarkany, et al (142) have shown that this is not due to simple site blocking and/or pore plugging, but is instead due to carbonyl groups in the resulting surface polymers which can effectively compete with acetylene for surface sites. There is no evidence that the extent of surface polymer formation in the presence of CO is significantly higher than in its absence (as proposed by Plante and Weiss (190)), only that the extent of deactivation caused by a unit weight of polymer formed in the presence of CO is higher (142).

The addition of a second metal, such as Pb (568,569), Ni (571), B (180,572), P (180), or Cu (89,137-141), to Pd results in catalysts which are more stable (lower rates of deactivation and/or ethylene selectivity decline) and generally more ethylene selective. This may be due to geometric isolation of Pd in an matrix of inactive metal which could reduce the production of species requiring multiple adsorption sites (543,566,567), reduce the extent of hydrogen spillover (570), and/or electronically alter the nature of the adsorbed species (568,569) or the relative strengths of acetylene and ethylene adsorption (571). The use of bimetallic or alloy catalysts appears to represent the best method of increasing catalyst lifetime and ethylene yields during selective
acetylene hydrogenation, but until methods for characterizing low loaded bimetallic catalysts are developed, they will be of little scientific use.

We can summarize the areas of acetylene hydrogenation phenomena in which significant questions remain. The first is the actual value of the reaction order in acetylene. The results of Margitfalvi, et al (134,135), LeViness (89) and LeViness, et al (138) (figure 8, p.38) suggest that although the reaction is zero order at acetylene pressures greater than about 8 torr, at lower pressures the reaction rate increases (negative order behavior) until it reaches a maximum at 1-2 torr acetylene, and thereafter decreases to zero (positive order behavior). These results were obtained on Pd-black (134,135) and one type of 0.04 wt% Pd/γ-Al₂O₃ (89,138). It would be desirable to investigate the acetylene reaction order over a wider variety of catalysts throughout the pressure range 0 to 10 torr. This may be done most easily by initial rate batch experiments. An accurate form of the kinetic equation will allow a better comparison of rate constant and activation energy data from the literature than is possible now.

The next area deserving further investigation involves the surface polymer formed in the absence of CO. Except for the results of Yajun, et al (194) - which seriously lack the details of their experimental procedure - the structure of this polymer is unknown. We might suspect the presence of even numbered linear and branched paraffins, along with some degree of mono- and perhaps di- and higher olefins, as well as possibly polyacetylene or similar high polymer precursors. The former species should be easily extracted in a hydrocarbon solvent such as
benzene or hexane. Suitable GC or GC/MS analysis will reveal their composition. The latter may be much harder to identify, but certain techniques (resonance Raman spectroscopy, TEM, SEM, IR, and MAS \(^{13}\text{C NMR}\)) exist and have been successfully used before. Only Yajun, et al (194) have reported polymer formation from ethylene as well as acetylene, but the details of this observation are not available. Most polymer appears to come from acetylene.

The extent of surface polymer formation is currently unknown. The results of Sarkany, et al (141) and Yajun, et al (194) place a minimum limit of 2.5-5% of the acetylene consumed, but their data suggest that the actual value may be significantly higher. As discussed previously (p. 66), any significant value of surface polymer selectivity will lower the apparent ethylene selectivity calculated assuming polymer formation is negligible. If it is not negligible, many of the reported ethylene selectivity values must be considered suspect. The extent of polymer formation may be measured directly by employing the pan of an electronic microbalance as the catalyst chamber and directly monitoring the weight increase during subsequent acetylene hydrogenation reactions. A reactor of this type has recently been used by Sarkany (254) to measure the extent of irreversible hydrocarbon adsorption during n-hexane conversions on Pt-black.

The effects of the surface polymer on catalyst activity and product selectivities are currently unclear. This question may be investigated in the same manner and at the same time as the surface polymer selectivities detailed above. Care must be taken to construct the equipment so that weight gain and catalyst activity/selectivity
measurements can be conducted simultaneously, to avoid the problems
encountered by LeViness, et al (138) and Sarkany, et al (141). These
investigators calculated surface polymer selectivities using two ideally
comparable experiments and sets of results, one with only weight gain
measurements, the other only gas phase reactant and product analysis.

The causes of catalyst deactivation and/or selectivity decline may
also come out of the above experiments, as the formation of polymer has
been implicated in both types of behavior. The effects of various
hydrogen and/or oxygen treatments on the amount of surface polymer and
subsequent catalyst activity and selectivities can be easily observed in
such a system.

The question of whether ethylene-only sites are a type of Pd or
support site might be answered by measuring both the overall and
intrinsic (from acetylene only) ethane and ethylene selectivities over a
series of catalysts of widely different metal loadings and/or similar
metal loadings on supports of different surface areas, or of very
different metal dispersions. If the ethylene only sites are the alumina
support and if the entire support is active, we should observe a large
effect on the overall ethylene selectivity by changing the alumina/Pd
to be or the alumina surface area. Changing the Pd metal dispersion
should have little or no effect. If the active alumina sites are only
those at or near the Pd-alumina interface (as proposed during
investigations of other systems (483,484,510,511,513,602,603)) we would
expect to see very little change in ethylene selectivities over any of
the different catalyst samples.
If, however, ethylene only sites are a different type of Pd, we should expect large differences in ethylene selectivities over samples of widely different dispersions. Changes in metal loadings and support surface areas will change ethylene selectivities only to the extent that they alter the metal dispersion and/or the stability of the different Pd surfaces.

The following report details the author's investigations of selective acetylene hydrogenation over Pd/alumina catalysts in an attempt to resolve some of these questions.
III. EXPERIMENTAL SECTION

A. Apparatus and Procedure

The reactor system constructed for this work appears in figure 21.

Figure 21. Reactor Apparatus.
It consisted of an all glass (8 mm ID) circulation loop connected through glass-stainless steel transition tubes and stainless steel flex tubes to a Perkin-Elmer TGS-2 Thermogravimetric Analyzer (TGA). Glass valves with teflon stopcocks (0-5 mm) controlled the path of gas flow throughout the glass portions of the reactor; stainless steel valves throughout the remainder. The TGA-Heise gauge (CC-88775, 0-1000 mm Hg absolute) connecting line was 3/16" (ID) stainless steel. All gas feed lines were 1/8 or 1/4" stainless steel. Stainless steel Swagelock fittings were used on all stainless tubing connections. Vacuum and/or stopcock grease was not used in any part of the system inorder to avoid any possible promotion of hydrogen spillover, as reported by Neikam and Vannice (474,520). In accordance with this principle, and to avoid mercury poisoning of the Pd, a turbomolecular vacuum pump (Leybold-Heraus Turbvac 150 with a Turbotronik NT-150/360 controller), rather than an oil or mercury diffusion pump, was employed.

The system volume was determined by pressure rise versus time measurements during filling from 10 torr to one atmosphere pressure with mass flow controller calibrated hydrogen and helium flows. Volumes of individual sections were measured by pressure changes during expansion from known volumes (see Appendix D, p. 527). The total system volume, from inlet valves 17,18,19, and 20 to the vent valve 14 and vacuum valves 10,13, and 16, was 2600 cc. The hydrocarbon inlet section volume (valves 1 through 17,18, and 19) was 83 cc. The outlet sample section volume (valves 7 through 14,15, and 16) was 53 cc. The Heise gauge and connecting lines volume (valves 10,11, and 15 through the gauge tube) was 157 cc. The total TGA volume (valves 4 and 6 through 11 and 20) was
2100 cc. Of this volume, the reactor chamber and connections to the circulation loop (valves 4 and 6 through the bottom of the wide hang down tube on the left of the TGA) accounted for 110 cc. The volume of the recirculation pump section (valves 2 and 3 to the pump) was 35.5 cc. The volume of the circulation loop itself was 171 (volume between valves 1, 7 and 9 (3, 4, and 6 closed, 5 open) was 75.5 cc; volume between valves 2 and 9 (13 closed) was 95.5 cc).

After numerous glass leaks had been detected and repaired, the measured TGA leak rate (initial pressure drop 1 atm to 4 μm, measured with a Leybold-Heraeus Thermotron TM 113 thermocouple gauge controller and a L-H 88671 TC gauge tube) was 182 μm/day. This corresponds to a leak rate of 5.60 X 10^{-6} std.cc/min. The TGA manufacturer reports a nominal leak rate through the TGA of 1 X 10^{-6} std.cc/min. The measured circulation loop leak rate was 965 μm/day (2.51 X 10^{-6} std.cc/min). The entire system leak rate was 332 μm/day (1.28 X 10^{-5} std cc/min).

Therefore the Heise gauge, circulation pump, and inlet and outlet lines leak rate was about 4.69 X 10^{-6} std.cc/min.

Reactor gas flows were set and monitored by factory calibrated mass flow controllers (Brooks 5850C series, see Appendix D, p. 547 for factory calibration reports). We measured flow rates of all flow controllers at a wide variety of settings; no deviations from factory calibrations were observed except with the HC gas flow controller. This unit was factory calibrated for ethylene. The gas mixture used in this work was only about 80% ethylene. Acetylene and hydrogen made up most of the remaining 20%. The flow controllers operate by comparing the gas temperature at two locations in the controller. The observed
temperature depends on the nature and the flow rate of the gas. The thermal conductivities of acetylene and ethylene (0.020 vs. 0.0178 W/min*K (657)) are very similar, but those of ethylene and hydrogen (0.0178 vs 0.182 W/min*K (657)) are not. The actual flow rate of the hydrocarbon mixture was calculated from the composition of reactor outlet streams with known He flow rates. The observed HC flow rate was always 15-20% higher than the flow controller readout for ethylene only.

A single tank of hydrocarbon reaction gas mixture was used throughout this work (Linde/Union Carbide custom mixture). The composition was 7.739% acetylene, 0.0255% ethane, 13.18% hydrogen, CO, H2S < 1 ppm, balance ethylene (vol/mol%). There were no detectable C4 (<10 ppm each), or C6+ (<100 ppm total) species.

The system was operated in a continuous flow recirculation (CSTR) mode. Helium (Linde/Union Carbide Chromatographic grade, 99.9999%, flow rate 0-50/0-100 std.cc/min) passed through a water and oil filter (Linde/Union Carbide #SG6182 type 4A molecular sieve with indicator) and entered the system through the TGA (valve 20). The reaction gas mixture (flow rate 0-10 std.cc/min) entered the system through valve 1 (figure 21). Typical operating flow rates were 14 ml/min He, 2 ml/min hydrocarbon (HC) mixture; the total flow rate was about 16 ml/min and the inlet acetylene concentration about 1%. The He flow ideally kept the reaction gas mixture out of the large TGA dead volume. In this case the reactor volume was 316.6 cc and the residence time about 20 minutes. Whether this was truly the case is considered in part C of this section (Experimental Error). The nominal capacity of the circulation pump (Cole Palmer J-7088-48 Coyote low flow teflon diaphragm pump (Pittman
13204 motor)) and model J-2630-25 manual power supply/speed controller) was 7000 ml/min. During CSTR reactions it was operated in the range 4000-5000 ml/min, for a recirculation ratio of 250-310.

The system was connected to a gas chromatograph (Hewlett-Packard 5710A with dual differential flame ionization detectors (FID's)) through two six way sampling valves, one on the inlet HC line; the other on the system outlet line. The configuration of the GC setup appears in figure 22. Inlet samples (0.250 ml) of the HC mixture only went directly to a 1/8" X 5.0 M stainless steel column packed with 80-100 mesh phenyl isocyanate (PICN) on Porasil C (Alltech part #27246, batch 263,
$T_{\text{max}}=60{^\circ}\text{C}$. The column was operated isothermally at room temperature. The effluent went directly through one side of the thermal conductivity detector (TCD, Antek, 165 milliAmper current, $T=100{^\circ}\text{C}$), then through the corresponding side of the FID (HP 5706A Dual Differential Electrometer, hydrogen flow 40 ml/min, air flow 450 ml/min, $T=150{^\circ}\text{C}$). This column completely separated hydrogen/methane, ethane, ethylene, acetylene, and n-butane in less than 10 minutes (He carrier gas pressure 45 psig, flow rate 30 ml/min).

Samples (2.0 ml) of the HC/He mixture from the reactor outlet went first to a three-way valve. Normally this valve was set to pass the sample on to a ten way, two position switching valve. The gas lines through this valve were configured so that in the first position the sample was sent to a column identical to the one on the inlet line ($1/8''$ X 5.0 M stainless steel packed with 80-100 mesh PICN on Porasil C, isothermal operation at room temperature, He $P=45$ psig), except that this column was equipped with another ten-way, two-position switching valve. This valve was set up so that the carrier gas flow through the column could be reversed after n-butane eluted, ideally eluting all other $C_4$ species and higher hydrocarbons together in one peak. In practice, this backflushing completely separated the remaining $C_4$ species (in two unresolved peaks) from species of carbon number 6 and higher. The effluent went back to the column switching valve then through the other side of the two detectors (detector current, temperatures and flow rates identical to inlet side).

The second position of the column switching valve sent the sample to a $1/8''$ X 5.5 M stainless steel column packed with 60-80 mesh
bis(methoxy) ethyladipate (BMEA) on Chromosorb P-AW (Alltech part #189996, $T_{\text{max}}=150^\circ\text{C}$). This column separated methane/hydrogen, ethane/ethylene, and acetylene/n-butane as three peaks, then completely separated the remaining $C_4$ species (1-butenes, trans-2-butene, cis-2-butene, and 1,3-butadiene) in 6 minutes (isothermal room temperature operation, He $P=45$ psig, 40 ml/min flow rate). After 1,3-butadiene had completely eluted, another ten-port, two-position valve configured for column backflushing was switched, eluting all $C_6$ and higher species in two major, partially resolved peaks. In some instances, the backflush was not performed until after 20-30 minutes, when the majority of the $C_6$ species (mostly hexenes with small amounts of hexane) had eluted. However, these $C_6$ peaks were small and relatively broad, so that the integration accuracy was poor, and the resulting $C_6$ backflush peak was also small and very broad. For these reasons this method was not used very often. All effluent went through both detectors as above.

During most experiments, outlet samples were sent to these two columns in alternating sequence. In some instances, the initial three-way valve was switched, sending the sample to a 3/16" X 3.5 M stainless steel column packed with 100-120 mesh 3% Dexpil 300 on Chromosorb W-HP (Alltech part #8428, $T_{\text{max}}=330^\circ\text{C}$). This column was in the GCoven proper and was operated isothermally at 30°C for 2 minutes (until all $C_2$ and $C_4$ species eluted - in one peak), then the temperature was increased at 8°C/min until no more peaks eluted. $C_6$ species eluted as small shoulders on the tail end of the first peak, with higher species eluting at approximately 4 minutes per two carbon numbers (He $P=30$ psig, flow rate
45 ml/min). With this column, only the FID was employed, and its temperature was increased to 350˚C.

This column was also employed to separate manually injected (injection port T=250˚C) samples of surface polymer extracts in 2-methyl pentane, ethanol, benzene, and carbon disulfide. The sample size (1-100 µl), He carrier gas flow rate (30-60 ml/min), initial temperature (25-100˚C) and temperature program (4, 8, and 16˚C/min for different amounts of time and in different combinations) were varied widely in an only partially successful attempt to separate and identify the species in these mixtures. A capillary column such as RSL-150/300 (Alltech #935110/965110) or SPB-1 (Supelco #2-3755) would have been much more appropriate, but we had none and the GC was set up for packed columns only.

Capillary GC/MS analyses of several polymer extract samples were performed by Mike Bulawa (Exxon Basic Chemicals, Baytown, TX). The results of these analyses will be presented in a later section.

Response factors of both detectors were calibrated with all species of interest throughout their observed pressure ranges. These response factors (area units per torr in the 2.0 ml (outlet) sample loop) appear in Table 24. The inlet sample valve was set up primarily to sample the inlet stream during 13C labeled experiments. We purchased 500 std.cc of 13CH3-13CH2, refurbished a quadrupole mass spectrometer (Balzers QMA-140) and connected it to the GC TCD effluent through a glass jet separator and associated vacuum hardware. A three-way valve between the TCD and FID allowed for the choice of MS or FID. For a variety of reasons, however, the MS was not connected to the department
computer system and we did not have the necessary funds to purchase a
PC and associated software for data acquisition. Therefore these
experiments were not conducted and the inlet sampling valve was rarely
used.

Table 24. GC Detectors Response Factors.

<table>
<thead>
<tr>
<th>Species</th>
<th>P Range (torr)</th>
<th>PICN Column</th>
<th>BMEA Column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>FID</td>
<td>TCD</td>
</tr>
<tr>
<td>H₂</td>
<td>5-38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.01-0.1</td>
<td>2330</td>
<td>136</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>1.2-7.7</td>
<td>4280</td>
<td>202</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.5-100</td>
<td>4140</td>
<td>240</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.01-7.7</td>
<td>4450</td>
<td>269</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>0.1-1</td>
<td>8700</td>
<td>329</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>0.1-1</td>
<td>8550</td>
<td>-</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>0.1-1</td>
<td>10660</td>
<td>435</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>0.1-1</td>
<td>11250</td>
<td>-</td>
</tr>
</tbody>
</table>

At the FID amplifier range necessary for accurate detection of C₄
and higher hydrocarbons (0-100 mV) the ethylene peak usually went off
scale with the PICN column and always did with the BMEA column. At the
same time the TCD sensitivity was too low to accurately measure the
small quantities of C₄ species, and column backflushing so severely
perturbed the TCD baseline that it had not stabilized until after the
backflush peaks had eluted. Backflushing invariably blew out the FID
flame; it had to be relit after each backflush. The net result of these
considerations was that TCD integrated areas were used for hydrogen and
C₂ species pressure calculations, while FID areas were used for methane
and all C₄ species. Sample chromatograms from the PICN and BMEA
columns, using both detectors, appear in figures 23 and 24.
He carrier gas (Linde/Union Carbide high purity grade, 99.995%, H₂O, N₂ < 5ppm), and FID air (Linde/Union Carbide dry grade, H₂O < 3ppm) and hydrogen (Linde/Union Carbide prepurified grade, 99.99%, O₂ < 10ppm, H₂O < 5ppm) were all passed through water/hydrocarbon traps (Linde/Union Carbide #SG6182, type 4A molecular sieve with indicator) prior to use. 2 micron filters (Nupro 2F series) were installed on all gas lines.

All catalysts used in this work were commercial Pd on alumina samples (Engelhard). The physical characteristics of the various samples appear in table 25. It must be stressed that these are nominal,

<table>
<thead>
<tr>
<th>Pd Loading (wt%)</th>
<th>Support Type</th>
<th>Pellet Size (in)</th>
<th>Surface Area (m²/g)</th>
<th>Porosity (cc/g)</th>
<th>Mean Pore Radius (Å)</th>
<th>Catalog Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>AT-10</td>
<td>1/8</td>
<td>4</td>
<td>0.25</td>
<td>600</td>
<td>2254705</td>
</tr>
<tr>
<td>0.5</td>
<td>AT-8</td>
<td>1/8</td>
<td>33</td>
<td>0.33</td>
<td>55</td>
<td>2254703</td>
</tr>
<tr>
<td>0.5</td>
<td>AT-2</td>
<td>1/8</td>
<td>90</td>
<td>0.35</td>
<td>30</td>
<td>2253701</td>
</tr>
<tr>
<td>0.5</td>
<td>AE-21</td>
<td>1/8</td>
<td>220</td>
<td>0.49</td>
<td>22</td>
<td>2264710</td>
</tr>
<tr>
<td>0.1</td>
<td>AT-2</td>
<td>1/8</td>
<td>90</td>
<td>0.35</td>
<td>30</td>
<td>2253951</td>
</tr>
<tr>
<td>0.02</td>
<td>AT-2</td>
<td>1/8</td>
<td>90</td>
<td>0.35</td>
<td>30</td>
<td>2254902</td>
</tr>
</tbody>
</table>

vendor supplied values only. We have not independently measured any of the figures in table 25. In addition we have no information about catalyst Pd dispersions. We have used these commercial catalysts in order to 1) save time and effort in not preparing the samples ourselves, 2) minimize variability between pellets so experiments with different samples could be directly compared, and 3) allow later researchers to
Figure 23. Sample Chromatogram from PICN Column.
Figure 24. Sample Chromatogram from BMEA Column.
easily locate these samples for detailed characterization studies, if desired. During experiments carried out on the catalysts listed above we observed no significant variations between different samples except for the 0.02 wt% Pd sample (2254902).

Catalyst pellets containing Pd turned dark brown/black almost immediately upon exposure to the reaction gas mixture. After operation, samples of the 0.02% Pd catalysts contained both black and white pellets. Apparently this catalyst sample was made up of both Pd containing and pure support pellets. This may have occurred because the original batch had a Pd content of somewhat more than 0.02 wt%. The pure support would have been added to bring the average bulk Pd content down to 0.02%. We conducted screening on these samples by exposing them to the reaction gas mixture for a short time (1/2 hour). Those that exhibited a color change were used for subsequent studies. No significant variations were observed with these samples. A Pd loading of 0.02 wt% was assumed for this sample during calculation of reaction rates per mole Pd.

At a typical total flow rate of 16 ml/min (2 ml/min HC mix, 14 ml/min He), approximately 50 mg of 0.5 wt% Pd catalyst gave acetylene conversions of about 50% at 40°C. This amount was approximately equal to the volume capacity of the TGA sample pan. During these experiments, those using 0.1 wt% Pd at T ≥ 60°C, and 0.02 wt% Pd at T ≥ 120°C, the entire catalyst sample was located on the catalyst pan. For experiments with 0.1 and 0.02 wt% Pd catalysts at temperatures lower than those listed, approximately 50 mg was placed in the TGA pan; the rest was placed in the bottom of the reactor U-tube in about 20 g of glass beads.
to prevent the pellets from laying on the bottom of the tube and causing possible problems with channelling or bulk diffusion effects. This setup is shown in figure 25.

Prior to each reaction, the TGA was calibrated in accordance with the operation manual. This entailed zeroing the weighing mechanism (Perkin-Elmer Autobalance AR-2) with only the hangdown wires and catalyst pans. With the much greater length of hangdown wire in the reactor side of the TGA, the balance could not be zeroed. Instead, the additional wire was removed and the balance zeroed (typically to ± 0.01 mg) with equal lengths of wire on each side. Next a 100 mg calibration weight was placed in the reactor side pan and the TGA weight suppression dial set so that at 100 mg suppression the balance was again zeroed to ±0.01 mg. Finally the recorder (Omega Omegaline 640, 0-10 mV) was calibrated so that full scale deflection at any weight range equalled 100% deflection on the recorder (eg. at 100 mg range, 0 mg weight caused no pen deflection, 100 mg weight caused 100% deflection). After the calibration was completed, the longer lengths of hangdown wire were reinstalled and their weight measured with the weight suppression dial (typically 11-16 mg).

We should note that it was neccessary to connect hang down wires together and to the pan stirrup with more than just the usual sharp bend at each end. The high gas circulation rate (4000-5000 cc/min) traveling up the hangdown tube (at 60 cm/sec) could cause oscillations in the pan height, separating connections made in this way and causing the catalyst and pan to fall to the bottom of the U-tube. Having an experiment end
Figure 25. Detail of Reaction Chamber/TGA Hangdown Tubes.
this way after perhaps five to ten days, or longer, operation can really
ruin your day (ditto for unannounced power failures). Wires were
usually wrapped around themselves at all connections in order to avoid
this most unwelcome result. We should also note that with increasing
use the hangdown wires become more and more bent. It is simply a result
of installing and removing them before and after each experiment. The
TGA noise increases quickly with increased "non-linearity" in the wires.
For this reason it was periodically necessary to completely replace the
wires used.

Catalyst samples were weighed in a lab analytical balance prior to
placing them in the pan/U-tube. Weights measured on this balance and on
the TGA differed by less than 2%. If all of the sample could be
accommodated in the pan, it was simply placed in it after weighing. If
some of the sample had to be put in the U-tube, all of the sample was
left on the analytical balance until weight gain from water absorption
had ceased. Samples lost between 3 and 10% of their weight (apparently
depending upon the humidity in the lab and the time they were exposed to
the atmosphere) during subsequent high temperature activation, mostly
due to water desorption, and it was necessary to make sure all pellets
started at identical water contents. In experiments with catalyst
pellets both in the pan and the U-tube, we assumed that any weight
change observed in the pan sample accurately reflected the changes in
the remainder of the sample. The calculated (in the case of samples in
both the pan and U-tube) or observed (samples in the pan only) weight
after pretreatment was the weight used in subsequent reaction rate
calculations.
All samples were activated by treatment in flowing oxygen (Linde/Union Carbide zero grade, 99.6%, total HC < 0.5 ppm, 20 ml/min through valves 1 and 4) at 200°C for two hours. The system was evacuated to <100 μm, then filled with He. Next flowing hydrogen (from the same supply as FID hydrogen, 20 ml/min through valves 1 and 4) was introduced and the temperature raised to 300°C for 2 hours. During both of these treatments, He flowed at 20 ml/min through the TGA and into the system. Because of the hangdown tube design, the catalyst experienced essentially 1 atm of oxygen or hydrogen.

It should be noted that although we do not know the dispersions of any catalyst samples used, the pretreatment detailed above should not have caused any changes due to redispersion in oxygen or sintering in hydrogen. Dogson and Webster (247) observed little or no changes in the metal surface area of Pd/alumina catalysts (1-10% Pd) at temperature lower than 400°C in air and 600°C in hydrogen. Similar results have been reported by other authors (248, 252).

After the hydrogen treatment, the temperature controller (Omega 6001K, 0-2500F) was set to the desired reaction temperature (40-120°C) and the system cooled overnight in flowing He. Evacuation after hydrogen treatment was not carried out at 300°C because of the small but definite leak in the system (besides the TGA, all the teflon stopcocks would be expected to leak, particularly in the absence of vacuum grease); the catalyst could be reoxidized by air at 300°C. This was observed by the low catalyst activity during the subsequent reaction when evacuation was carried out at 300°C. Instead, the system was
evacuated in the morning at reaction temperature prior to the introduction of He and the HC mixture.

After evacuation valve 1 was closed and the HC mixture, bypassing the mass flow controller, filled the inlet line to 1 or 2 psig. The remainder of the system was rapidly filled with He, also bypassing the mass flow controller. Valves 5, 10, 13, 15, and 16 were closed, 14 and 20 were opened, He flow began at the desired rate, and the circulation pump was turned on. Finally valve 1 was opened and the HC mixture flow turned on.

The first gas sample was taken after about 1/2 hour operation. This sample was sent to the PICN column for hydrogen, C₂ species, n-butane, and total C₄ and C₆₄ analysis. This routine took about 20 minutes to complete. Immediately thereafter another sample was taken and sent to the BMEA column for C₄ and total C₆₄ analysis. This routine took about 15 minutes. After this sample had been taken, the circulation pump was shut off for about 10 seconds and the catalyst weight measured with the TGA. The high rate of gas circulation lifted the balance pan, causing readings to be typically 0.5-1.0 mg lower than weights measured with the pump off. In addition, the level of background noise (weight fluctuations) was fairly high (± 0.2-0.5 mg) when the pump was on. Shutting off the pump did perturb the system, specifically increasing the rate of ethane formation by acetylene depletion/ethylene reaction in the stagnant gas around the catalyst pellets. Experiments with and without shutting off the pump showed that in order not to observe this artificially high ethane concentration it
was necessary to wait for up to 30 minutes before taking another gas sample (see Appendix G, p. 595).

During the initial stages of reaction (up to 36 hours), the rate of change of the catalyst activity and various product selectivities was high, and samples were taken often (1 of each type per hour). As the time of operation increased the rate of change of all measured quantities, including the catalyst weight, decreased. Therefore the time span between gas analyses/weight measurements was gradually increased, reaching a limit of once every one or two days during operation until catalyst death. Experiments were run for 48-500 hours, depending on the reaction temperature, metal loading, inlet acetylene concentration, information desired, and the power outage frequency.

Used catalyst samples were treated in a number of different ways. The amount and effects of volatile surface polymers were investigated by evacuating the system at the reaction temperature until no further weight loss was observed in a 24 hour period. This typically occurred after 72 to 96 hours. He and the HC mixture were introduced at identical flow rates and the catalyst activity and selectivities before and after evacuation compared.

Hydrogen treatment alone and oxygen-hydrogen treatment were conducted in order to measure their effects on the amount of surface polymer as well as the subsequent activity and product selectivities. Evacuation at temperatures greater than the reaction temperature (100-300°C) was also investigated.

Other used samples were placed in various solvents (2-methyl pentane, carbon disulfide, ethanol, and benzene). After 1/2 hour to
several days, samples of the solvent were withdrawn and injected on the 3% Dexsil 300 column to analyze for soluble higher hydrocarbons. A typical chromatogram appears in figure 26.

After these solvent extractions, the catalyst pellets were still dark brown/black. We were not able to dissolve the species responsible for this discoloration in any solvent we used. Several catalyst pellets were placed in hydrofluoric acid, which digested the alumina support and presumably dissolved the Pd also. Thin (< 0.1mm) "sheets" (typically 0.5 by 1mm) of brown material, which we have not yet been able to identify, were left in solution.

The effects of acetylene/hydrogen pressure on the rate of both gas phase and surface polymer formation were investigated during differential conversion experiments at 40°C with acetylene pressures between 1 and 22 torr. Under these conditions (low Pd content - 50 mg 0.1 wt% Pd - and high total flow rates - 35-50 ml/min) acetylene and hydrogen conversions were indistinguishable from zero. The rate of gas phase polymer formation was measured by GC analysis and flow rate values; the rate of surface polymer formation by catalyst weight gain in the TGA.
Figure 26. Sample Chromatogram from Dexsil Column.
B. **Symbol Definition and Calculation Procedure.**

During past investigations of selective acetylene hydrogenation, many different definitions of catalyst activity and selectivity have been used. This makes comparison between different investigations both difficult and tedious. Throughout the remainder of this work we will use a consistent set of variables to describe these experimental observations.

Acetylene conversion is defined as the molar rate of acetylene reaction over the molar rate of acetylene entering the reactor. This may be represented as:

\[ X_{C_2H_2} = \frac{-\dot{r}_{C_2H_2}}{Y_{C_2H_2}(n_{HC})} \]

where \( X \) is the fractional conversion, \( \dot{r} \) the molar reaction rate, \( y_0 \) the mole fraction of acetylene in the HC mixture stream, and \( n_{HC} \) the HC mixture molar flow rate.

The acetylene reaction rate was calculated from a standard CSTR material balance, rate=\text{out}+\text{accumulated-in}. The rate of acetylene entering the reactor is the denominator in the expression above \( (Y_0C_2H_2(n_{HC})) \). The rate of acetylene leaving the reactor is the product of the acetylene mole fraction and the total flow rate (mole/min) leaving the reactor. The corresponding term for this rate is \( yC_2H_2(n_r) \). Assuming that the change in the number of moles due to reaction is much smaller than the total molar flow rate, the second term in this expression may be replaced by \( n_r=(n_{HC}+n_{H_2}) \). Molar flow rates were
calculated from mass flow controller settings, converting standard (70°F and 14.7 psia) cc/min to moles/min assuming the gas behavior was ideal.

The accumulation term was calculated from the samples immediately before and after the one in question. Assuming that the reactor may be accurately modeled as a CSTR, the concentration of any species leaving the reactor is identical to the concentration of the species everywhere in the reactor. For any sample n, the rate of accumulation is given by:

$$\text{acc.} = \frac{(Y_{n+1} - Y_{n-1})}{(t_{n+1} - t_{n-1})} \frac{(PV/RT)}{}$$

where \( t_i \) is the time (minutes) sample \( i \) was taken, \( y_i \) is the mole fraction of acetylene measured in sample \( i \), \( P \) is the total system pressure (1 atm), \( V \) the reactor volume (316.6 cc), \( R \) the gas constant, and \( T \) the reactor system temperature (293 K). The value of the last term, \( PV/RT \), is 0.0132 moles. The acetylene reaction rate measured during sample \( n \) is given by:

$$r_n = y_n(n_{ac} + n_{w}) + \frac{(Y_{n+1} - Y_{n-1})}{(t_{n+1} - t_{n-1})} \frac{(PV/RT)}{} - Y_0 C_2 H_2 (n_{ac})$$

Reaction rates of ethane, \( C_4 \), and \( C_6 \), species were calculated in identical ways, although the inlet ethane mole fraction was very small (0.0255%), and inlet \( C_4 \) and \( C_6 \) were zero.

The rate of surface polymer formation was calculated in a somewhat different manner. Catalyst weight measurements were taken every hour, at most, during the initial stages of each reaction. In this region the rate of weight gain was highest, and it always decreased during further operation. As the rate of polymer formation decreased, the time between measurements was increased up to a limit of perhaps once every 2 days.
during operation to catalyst death. A plot of catalyst weight versus
time generally fit a fairly smooth curve (see Results and Discussions

Rates of polymer formation calculated from the observed catalyst
weights and the time between measurements, however, fluctuated pretty
severely. This was especially true when the time between measurements
was small (1 hour) or the rate of formation very low (0.1 mg/day).
Therefore, the measured weights were plotted against time and a smooth
curve drawn through them. Rates of polymer formation were calculated
from this curve, not from weights as directly measured.

In order to calculate molar rates of polymer production, we must
know the structure of the polymer formed. Analyses of the polymer
fraction which dissolved in hydrocarbon solvents has shown that these
are predominately normal paraffins of even carbon numbers, from 8 to at
least 30, although more than half are just carbon number 10 to 18. In
addition, numerous branched paraffins, linear and branched mono-olefins,
and some di-olefins and aromatics are present. The structure of the
insoluble species is presently unknown.

Instead of trying to measure the rate of production and structure
of each of these species, we have assumed that the average molecular
formula is given by \((C_2H_4)_n\), or an acetylene equivalent molecular weight
of 28 g/gmole. This appears to be a reasonable assumption for the
soluble species. An equivalent value for the insoluble species is
unknown, but must be between 24 and 28 g/gmole (between \((C_2)_n\) and
\((C_3H_4)_n\)). 28 g/gmole was assumed to represent all of the surface polymer
species. The actual value may be lower, which would increase the
calculated polymer selectivities by up to 15% (relative). The rate of polymer formation was calculated as the molar rate of acetylene reacting to form surface polymers, or \( \Delta w / (\Delta t(28)) \), and is the minimum value possible.

Product selectivities were calculated from the molar rate of production of each species times the number of acetylene molecules required to form each molecule divided by the reaction rate of acetylene. In this notation, ethane selectivity \( (S_{\text{C}_2\text{H}_6}) \) is simply \( (100\%) (r_{\text{C}_2\text{H}_6}) / (-r_{\text{C}_2\text{H}_2}) \). \( \text{C}_4 \) selectivity \( (S_{\text{C}_4}) \) is \( (200\%) (r_{\text{C}_4}) / (-r_{\text{C}_2\text{H}_2}) \). \( \text{C}_6 \) selectivity \( (S_{\text{C}_6}) \) is \( (300\%) (r_{\text{C}_6}) / (-r_{\text{C}_2\text{H}_2}) \). In calculating \( S_{\text{C}_6} \), we have assumed that the majority of these species are of carbon number 6. Analyses of this fraction show that it is at least 50% \( \text{C}_6 \). The total gas phase polymer selectivity, \( S_{\text{surf}} \), is simply \( S_{\text{C}_4} + S_{\text{C}_6} \). Surface polymer selectivities \( (S_{\text{surf}}) \) have been calculated from the acetylene equivalent molar rate of polymer production divided by the reaction rate of acetylene, or \( (100\%) (\Delta w) / (\Delta t(28)) (-r_{\text{C}_2\text{H}_2}) \).

Ideally we would also be able to accurately measure the rate of ethylene production and calculate the selectivity to ethylene \( (S_{\text{C}_2\text{H}_4} = r_{\text{C}_2\text{H}_4} / (-r_{\text{C}_2\text{H}_2})) \). Although the initial ethylene/acetylene ratio is only 10 (compared to 200 or greater in previous works), the accuracy of these measurements was not high enough. In order to distinguish between an ethylene selectivity of 30 and 40% at 50% acetylene conversion, the GC detectors must be capable of distinguishing 10.15% ethylene from 10.20 (relative error \( \ll 0.5\% \)). This was not the case, particularly as the TCD was used to measure the partial pressure of ethylene.
Selectivities as we have defined them should sum to 100% if every
product species is included. The sum of the product selectivities
considered here - including ethylene calculated from GC data - was
generally between 90 and 110%. This suggests that we have included all
major product species. The variation in $S_{C_2H_4}$ was highest, followed by
$S_{C_6H_6}$, $S_{C_4}$, $S_{surf}$, and finally $S_{C_2H_6}$. For this reason, all selectivities
other than $S_{C_2H_4}$ were summed and subtracted from 100%. This value was
used to define $S_{C_2H_4}$. The variation in $S_{C_2H_4}$ was still high as it
includes the variation in all other selectivity values, but it was much
better than using values calculated from the ethylene GC areas.

Similarly hydrogen integrated areas were very difficult to measure
accurately, and it was also difficult to convert the measured area into
a partial pressure value. These problems arise from the use of helium
as the GC carrier gas. The thermal conductivities of hydrogen and
helium are very similar (0.121 vs. 0.144 W/min*K (657)) and the hydrogen
TCD response factor is low (less than 5/200 of the response of
acetylene, table 24, p. 173). In addition, plots of TCD areas versus
hydrogen pressure in He carrier gas can exhibit one or more inflection
points, so that any TCD area may represent more than one possible
hydrogen pressure. While we did not observe this behavior during
hydrogen calibration of the TCD, we cannot rule it out at all conditions
in this study.

Perhaps the simplest solution to this particular problem would
have been using nitrogen as the GC carrier gas. The thermal
conductivities of hydrogen and nitrogen (0.121 and 0.0250 W/min*K (657))
are sufficiently different that the TCD response factor is high and does
not exhibit inflection points. Although the use of nitrogen would have greatly lowered the response factors of acetylene, ethylene, and ethane, we could have injected smaller samples or increased the FID amplifier range so that ethylene peaks did not go offscale. In either case ethylene could have been accurately measured with the FID, and hydrogen with the TCD and nitrogen carrier gas.

This rather straightforward solution was not employed for several reasons, all relating to the planned $^{13}\text{C}$ labeled ethylene experiments using the MS (see p. 172). In order to interpret isotope distributions from the MS, we would also require the relative composition of the gas samples introduced. This could most easily be accomplished by passing the GC effluent through the TCD before the MS. Of course it would have also been possible to use a splitter to send some of the sample to the FID and the rest to the MS, but this would raise other problems concerning the split ratio (and the splitter stability) and require more labeled species in each experiment.

The MS information we were most interested in was the specific amount of $^{13}\text{C}$ in ethane versus ethylene in order to calculate the relative amounts of ethane produced directly from acetylene (the intrinsic ethane selectivity) and from ethylene hydrogenation. Nitrogen, at mass 28, would render these measurements impossible by its presence alone, and would severely increase the background noise by its tendency to ionize in the quadropole. The analysis system was set up as it was for all of these reasons. We did not expect or foresee the problems that ultimately canceled these labeled experiments.
In light of these considerations, the reaction rate and reactor exit partial pressure of hydrogen were calculated from the inlet composition and flow rate, and the production rates of all other species considering the hydrogen reaction stoichiometry of each. The rate of hydrogen consumed to form ethane is two times the rate of ethane production. \( \text{C}_4 \) species were predominantly (90\%) butenes except in the very early stages of reaction when 1,3-butadiene was dominant. We therefore assumed only 1 molecule of hydrogen was consumed for each acetylene molecule forming \( \text{C}_4 \) species (two times the rate of \( \text{C}_4 \) production). The composition of the \( \text{C}_6 \) fraction is not known in such detail, but period analyses revealed it was mostly (45-50\%) hexenes. Assuming they were all hexenes would correspond to a hydrogen consumption rate of 3 times the rate of \( \text{C}_6 \) production (also one hydrogen per acetylene). With the assumption that the mean formula of the surface polymer may be accurately represented by \( (\text{C}_2\text{H}_4)_n \), polymer formation also requires one hydrogen per acetylene. Ethylene of course also requires one hydrogen molecule per molecule.

The net result of these observations and assumptions is that the rate of hydrogen consumption could be calculated as the sum of the acetylene consumption and ethane production rates, \(-\text{C}_2\text{H}_2+\text{C}_2\text{H}_6\). From this information, the hydrogen concentration and flow rate of the inlet gas, and the total flow rate out of the reactor, the calculation of hydrogen partial pressures is relatively straightforward.

In order to calculate reaction rate constants and compare them over the various catalyst samples, acetylene consumption rates were corrected for the amount of catalyst employed, the Pd metal loading, and
hydrogen and (sometimes) acetylene partial pressures. Again assuming CSTR behavior, the kinetic expression is:

$$-r_{C_2H_2} = k(P_{H_2})^m(P_{C_2H_2})^n$$  or  $$k = -r_{C_2H_2}(P_{H_2})^{-m}(P_{C_2H_2})^{-n}$$

The majority of past investigations have observed first order behavior in hydrogen (m=1, table 21, p. 154). We have used this value in all calculations. The reaction order in acetylene is more controversial. We have considered values between -1 and 1. None of the values in this range fit all of the data, particularly experiments conducted at different acetylene conversions. This behavior will be considered in greater detail in a following section. As most experiments were conducted with 1% inlet acetylene and at comparable acetylene conversions (50-60%), we have used a value of m=0 (zero order in acetylene). Under these conditions the units of the rate constant are moles of acetylene reacted per mole Pd per minute per torr hydrogen (mole/mole*min*torr). A more conventional rate constant, such as $K_w$ (min$^{-1}$) can be calculated by converting torr (P) hydrogen to hydrogen concentration (n/V) using the ideal gas law, moles of acetylene (n) to acetylene concentration (n/V) by correcting for the reactor volume (316.6 cc), and removing the Pd dependence by multiplying by the moles of Pd in the catalyst sample.

Calculating rate constants per mole Pd was neccessary in order to compare reactions with different amounts of catalysts and catalysts of different Pd loadings, while the designation mole/torr (rather than mole/mole, which would cancel leaving (mole Pd)$^{-1}$(min)$^{-1}$) was used to emphasize that although the reaction is first order in hydrogen, we are measuring the reaction rate of acetylene.
The activity and product selectivities observed over different catalyst samples at a variety of temperatures have been compared versus both operation time and the amount of surface polymer on the catalyst, expressed as mg per ml catalyst pore volume. The units of the latter were chosen from a number of possibilities, including ml polymer per ml pore volume, mg per square meter surface area, mg per gram catalyst, and mg per gram Pd. The first was not possible because we have been unable to identify the insoluble polymer species, and the last three did not show any fundamental relationships between different experiments. The chosen units did, as we might expect from the fact that the surface species must exist somewhere on the surface. The catalyst pores appear to be a reasonable location.

A typical computer program used to calculate acetylene conversions, product selectivities, polymer loadings, and reaction rate constants, and the results of these calculations for all experiments conducted in this study, appear in Appendix E (p. 532). Experiment numbers listed in figure captions in the following sections refer to the data presented in this appendix.
C. **Experimental Error**

The most important condition when considering experimental error in this reactor system is the assumption that only the catalyst pan hangdown tube and the circulation loop contain the reaction gas mixture. If this is not true, then the assumption of CSTR behavior is incorrect and analysis of the data may be considerably more difficult, if not impossible.

During all experiments we have conducted an overall carbon balance on the system. From the helium flow rate, which is known, the composition of the outlet stream, the rate of catalyst weight gain, and changes in the composition of the gas in the reactor we have calculated an apparent inlet HC mixture flow rate. This calculation includes the CSTR assumption with the reactor volume equal to 316.6 ml, so the normal CSTR unsteady-state behavior is accounted for. In almost every experiment, the calculated inlet flow rate increased steadily during the first 10 hours of operation and then remained fairly constant throughout the duration of the experiment (figure 27, or see tables in Appendix E, column "F (ml/min)"). Alternatively, we can compare the initial rise in HC concentration to that predicted by an ideal CSTR model (figure 28).

There are three possible explanations for this behavior. The first is that the reactor is not perfectly backmixed so that the outlet concentrations are not representative of the overall concentrations in the reactor. The second is that the calculated inlet flow is representative of the true inlet flow, so that the mass flow controller
Figure 27. Comparison of steady state inlet HC mixture flow rate with calculated values during initial operation.

Figure 28. Comparison of real reactor behavior with an ideal CSTR.

takes nearly 10 hours to reach the chosen flow rate. The third is that the volume of the reactor is greater than 316.6 ml. The last would require diffusion of one or more of the HC mix species into the housing
of the TGA and might invalidate our use of the CSTR model, as there is no recirculation through the TGA. We have investigated all of these possibilities in detail.

We have measured the recirculation pump flow rate at settings in the typical range of operation. During all experiments, this rate was at least 4000 ml/min. At a typical total inlet flow rate of less than 20 ml/min, the recirculation ratio is greater than 200. This is normally high enough to ensure complete backmixing. We have also shut off the inlet flows to the reactor and isolated the circulation loop from the TGA immediately after taking a sample. During that sample analysis the gas in the loop was continuously circulated at 7000 ml/min, guaranteeing a uniform composition. After the initial analysis was completed we expanded the gas in the loop into the outlet sampling section and injected a sample. After correcting for the pressure drop due to expansion, the total amount of hydrocarbons and the specific composition was within 2% of that measured in the initial sample. We therefore conclude that the reactor is perfectly backmixed.

In order to investigate the stability of the HC mass flow controller, we have conducted flow-through experiments without using the TGA or the circulation pump. In this case, the system was evacuated, then filled with the HC mixture up to valves 4 and 5 (figure 21, p. 165). The remainder of the system was filled with He, and He flowed through the TGA to the circulation loop through valve 6, then out through the sampling section to the vent. After valve 5 was opened and HC mixture flow began, we sampled the outlet stream. The composition of this outlet flow was constant and corresponded to a typical steady state
experimental inlet flow rate (e.g. 2.35 std.cc/min at a setting of 2.00). Therefore the mass flow controller does not require ten hours to warm up (the HC inlet flow is constant).

More importantly, after this flow-through steady state was reached, we turned on the circulation pump and opened the flow to the TGA hangdown tube (valve 4 open; 5 closed). We again observed a slower increase in reactor HC pressure than that predicted by a CSTR model. After the reactor HC pressure had reached a steady value, the calculated inlet HC flow rate was identical to that measured in the flow-through experiment. Clearly some of the HC mixture was diffusing into the TGA housing. After the steady state had been reached, we shut off the inlet flows and isolated the TGA from the rest of the system. The circulation loop was evacuated, then opened to the TGA, allowing gas in the TGA to expand into the loop. After this gas had been circulated in the loop for about 15 minutes, it was expanded into the outlet sampling section and a portion injected into the GC. This procedure was repeated until no change in composition from the TGA gas was observed.

From this information, it was possible to calculate the amount of HC gas (in std.cc's) that was in the TGA after the steady state had been achieved. We measured approximately 80 std.cc's in the TGA after an unsteady state period where approximately 100 std.cc's were "missing" from the overall material balance (assuming constant inlet flow and perfect backmixing in the reactor). The amount of HC mixture in the TGA corresponds to a mole fraction of 80/2100, or 0.038 (3.8%), compared to a value of 2.35/16.35, or 0.144 (14.4%) in the reactor.
Because helium is flowing through the TGA and into the reactor, it is not surprising that the steady state concentration in the TGA is lower than that in the reactor. The HC gas in the reactor must diffuse up the hangdown tube against the helium flow. It is theoretically possible to calculate the rate of diffusion against this helium flow, given the tube diameter and length, the concentration gradients of each species, the helium flow rate, and suitable boundary conditions. The tube in question is 1.2 cm diameter and 7.6 cm long, followed by 12.7 cm of 2.5 cm diameter tube (figure 25, p. 179). The helium flow rate is 14 cc/min (9.7 and 2.2 cc/min, respectively, in the two tubes). We have attempted these calculations, but the results are strongly dependent on the chosen boundary conditions. The conditions at the union of the circulating flow and the helium flow are of particular importance here, and are for all practical purposes unknown.

The circulation pump is a teflon diaphragm design, with a single stroke capacity of about 1.5 cc. Although the flow becomes more continuous with increasing pump speed, flow rate measurements with a soap bubble flow meter show that the flow is still pulsating at the conditions of operation. Therefore although the overall recirculating flow appears to be laminar (Reynold's number = 36), on a smaller scale there is certainly some degree of turbulence. In addition, pressure changes due to the action of the pump diaphragm may cause some degree of forced convective flow up the hangdown tube of the TGA. For these reasons, we have not attempted to solve the theoretical expression for diffusion into the TGA, but have considered experimental results only.
We might suspect that the gas phase hydrocarbon species will diffuse into the TGA with rates proportional to their reactor concentrations (overall concentration gradients). This supposition is supported by measurements of the composition of gases in the TGA during recycled operation without any catalyst in the reactor. Under these conditions, the total concentration of hydrocarbons in the TGA is much smaller than in the reactor (3.8 vs. 14.4%), but the relative concentration of each species is approximately the same.

The limiting cases of diffusion into the TGA during the initial unsteady state conditions will be 1) only ethylene (the major - 80% - component of the gas phase) diffuses. In this case, the inlet flow rate is the observed steady state value, while the outlet flow rates of all species except ethylene are defined by the observed total outlet flow rate and the outlet concentration of each; or 2) each species diffuses into the TGA in proportion to its concentration in the reactor. In this case, the inlet flow rate is the observed steady state value, while the outlet flow rate is the steady state outlet flow. The net result of the second case is that we treat the TGA as another outlet of the reactor system, where the composition is identical to that measured at the conventional reactor outlet. In reality, we suspect that the actual situation lies somewhere between these two extremes, as there should be some reactor concentration below which a hydrocarbon will not diffuse into the TGA (the concentration gradient too small to overcome the He flow down the 12 mm ID tube).

We have taken the raw data from a typical experiment and compared the calculated values of catalyst activity and product selectivities
subject to these two limiting assumptions and the case where diffusion into the TGA is ignored (inlet and outlet HC flows are those calculated from the overall carbon balance, Appendix F, p. 587)). From these results, it is apparent that there is little or no difference in activity and selectivity values calculated assuming either type of diffusion, although values calculated assuming no diffusion are significantly different.

We know that diffusion into the TGA occurs and that in the time of operation where the concentration of hydrocarbons in the TGA is increasing (up to about 10 hours operation), the behavior is identical regardless of which species is diffusing. We must now consider what happens when an apparent equilibrium is established and diffusion from the TGA back into the reactor may occur if the relative concentrations in the reactor change.

If only ethylene diffuses into the TGA, this will have little or no effect, as the concentration of ethylene in the reactor is for all practical purposes constant, and back diffusion will not occur to any great extent. In addition, production and/or consumption rates of ethylene are not calculated directly, only as a difference from the other product selectivities.

Experiments without any catalyst show that at least at their inlet concentrations, hydrogen and acetylene also diffuse into the TGA so that the relative composition of the hydrogen/acetylene/ethylene mixture is equal to that in the reactor, although the total concentration of this mixture - in He - is significantly lower in the TGA. It is therefore
likely that more than one, and perhaps all, species actually diffuse into the TGA.

We have observed a total HC mixture mole fraction of 0.038 in the TGA in diffusion equilibrium with a mole fraction of 0.144 in the reactor. The ratio of these values is 0.144/0.038 = 3.8. The total TGA volume is approximately 2100 cc. As this includes the feed lines into the TGA, where the HC mixture concentration should be very small, the volume containing the mixture is actually less than 2100 cc, but we will use this value here. The measured reactor volume is 316.6 cc. The ratio between these values is 2100/316.6 = 6.6. We therefore have a reservoir of HC mixture that contains 6.6/3.8 = 1.74 times as much total mixture as the reactor. The reactor, however, is subject to continuous inlet and outlet flows of 14 std.cc/min He and 2.35 std.cc/min HC.

During the very initial stages of operation, when the HC mixture concentration gradient between the reactor and the TGA is greatest (i.e. when the TGA concentration is zero), we have calculated a maximum HC diffusion rate of 0.25 std.cc/min into the TGA. This represents 10.6% of the total inlet HC flow. This net flow decreases to zero after approximately ten hours operation. The total amount in the TGA is 0.038(2100) = 80 cc. The average rate of diffusion into the TGA over this time span is 80/(10*60) = 0.133 cc/min. In the absence of diffusion, we would have a CSTR reactor with a mean residence time of approximately 20 minutes. In the absence of reaction, the unsteady state equation describing this system is \( y/y_0 = 1 - \exp(-\Theta) \), where \( \Theta = t/\tau \) and \( \tau \) is the residence time. Therefore after 20 minutes operation (\( \Theta = 1 \)), the reactor HC mixture concentration should be 63.2% of the steady
state value. After 40 minutes ($\Theta = 2$), $y/y_0 = 0.865$ (86.5%). After 60 minutes ($\Theta = 3$), $y/y_0 = 0.95$ (95%).

For all practical purposes the change in reactor concentration - from zero to 90% of the final value (2.10/2.35) - should have taken place in less than 1 hour, and the maximum diffusion rate is 10.6% of the total HC inlet flow. If the initial acetylene conversion was zero until net diffusion equilibrium was achieved (after 10 hours), and then would have increased to 100% in one hour in the absence of diffusion, the maximum rate of acetylene diffusion back into the reactor would be $0.07739(0.25) = 0.0193$ std.cc/min. The inlet acetylene flow rate is $0.07739(2.35) = 0.181$ std.cc/min. The apparent conversion would then be approximately $0.0193/0.181 = 0.89$ (89%) after one hour, and would gradually increase to 100% during the next ten hours. A similar argument can be made for the apparent reaction rate of any other species.

In the experiments conducted in this work, major changes in acetylene conversion and product selectivities always took place during the initial stages of reaction, although the duration of these changes depended on the catalyst metal loading, the reaction temperature, and the inlet acetylene concentration. In the first ten hours of operation there were never any observed inflection points in any species gas phase concentrations, except for perhaps 1,3-butadiene. Therefore the net result of diffusion from the TGA to the reactor in this regime would be to decrease the apparent rate of change of any given species, but would not alter the direction of this change. In addition, none of the hydrocarbon species concentrations tended to zero until catalyst
deactivation decreased the acetylene conversion to values approaching zero. This process, however, took a minimum of 24 and as many as 500+ hours, and the rate of change was very small.

We therefore conclude that although the HC mixture did diffuse into the TGA, causing some deviations from true CSTR behavior, the values of catalyst activity and product selectivities calculated by the methods described earlier are largely valid. The observed changes in acetylene conversion, ethane selectivity, and 1,3-butadiene and 1-butene in the C4 fraction probably occurred somewhat faster than we have calculated, but the direction of the change and the final magnitude of each value will be relatively unaffected by diffusion in the TGA.

The calculated inlet HC flow rates varied to some degree after the first ten hours operation (table 26), but we used only one more or less average value for the calculation of catalyst activity and product selectivities. The maximum observed deviations from the value used in the calculations of any given experiment are generally less than ± 4%. In several cases, the maximum deviation is as high as 6%, and even 14.4% in one case. However, these values are not representative of the measured flow rates. The standard deviations are much lower; all but one less is than 1% relative, and that is only 1.54%.

The inlet HC flows were calculated assuming that the helium inlet flow was constant at the setpoint value. The overall carbon mass balance used the HC mixture composition, the rate of weight gain of the catalyst (subject to the assumption that the mean polymer formula is \((C_2H_4)_n\)), the change in the number of moles of carbon in the reactor
Table 26. Variation of steady state inlet HC flow rates observed during continuous operation.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Flow Rate (std.cc/min)</th>
<th>Deviation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Used</td>
<td>Max</td>
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<tr>
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</tr>
<tr>
<td>30</td>
<td>2.500</td>
<td>2.525</td>
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</table>

(calculated from the change in the outlet composition and the reactor volume), and the composition of the outlet flow.

We have measured the composition of the HC gas mixture on a number of different occasions and observed a composition of 13.18 ± 0.28% hydrogen (± 2.1%), 0.0255 ± 0.01% ethane (± 39%), 79.05 ± 0.25% ethylene (± 0.32%), and 7.739 ± 0.030% acetylene (± 0.39%). The relative deviations between detector calibration runs were of the same magnitude, except for ethane which was difficult to measure in the HC mixture with the TCD because of its very low concentration. Calibrations at higher ethane partial pressures, more representative of the reactor concentration during operation, showed relative deviations similar to
those of ethylene and acetylene. The observed outlet HC species concentrations used to calculate the overall carbon balances were therefore quite accurate.

The reactor volume was measured several times by pressure rise versus time plots with different mass flow controlled gas flows and the deviations between these values were also very small (see Appendix D, p. 527). The mass flow controllers are both rated at ± 0.5%, and as the calculated HC inlet flow rates actually contain the error from both flow controllers (the helium flow was assumed constant), the variation in calculated HC inlet flows during operation can be attributed mainly to the error in the flow controllers themselves.

We have no real explanation for the different steady state inlet HC flow rates observed during different experiments at the same flow controller setting. At a controller setting of 1.5 std.cc/min, we observed flows between 1.68 and 1.85 std.cc/min, while at a setting of 2 std.cc/min we observed 2.18-2.65. At a controller setting of 2.5, we observed a value of 2.86. The average flow rate at a setting of 1.5 is 1.76, RMS standard deviation 0.028 (1.6%), while the average at a setting of 2.0 is 2.437, RMS standard deviation of 0.062 (2.6%). The ratios of the set point value to the average are 1.17 and 1.22, respectively (1.14 at a setting of 2.5).

We have been tempted to attribute the changing observed rate to the age of the flow controller, as the observed values tend to increase down table 26, which is in chronological order except for the last four values (#25 and 26 were conducted between 27 and 30). This might be due to a gradual build-up of organic residue in the controller orifice.
However two of the lowest values observed on a controller setting of 2 were two of the last ones (25 and 26). It appears that even though the accuracy during any one run at a given setpoint is generally very high, the reproducibility between runs, when the controller was closed (but not shut off except during power failures), is somewhat lower. Changes in the helium flow rate also cannot be ignored, but we have no evidence supporting the conclusion that they occurred. The very high purity of the helium used during reactions (99.9999%) would suggest that we can discount contamination of this controller causing changes in the flow rate.

Because of the way we have defined product selectivities, changes in the reactor composition due to diffusion effects of any kind will have little effect on ethane and C₄⁺ selectivities, as the extent of diffusion of these species should be comparable to that of acetylene. We have more confidence in these values than in any other, except at low (<5%) acetylene conversions. As acetylene conversion decreases the relative error in the rate of acetylene consumption increases. At the same time, the relative error in the rates of ethane and C₄⁺ species production also increases. Defining selectivity as rate over rate compounds the errors in each measurement.

For this reason, we have little faith in ethane and C₄⁺ selectivities at conversions less than 5%, and feel that values calculated at conversions of less than 10% should be considered approximations only. The C₄⁺ backflush peaks were especially difficult to integrate accurately at low concentrations due to their broadness (see figure 23, p. 175). Ethylene selectivities, calculated as the
difference between 100% and the sum of all other product selectivities, are of course meaningless at these acetylene conversions.

Catalyst weight measurements were also quite accurate. The balance was zeroed and calibrated to ±0.01 mg before each run, while weights of 30-65 mg of catalyst were placed in the pan. Typical initial rates of weight gain were 0.5 mg/hr. The variation between measurements taken at the same time was of the order ± 0.05 mg. We took readings at time intervals calculated to yield a weight increase of at least 0.5 mg since the last one. During operation to catalyst death, a 0.5 mg weight gain might not be reached for more than a week. While in this range the error is somewhat greater, the rate of weight gain in this region was very small and the calculated selectivity always approached zero.

The surface polymer selectivity is by definition strongly affected by the rate of acetylene consumption. However, at initial measured conversions of 50%, no matter how large the effects of diffusion might be - and we suggest they are not large - the real acetylene conversion could not be greater than 100%, in which case real surface polymer selectivities would be half as large as we have calculated them to be, and no smaller. Of course if the real acetylene conversion was less than we have calculated, surface polymer selectivities would be substantially larger than those we arrived at.

We should note that the catalyst weight gains observed cannot be due to physical absorption of water or heavy hydrocarbons in the feed, as alumina blanks pretreated in the standard way showed no measurable weight gain (< 0.1 mg) during operation under conditions where a catalyst sample gained a minimum of 3 mg. In addition, experiments with
only the Pt hangdown wires and pans showed no weight gain during operation at temperatures between 40 and 120°C. The acetylene conversion over the Pt pan and wires alone was less than 2% at 120°C, and could not be distinguished from zero at lower temperatures.

The magnitude of the reaction rate constants will also be strongly affected by the rate of acetylene reaction. Based upon the discussion of diffusion effects above, we conclude that the magnitude of the rate constant is accurate, although when large changes occur, the rate of change may be dampened by acetylene diffusion into the TGA — in the case of decreasing conversions — or by diffusion from the TGA back into the reactor — in the case of increasing conversion. Unless there is an inflection point in the real concentration versus time behavior of acetylene in a time span of substantially less than 10 hours, such changes in conversion cannot be attributed to diffusion to or from the TGA.

Great care should be taken when comparing the magnitudes of the rate constants between different catalyst types. Metal loadings are nominal, vendor supplied only and metal dispersions are unknown. Any changes or apparent trends in rate constant values between different types could easily be due to changes in either metal loading or dispersion, particularly the latter.

In summary then, diffusion of hydrocarbons and hydrogen between the reactor and the TGA definitely does occur during recycle operation, in spite of the helium flow against it in the TGA hangdown tube. Net diffusion equilibrium between the reactor and the TGA is reached in about 10 hours from the initial condition of about 14.4% HC mix in the
reactor, zero in the TGA. The TGA equilibrium concentration is about 3.8% HC mixture in helium. Therefore, the reactor system does not behave as a true CSTR. However, because of the direction of changes in consumption and/or production of the various species in the reaction system, and the time scales on which they occur, we conclude that this diffusion does not affect the magnitude of the steady values obtained, but only the time necessary for the changes to be completed.

Calculated values of catalyst activity and product selectivities then do accurately reflect the reactions occurring on the catalyst surface. The accuracy of ethane, \( C_4 \), and ethylene selectivity measurements breaks down rapidly at acetylene conversions approaching 10%, and are probably meaningless at conversions less than 5%. Surface polymer selectivities cannot be less than 1/2 of the values we have calculated, and could theoretically be much higher, but given the constraints on the effects of diffusion on acetylene conversion, we believe these values are accurate.
IV. RESULTS AND DISCUSSION

A. The Formation of Polymer

1. Results

The formation of both gas phase and surface polymers was observed during all experiments conducted in this study. The rate of surface polymer formation during operation at 40°C decreased with catalyst metal loading (figure 29). 0.5 and 0.1 wt% Pd catalysts approached limiting values of 800 mg polymer/ml catalyst pore volume. The 0.02 wt% Pd sample was not operated for sufficient time to reach this polymer loading value; comparison of the behavior of the three different samples suggests that this would not be achieved until at least 1000 hours of operation.

![Graph showing polymer formation over time](image)

Figure 29. Surface polymer formation during operation at 40°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 28, 1, 8, 21)
Although the rates of polymer formation, on a per total catalyst basis, over these samples are very different, these differences are largely removed when these rates are divided by the acetylene consumption rate observed in each case (expressed as selectivities). Figures 30-32 show the total, surface, and gas phase polymer selectivities, respectively, calculated during these experiments. From figure 30 it appears that although the initial total polymer selectivity increases with decreasing metal loading, after 50 hours operation all samples exhibit similar values. Figures 31 and 32 show that this increase in total polymer selectivity with decreasing metal loading is mainly due to differences in the surface polymer selectivities, as gas phase polymer values are essentially identical.
Figure 31. Surface polymer selectivities observed during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 32. Gas phase polymer selectivities observed during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Because the amount of polymer on each catalyst sample at any given time is different, we have also compared polymer selectivities at equal polymer loadings, as one might expect the amount of polymer to affect
the rate of further polymer formation (figures 33–35). This operation expands the initial points, where the rate of surface polymer formation is highest, and compresses the later points, where the rate approaches zero. On this basis the total polymer selectivity is initially highest on the 0.02 wt% Pd sample, but with increasing surface polymer loading it decreases to less then the values observed over the 0.5 and 0.1 wt% samples, which remain fairly constant (figure 33).

![Graph](image)

**Figure 33.** Total polymer selectivities compared at equal polymer loadings during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Surface polymer selectivities are all initially 25–35%, but decrease with increasing polymer loadings as would be expected (figure 34). After the rapid initial decrease, surface polymer selectivities increase with increasing metal loading. Gas phase polymer selectivities compared on this basis are still very similar, although the initial values over the 0.02 wt% catalyst are somewhat higher than the others,
and it appears to be decreasing rapidly during further surface polymer build-up (figure 35).

Figure 34. Surface polymer selectivities compared at equal polymer loadings during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 35. Gas phase polymer selectivities compared at equal polymer loadings during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.
Similar experiments were conducted using the 0.1 and 0.02 wt% Pd catalysts at 80°C. The 0.5% sample is not included here because the rate of polymer formation was so high that the catalyst deactivated too quickly to collect meaningful rate data, and the reaction appeared to be pore diffusion limited at all times (see section IV C Catalyst Activation and Deactivation, p. 333). The rate of polymer formation is still higher on the 0.1% sample (figure 36), although both rates are higher than at 40°C.

![Graph](image)

Figure 36. Surface polymer formation during operation at 80°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 12, and 25)

The total surface polymer selectivity is again initially higher on the 0.02% sample, but decreases to approximately the 0.1% value after about 30 hours of operation (figure 37). This decrease is more dramatic when these experiments are compared at equal polymer loadings (figure 38), due to the lower rate of polymer formation on the 0.02% sample.
Figure 37. Total polymer selectivities observed during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 38. Total polymer selectivities compared at equal polymer loadings during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

The surface polymer selectivities on a time basis are again higher for the 0.02% sample (figure 39), while on a polymer loading basis, the 0.02% value decreases rapidly to less than the 0.1% value (figure 40).
Figure 39. Surface polymer selectivities observed during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 40. Surface polymer selectivities compared at equal polymer loadings during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Gas phase polymer selectivity values and trends versus both time and polymer loading were essentially identical to those observed at 40°C (figures 32 and 35), and are not presented here.
We have investigated the effects of reaction temperature on the formation of both surface and gas phase polymers. With a 0.1 wt% Pd catalyst the rate of polymer formation increases with reaction temperature between 40 and 70°C (figure 41). However, the rates at 70 and 80°C are essentially equal. Trends in the rate of acetylene consumption during these experiments suggest that the reaction over the sample at 80°C was pore diffusion limited throughout the operation (see section IV C, p. 333). We can not be sure at this point if this effect is real (the real rate of surface polymerization has not increased), or if it is due to pore diffusion limitations.

![Figure 41. Surface polymer formation during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst (Experiments 8, 10, 11, and 12).](image)

Total polymer selectivities were somewhat higher at 40°C than at higher temperatures, but the difference was not large and the values at 60-80°C were very similar. The same is true for gas phase polymer selectivities. Surface polymer selectivities, however, decreased with
increasing temperature (figure 42). Unlike the comparisons of different metal loadings, where surface polymer selectivities increased with decreasing metal loading on a time basis (figure 31) but decreased with the same on a polymer loading basis (figure 34), these also decrease with increasing temperature on a per polymer basis (figure 43). Because the reaction at 80°C appeared to be pore diffusion controlled throughout its duration, we have not used this catalyst at temperatures higher than this.

![Graph showing surface polymer selectivity at different temperatures](image)

**Figure 42.** Surface polymer selectivities during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

We have investigated the formation of polymers on a 0.02 wt% catalyst at temperatures between 40 and 120°C. The rate of surface polymer formation is always higher at 80°C than at 40°C, but the initial rate at 80°C is higher than the initial rate at 120°C (figure 44). After about 20 hours, the rate at 80°C has decreased sufficiently for the rate at 120°C to surpass it. Except for this initial reversal, the behavior
Figure 43. Surface polymer selectivities compared at equal polymer loadings during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

Figure 44. Surface polymer formation during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst (Experiments 21, 25, and 26).

is identical to that observed over the 0.1 wt% Pd catalyst between 40 and 80°C. Surface polymer selectivities decrease with reaction temperature (figure 45), also in agreement with the results on the 0.1
Figure 45. Surface polymer selectivities during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

wt% sample (figure 42). Surface polymer selectivities compared at equal polymer loadings are identical at 40 and 80°C, but are drastically lower at 120°C (figure 46). The surface polymer selectivity in this

Figure 46. Surface polymer selectivities compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.
experiment was the lowest we observed at any condition of operation. The 0.5 and 0.1 wt% catalysts were not used at this temperature (in order to investigate whether they too would exhibit very low surface polymer selectivities) because of the very rapid deactivation we would expect under these conditions and the fact that both catalysts already became pore diffusion controlled at much lower temperatures.

Gas phase polymer selectivities observed during operation decreased with increasing temperature (figure 47), unlike those with the

![Graph](image)

**Figure 47.** Gas phase polymer selectivities during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

0.1 wt% catalyst. However, the range of temperatures used in this case is twice that used with the 0.1% sample, and it is possible that a similar trend would be observed if the temperature range of the 0.1% sample was increased to 80°C. Compared at equal polymer loadings, the gas phase polymer selectivities observed at 40 and 80°C are equal (figure 48). The value at 120°C up to polymer loadings of about 400
Figure 48. Gas phase polymer selectivities compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

mg/ml catalyst pore volume is substantially lower than those at 40 and 80°C. However there is a problem with this measurement.

The reactor circulation loop was not heated during operation; only the hangdown-tube containing the catalyst was at the reaction temperature. It is therefore theoretically possible that gas phase polymers could condense on the glass walls of the circulation system. This was never observed during any of these experiments. However after the experiment at 120°C, the walls of the TGA hangdown tube containing the catalyst sample (which was at 120°C) were coated with a thick brown liquid. Apparently some of the gas phase polymers which were volatile at 120°C decomposed upon contact with the heated glass tube. Since this material did not dissolve in any hydrocarbon solvent we used, we could not measure the quantity or composition of it (it was finally burnt off with a glass torch). The actual gas phase polymer selectivity is
therefore higher than that appearing in figures 47 and 48, although we do not know how much higher.

Because total polymer selectivities are simply the sum of the surface and gas phase values, these suffer from the same problem as the gas phase selectivities at 120°C. Therefore although the total polymer selectivity during operation decreases with increasing temperature (figure 49) and values at 120°C compared at equal polymer loadings are

![Graph showing total polymer selectivities at different temperatures](image)

**Figure 49.** Total polymer selectivities during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

significantly lower than those at 40 and 80°C (figure 50), we cannot be sure if these apparent trends are accurate. Based upon the results at 40 and 80°C, we might suspect that the total polymer selectivity at 120°C is lower at all operation times, but is substantially equal at equal polymer loadings.

Regardless of the actual change in gas phase polymer selectivity with increasing temperature, it is clear that the surface polymer selectivity, compared at equal polymer loadings, decreases sharply
between 80 and 120°C (figure 46). If gas phase polymer selectivities at 120°C are equal to those observed at lower temperatures (figure 48), then the total polymer selectivity at 120°C will be lower than those at lower temperatures by the difference between surface polymer selectivity values (figure 46).

The effects of the support surface area on polymer selectivities have been investigated on a series of 0.5 wt% Pd catalysts on aluminas of 4, 33, 90, and 220 m²/g. Both the rate of surface polymer formation and the final polymer loading at catalyst death increase with increasing support surface area from 4 to 90 m²/g (figure 51). On the 220 m²/g support, however, both values are equal to those observed over the 4 m²/g sample and are considerably lower than the 33 and 90 samples.
Figure 51. Surface polymer formation during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas. (Experiments 1, 3, 6, and 7).

The total polymer selectivity of the 4 m²/g sample, on both a time and polymer loading basis, was somewhat lower than those of the other samples, but the difference was small (5%) and all of the other values were essentially equal. There was no real difference in the gas phase polymer selectivity values of any sample (figure 52).

Although no clear trends with support surface area are apparent (figure 53), surface polymer selectivities over the 220 m²/g sample are high the longest, while those over the 4 m²/g sample are initially the lowest. At equal polymer loadings, there is a definite trend of increasing surface polymer selectivities with increasing surface area with the 4, 33, and 90 m²/g samples (figure 54) but the 220 m²/g sample exhibits values in the same range as the 33 m²/g sample, between the extremes of the 4 and 90 m²/g samples.
Figure 52. Gas phase polymer selectivities compared at equal polymer loadings during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

Figure 53. Surface polymer selectivities during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

The acetylene consumption behavior of the 4 and 220 m²/g samples suggests that the reaction is pore diffusion limited on both (see
Figure 54. Surface polymer selectivities compared at equal polymer loadings during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

section IV C, p. 333). This may explain the remarkable correspondence of their polymer loading values during operation (figure 51), and perhaps the lack of any clear trend in surface polymer selectivity versus support surface area (figure 54).

The effects of the acetylene feed concentration have been investigated during reactions over the 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst at 40°C. The rate of surface polymer formation with a feed concentration of 1.05% is considerably higher than with 0.35% (figure 55). The total and gas phase polymer selectivities are equal in both of these cases, as are the surface polymer selectivities at identical times (figure 56).

Because the surface polymer selectivities are identical on a time basis while the polymer loadings are different, the surface polymer selectivities at equal polymer loadings must be different (figure 57).
Figure 55. Surface polymer formation during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations (Experiments 3 and 4).

Figure 56. Surface polymer selectivities during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations.

In this case, the surface polymer selectivities observed with 1.05% acetylene feed are always higher than those observed with 0.35%.
Figure 57. Surface polymer selectivities compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations.

The effects of different catalyst treatments have been investigated on a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst operated with approximately 1% inlet acetylene feed at 40°C. The original catalyst sample was pretreated in the standard way (2 hours in flowing O₂ at 200°C followed by 2 hours in flowing H₂ at 300°C). After 220 hours operation (1), the system was evacuated until no further catalyst weight loss occurred in a 24 hour period. This took 90 hours and removed 26.8% of the surface polymer from the sample. The reaction was then restarted at 40°C with identical inlet flow rates. After 27 hours further operation (2), the catalyst was treated with flowing H₂ at 300°C for 2 hours, then cooled back to 40°C. This treatment removed 94% of the surface polymer present. The reaction was restarted, again at identical flows. After 220 hours further operation (3), the sample was treated with flowing O₂ for 1/2 hour at 200°C, followed by flowing H₂ for 2 hours at 300°C. This
treatment removed 53.6% of the surface polymer present. After cooling to 40°C, the reaction was begun again at the same flow rates and continued for 50 hours (4).

The catalyst was active for polymer formation after each of these treatments (figure 58). The overall rates of surface polymer formation appear to be quite similar, although the rate after evacuation (2) is obviously higher than after the other three treatments.

![Graph showing polymer formation over time](image)

Figure 58. Surface polymer formation observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 21). 2. Same sample after 90 hours evacuation at 40°C (Exp. 22). 3. Same sample after hydrogen treatment (Exp. 23). 4. Same sample after oxygen-hydrogen treatment (Exp. 24).

The total polymer selectivities as functions of time are generally highest on the initial sample (1), followed by the oxygen-hydrogen treated (4), the hydrogen treated (3), and the evacuated (2) samples, although initially the oxygen-hydrogen treated value is highest (figure 59).
Figure 59. Surface polymer formation observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 58 for symbol definition.

Because each experiment other than the first begins with a non-zero surface polymer loading, comparisons at equal polymer loadings do not necessarily have the same significance as those considered earlier. Figure 60 shows the total polymer selectivities of all four experiments compared at equal polymer loadings. Evacuation (2) has removed only about 1/4 of the total surface polymer, and its only apparent effect on the total polymer selectivity is to increase it slightly higher than the value observed during initial operation. Hydrogen treatment (3) removed more than 3/4 of the surface polymer and decreases the subsequent total polymer selectivity relative to both the initial and post-evacuation values. Oxygen-hydrogen treatment (4), on the other hand, removed about 50% of the surface polymer but results in a drastic increase in the subsequent total polymer selectivity. The initial values after this treatment are higher than all others at equal polymer loadings, and in addition are higher than the others at all polymer loadings.
Figure 60. Total polymer selectivities compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 58 for symbol definition.

Surface polymer selectivities are generally highest over the initial sample, followed by the hydrogen treated, oxygen-hydrogen treated, and finally the evacuated sample, although the very early values over the hydrogen and oxygen-hydrogen treated samples are very high (figure 61).

The comparison of surface polymer selectivities at equal polymer loadings is again more complicated. In each case other than the initial one, surface polymer selectivities after treatment are much higher than the values typically observed at that polymer loading (in the absence of, or at different surface polymer loadings than, the various treatments) and decrease much faster than initially (figure 62).
Figure 61. Surface polymer selectivities observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 58 for symbol definition.

Figure 62. Surface polymer selectivities compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 58 for symbol definition.

Gas phase polymer selectivities are remarkably similar over all catalyst samples used, regardless of the treatment (figure 63).

However, because the polymer loading is different in each case, and
Figure 63. Gas phase polymer selectivities observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 58 for symbol definition.

because of the large changes in surface polymer selectivity versus small changes in total polymer selectivities following each pretreatment, gas phase polymer selectivities from the various treatments (at equal polymer loadings) must be different in the opposite direction of surface polymer selectivity changes (figure 64).

Compared at equal polymer loadings, the net effect of each of these treatments is to sharply increase the surface polymer selectivity and sharply decrease the gas phase polymer selectivity, even though the total polymer selectivity may be decreased slightly (hydrogen treatment), increased slightly (evacuation), or increased sharply (oxygen-hydrogen treatment).

The previous series of experiments was carried out with catalyst samples that had polymer loadings of about 200 mg/ml catalyst pore volume. It was in the range zero to 200 that catalyst activation and
ethane selectivity increases occurred (see sections IV C and IV D, respectively). Catalyst deactivation, however, generally did not occur until polymer loadings of 600-800 mg/ml pore volume. We calculate that it would require at least 1000 hours operation to achieve such a polymer loading on a 0.02 wt% sample at 40°C. A 0.5 wt% sample required only about 40 hours to reach such a polymer loading, and this was used to investigate the causes of deactivation.

A sample of 0.5 wt% Pd on 90 m²/g Al₂O₃ was pretreated in the standard way, then operated at 40°C for 40 hours with approximately 0.8% inlet acetylene. The catalyst activity was less than 1/4 of its maximum value at this point. The sample was then evacuated for 72 hours, until no further weight loss was observed. This evacuation removed 28.3% of the surface polymer present. After restarting the reaction at identical conditions (temperature and flow rates), the activity was slightly
higher than the maximum observed during the initial experiment. It decreased to less than 1/4 of the maximum value in only 25 hours. Next, the sample was evacuated for 2 hours at 200°C, followed by 3 hours at 300°C. This removed 78.5% of the polymer present, but left the sample completely inactive for further reaction.

The polymer loadings observed during these operations (figure 65) were very similar to those observed over an identical catalyst sample discussed previously (figure 29, p. 211). In contrast to the evacuated 0.02 wt% sample (figure 58, p. 232), the rate of surface polymer formation after evacuation was lower than the initial rate, even though the percentage removal was the same in each case (26.8 and 28.3%). Of course the total polymer loading was higher both before and after evacuation on this catalyst sample (711 and 520 versus 192 and 145 mg/ml pore volume).

![Graph showing polymer formation over time](image-url)
The total polymer selectivity after evacuation was lower than during the initial experiment (figure 66), as it was after evacuation of the previous 0.02 wt% sample (figure 59, p. 233). When compared at equal polymer loadings, however, the total polymer selectivity of this sample was slightly decreased (figure 67) in contrast to the 0.02% sample, which was slightly increased (figure 60, p. 235).

In agreement with the previous results over the 0.02 wt% catalyst, the surface polymer selectivity as a function of time is reduced compared to the initial values (figure 68), while comparison at equal polymer loadings shows an increase in surface polymer selectivity versus the initial experiment (figure 69).

The gas phase phase polymer selectivities compared by time of operation are nearly identical (figure 70), in agreement with the various 0.02 wt% catalyst treatments (figure 63, p. 236). Compared on
Figure 67. Total polymer selectivity compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

Figure 68. Surface polymer selectivities observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

an equal polymer loading basis, the gas phase polymer selectivity after evacuation is somewhat lower than the initial experiment values (figure
71), although not nearly as much lower as the 0.02 wt% values after evacuation (figure 64, p. 237).

**Figure 69.** Surface polymer selectivities compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

**Figure 70.** Gas phase polymer selectivities observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).
Figure 71. Gas phase polymer selectivities compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

We have also investigated the effects of the HC mixture pressure on the rates of both surface and gas phase polymer formation under differential conversion conditions (low Pd content and high total gas flow rates) at 40°C over 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst samples. The rate of surface polymer formation is nearly independent of the HC mixture pressure at acetylene pressures above about 5 torr, and decreases rapidly at lower pressures (figure 72). From this figure alone, we cannot definitely conclude that the behavior is zero order in both acetylene and hydrogen; because the hydrogen/acetylene ratio is constant at all times, we would expect identical behavior if it were first order in hydrogen and negative one order in acetylene. We can only conclude that at this hydrogen/acetylene ratio, it is zero order in total pressure.
Figure 72. The dependence of the rate of surface polymer formation on acetylene partial pressure at differential conversions over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst at 40°C. (Experiments 13-20).

During these differential conversion experiments, we also measured the rates of production of the gas phase polymer species. These measurements were complicated by initial behavior of this reaction system. As shown previously, the gas phase polymer selectivity increased during the initial stages of operation over all catalysts. In addition, the activity of almost every catalyst increased during the same time period. We therefore have a problem deciding at what time to measure these rates. On this 0.1% catalyst at 40°C, the rate of surface polymer was essentially linear up to three hours of operation.

We therefore chose to measure the surface polymer production rates as the overall rate after three hours, while samples of the outlet gas mixture were taken throughout this operation. Figures 73 and 74 show the results of all of these measurements, rates of production at the observed acetylene pressures, for C₄ and C₆, species, respectively.
Figure 73. The dependence of the rate of C4 formation on acetylene partial pressure at differential conversions over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst at 40°C. (Experiments 13-20).

Figure 74. The dependence of the rate of C₆⁺ formation on acetylene partial pressure at differential conversions over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst at 40°C. (Experiments 13-20).

The spread of rates and acetylene pressures during any single experiment is not too large, but the variation between experiments, particularly the two at about 3 and 4.5 torr acetylene, respectively, is
quite large. It may of course be possible that these rates do vary with pressure in this manner, but it would probably be unwise to make this conclusion from these data alone. Based on the more accurate results of the pressure dependence of surface polymer formation, it would probably be more prudent to tentatively conclude zero order dependence on total pressure in this case.

We should note that the total rate of gas phase polymer formation is approximately 0.12 moles/mole Pd·min, versus a surface polymerization rate of 0.6-0.8 at the same conditions, in agreement with the previous observations of relatively high surface and low gas phase polymer selectivities during initial operation.
A. The Formation of Polymer

2. Discussion

From the results presented in the previous section it is apparent that surface polymer formation is not negligible, particularly during the initial stages of reaction. The lowest surface polymer selectivities observed on fresh catalysts are 5% over 0.02 wt% Pd on 90 m²/g Al₂O₃ at 120°C (figure 45) and 8% over 0.5 wt% Pd on 4 m²/g Al₂O₃ at 40°C (figure 53). Values are higher, generally between 15 and 35%, at all other conditions employed in this study. Because this has not been observed previously and contradicts the normal assumption that this selectivity is negligible, we must establish that it is not an artifact of some kind.

We have conducted experiments with a number of pure Al₂O₃ samples in order to test whether catalyst weight gain is due to physical adsorption of feed contaminants, particularly water or heavy hydrocarbons. The observed weight gains during these tests was less than 0.1 mg on a sample of about 50 mg at conditions where a catalyst gained at least 3 mg on a sample also of about 50 mg. Similarly the Pt hangdown wires and pans showed no measurable weight gain during operation between 40 and 120°C.

In addition, evacuation at reaction temperature removed about 30% of the total catalyst weight previously gained. Material balance calculations from polymer samples extracted from spent catalysts in various hydrocarbon solvents and analyzed in the GC suggested that this fraction accounted for approximately 30% of the total weight gain. It would seem likely that the same species were removed in each case, and
the GC analysis confirms the presence of hydrocarbons of carbon numbers much greater than 2 (see section IV B, The Polymer Composition, p. 260, for more details). The remaining 70% of the surface species could not be removed by evacuation or solvent extraction, ruling out water or heavy hydrocarbon feed contaminants as the cause of this weight gain. The species could, however, be at least partially removed by hydrogen and/or oxygen-hydrogen treatment at elevated temperatures (figure 58). During hydrogen treatment at 300°C, a large number of hydrocarbons, including benzene, acetylene, and ethylene, were observed in the reactor outlet stream. Digestion of spent catalysts in hydrofluoric acid left thin brown sheets of an unknown material in solution, suggesting some type of carbon containing species.

Considering all of these data, we conclude that the calculated surface polymer selectivities do represent the actual formation of polymers on the catalyst surface, and are not due to any artifact.

These surface polymer selectivities are perhaps surprisingly high. We must now consider whether there is any precedent for the rates of polymer formation observed here. Sarkany, et al (141) reported a rate of polymer formation of 0.30 mg/gcat*hr during the first 12 hours of operation with a 0.04 wt% Pd/g-Al₂O₃ catalyst. Unfortunately, the temperature at which this reaction was conducted is not included in this paper. The feed gas contained 0.29 mol% acetylene, and most acetylene conversions reported in this work were around 60%. Assuming that this is the case here, the acetylene pressure during this experiment was about 0.9 torr, with an initial hydrogen/acetylene ratio of 1.5. The
rate of surface polymer formation corresponds to 0.048 moles polymer/mole Pd*minute.

Since we have not employed catalysts of 0.04 wt% Pd metal loading, we will choose the 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst for comparison. At 40°C, we observed an initial surface polymer formation rate of about 1.3 mg/gcat*hr, or 0.41 moles/mole Pd*minute. The inlet acetylene concentration was 0.91 mol%, and the conversion 45%. This corresponds to an acetylene pressure of about 4 torr, with an inlet hydrogen/acetylene ratio of 1.7. From figure 72, we would expect the rate of polymer formation at 4 torr acetylene to be considerably higher than at 0.9 torr, and this might explain some of the ten-fold difference in rates (0.048 in (55) and 0.41 here). In addition, it appears likely that the rate measured by Sarkany, et al (141) was conducted at 25°C. Assuming a polymerization activation energy of 12 kcal/mole — that the activation energy for polymerization is approximately equal to that of hydrogenation — the rate measured by Sarkany, et al (141) corresponds to a rate of about 0.13 moles/mole Pd*min at 40°C. This is only 3 times lower than the rate we observed, and this difference can be easily explained by the 4 fold difference in acetylene pressures during these two experiments.

Yahun, et al (194) report a maximum rate of polymerization of 0.60 mg/gcat*hr at 40°C over a 0.035 wt% Pd on Al₂O₃ catalyst. They report an inlet acetylene concentration of 0.4 mol%, a conversion of about 80%, and an inlet hydrogen/acetylene ratio of 1.5-4.0. The total system pressure is not clearly stated, but appears to be about 5 atm. This would correspond to 15.2 torr inlet and 3 torr outlet acetylene (the
reaction was conducted at plug flow conditions). The rate of polymerization is 0.11 moles/mole Pd*minute. This number is more difficult to reconcile with ours. From figure 72 we would not expect the rate of polymerization between 15 and 3 torr acetylene to be much higher than the one we measured at 4 torr, but we would expect it to at least be equal to ours. However, Yahun, et al (194) report that the rate of polymerization versus the hydrogen/acetylene ratio goes through a maximum. They do not give any details of this observation, and the actual hydrogen/acetylene ratio during their experiment is only stated as 1.5-4.0. Assuming that the maximum occurs somewhere at hydrogen/acetylene ratios less than one, we might be able to reconcile the differences here if their hydrogen acetylene ratio is closer to 3 or 4 than 1.5, but these assumptions do not appear to be justified at this time.

It is clear that while the rates of surface polymerization observed in this work are larger than those previously reported, they are not unreasonably large. Yet we have calculated initial surface polymer selectivities of 15-35% (about 32% on the 0.02 wt% Pd catalyst), while Yahun, et al (194) report an average value of 2.5-5% of the total inlet acetylene, and Sarkany, et al (141) report that the surface polymer selectivity was about 2% and was therefore ignored in subsequent calculations. It is not clear if the latter value is an initial value, or an average taken over the duration of the experiment. If the latter is true, the initial surface polymer selectivity must have been at least 4%, as their conversion was constant throughout the reaction and the average rate of polymerization was 0.15 mg/g_{cat}*hr (versus 0.30 at 6
hours). Similarly, since the average conversion observed by Yahun, et al (194) was about 75%, their average selectivity would be 3.3-6.7%. These values are considerably lower than those observed here.

However, if we calculate average polymer selectivities from this work, we find values much closer to those reported by Yahun, et al (194) and Sarkany, et al (141). This occurs because surface polymer selectivities always decrease rapidly during operation (figure 31). The average surface polymer selectivity observed over the 0.02 wt% Pd sample is about 14%. Polymer selectivities calculated in this way are not very useful though, as they depend strongly on the time of operation. Had we continued the reaction on this catalyst for another 200 hours, we would calculate a much lower average value (approaching 5%), while considering only operation up to say 25 hours would yield a much higher value (about 25%). Clearly this is not an accurate way to compare the behavior of different experiments.

Surface polymer selectivities observed over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with 1.05 and 0.35% inlet acetylene concentrations were essentially identical on a time basis (figure 56), while those observed with 1.05% inlet acetylene were always higher compared at equal polymer loadings (figure 57). The maximum acetylene conversions were 61 and 42%, representing acetylene pressures of 3.1 and 1.54 torr, respectively. The initial rates of surface polymer formation were 0.28 and 0.13 moles/mole Pd*min, confirming the lower rate predicted for lower total HC mixture pressures in figure 72. The rate of acetylene consumption was of course lowered by almost the same extent, as shown by the nearly identical surface polymer selectivities observed.
The rates of acetylene consumption observed during these two experiments fit a first order hydrogen, zero order acetylene model fairly well (see figure 154, p. 350), suggesting that the polymerization rate under these conditions also behaves in this way and that the positive order observed in this pressure range in figure 72 is due to a positive reaction order in hydrogen, not acetylene. This positive order behavior confirms our earlier assumption that the polymerization rate observed by Sarkany, et al (141) at 0.9 torr acetylene and 25°C (0.048 moles/mole Pd*min) might be expected based upon our observed rate at 4 torr acetylene and 40°C (0.41). Correcting Sarkany, et al's value to 40°C with an activation energy of 12 kcal/mole yields a value of 0.13 moles/mole Pd*min, the same value we have calculated for 1.54 torr and 40°C over this 0.5 wt% Pd catalyst. Correcting their value over a 0.04 wt% Pd catalyst to 1.54 torr acetylene would yield a rate somewhat higher than ours over this 0.5 wt% Pd catalyst, consistent with our observation that the initial surface polymer selectivity is higher over catalysts of lower Pd loadings (figure 31 and 34).

We complete this section of our discussion by concluding that the rates of surface polymer formation observed in this work are not without precedent in the literature, and appear to represent reasonable rates of actual polymerization occurring on the catalyst surface, rather than artifacts of any type. Surface polymer selectivities calculated from these polymerization rate data and acetylene consumption rates appear to be somewhat higher than we would expect from the data of previous investigations. However there are conceivable circumstances in which the various values can be reconciled, particularly if the selectivity to
polymer goes through a maximum with hydrogen/acetylene ratios, as reported by Yahun, et al (194). There is precedent for this assumption in past investigation of gas phase polymerization selectivities. The rate of acetylene polymerization in the absence of hydrogen is essentially zero (67,194,210), while the gas phase polymer selectivity generally decreases with increasing hydrogen/acetylene ratios (37,70,109). It must therefore pass through a maximum, and we might expect the surface polymer selectivity to behave similarly.

This conclusion, however, is contradicted by other results. Sheridan (70) reported that the percentage of acetylene producing species other than ethane and ethylene (polymers) only decreased from 38 to 20% with a change in the hydrogen/acetylene ratio of 1:4 to 5:1. LeViness (89) reported C₄ selectivities of 20-30% during batch reactions with hydrogen/acetylene ratios greater than 17.

Based upon our values of surface polymer selectivities, it is imperative that we include them in calculating ethylene selectivities. Had we assumed that the surface polymer selectivity is negligible, calculated ethylene selectivities would have actually been the sum of the real ethylene selectivity and the polymer value. As the surface polymer selectivity decreased during the initial stages of reaction, calculated ethylene selectivities would have appeared to decrease rapidly, although this would not have necessarily been the case (they could, of course, be decreasing in this time of operation anyway, but the extent of the decrease would be increased by ignoring surface polymers).
The parameters that affect surface polymer selectivities, and the extent of their effects, are still poorly understood. The hydrogen/acetylene ratio may or may not have a large effect, and the range of ratios where this might occur is presently unknown.

For these reasons, we cannot conclude that surface polymer selectivities are always as high as those observed here. We can, however, conclude that they could be, at least under some conditions, and urge future researchers not to assume they are negligible until measurements show that to be the case. Previous ethylene selectivities calculated by the difference between 100% and the sum of all other product selectivities, not including the surface polymer value (89,108,109,137-144,190), must be considered suspect. Those that also ignored gas phase polymerization products (110-112,132) must be considered wrong, as the total polymerization selectivity is generally in the range of 40-50%.

Surface polymer selectivities always decreased during operation, usually fairly rapidly in the initial stages of operation (figures 31,39,42,45,53,56,61,68). During the same stages of reaction, gas phase polymer selectivities increased fairly rapidly (figures 32,47,52,63,70). Total polymer selectivities generally changed to a much smaller degree (figures 30,38,49,59,66), although substantial initial decreases were observed in some cases. It appears that at least some of the initial increase in gas phase polymer selectivity is a direct result of the decrease in surface selectivity. This is most apparent after the various treatments conducted on a 0.02 wt% Pd catalyst (figures 59-64). Here the treatments which removed some of the surface polymer had a much
larger effect on surface and gas phase polymer selectivities compared to the effect on the sum of the two (total polymer selectivity).

The ability of various aluminas to adsorb hydrocarbons is well known, and forms the basis for their use as GC column packings and hydrocarbon filters. We would expect that heavier hydrocarbons would be retained on the alumina until their amounts reached a certain value, after which they would appear in the gas phase. Removing the surface species by evacuation or higher temperature hydrogen or oxygen-hydrogen treatments would cause this initial behavior to be repeated, as we observe. The much smaller changes in the total polymer selectivity, usually in the downward direction, could be caused by selective poisoning of sites responsible for polymerization by the surface polymers or to changes in the nature of the active sites themselves. This latter hypothesis will be considered in greater detail in a later section (IV C, Catalyst Activation and Deactivation).

This interpretation of the causes of the initial changes in surface and gas phase polymer selectivities is supported by the results of experiments at different temperatures. Surface polymer selectivities decrease with increasing temperature over the 0.1 wt% catalyst between 40 and 80°C (figures 42 and 43), and over the 0.02 wt% catalyst between 40 and 120°C (figures 45 and 46). Sheridan (70) reported an decrease in total polymer selectivity from 28 to 20% between 0 and 120°C, although he did not report the distribution between the surface and the gas phase.

This behavior might be due to a lower real activation energy for polymerization than hydrogenation. The observed value certainly is
lower. We have no way of calculating the real polymerization activation energy, however, because of changes in adsorption-desorption parameters with temperature, which are unknown. The composition of the gas phase polymers suggests that 1,3-butadiene is the only species which might be able to compete with acetylene and ethylene for surface adsorption sites, and even here it is not completely clear if this is the case (see section IV B, The Polymer Composition, p. 260). At any rate, it would appear that the growth of at least the gas phase polymer species occurs during one residence time on the Pd surface. Increasing temperature will decrease the pseudo-equilibrium surface concentration of lower molecular weight polymers, particularly C₄ and C₆ species, whose boiling points are lower than 80°C. In addition, the highest observed partial pressure of any polymer species was on the order of 1.3 torr (1-butene), far below the saturation partial pressures at these reaction temperatures.

Increasing reaction temperature would then decrease the surface concentration of lower molecular weight species, and extend the range of molecular weights which are driven off the catalyst surface. The net result would be a decrease in the relative amount of high molecular weight surface species, as we observe.

If this were the only effect of temperature, and if the activation energies of polymerization and hydrogenation were identical, then we would expect to find a corresponding increase in gas phase polymer selectivities so that the total polymer selectivity remains constant with temperature. Total polymer selectivities were indeed essentially unchanged over the 0.1 wt% catalyst between 40 and 80°C, but this
temperature range is rather narrow. Over the 0.02 wt\% sample, total polymer selectivities decrease with increasing temperature on a time scale (figure 49), but the values observed at 40 and 80°C are identical when compared at equal polymer loadings (figure 50). The value observed at 120°C is substantially lower than the other two, but there are problems with the reliability of these data.

After this experiment was terminated, we found a thick brown liquid covering the inside of the reactor hang-down tube. This was apparently caused by the decomposition of gas phase polymer species on the glass surface. Observed gas phase selectivities are therefore somewhat lower than the real rates of production would suggest. The extent of this artificial decrease is unknown, but as values of gas phase polymer selectivities are equal at polymer loadings higher than about 400 mg/ml pore volume (figure 50), we might suspect that they were actually equal at lower loadings too. This would suggest that the actual activation energies for hydrogenation and polymerization are very similar, if not identical, but we do not have sufficient data to make such a conclusion at this time.

The behavior of polymer selectivities at different metal loadings and support surface areas are harder to analyze, particularly as metal dispersions are unknown. Initial rates of polymerization, on a per Pd basis, were roughly identical on catalysts of different metal loadings. This immediately leads us to expect the trends in the amount of polymer per catalyst pore volume apparent in figures 29 and 36. Initial total polymer selectivities are higher on catalysts of low metal loading (figures 31, 33, 37, and 38), although on a polymer loading basis they
rapidly decrease to values lower than those observed with catalyst of higher metal loadings (figures 33 and 38). Identical behavior is exhibited by the surface polymer selectivities (figures 31, 34, 39, and 40). Gas phase polymer selectivities are more nearly equal over all samples.

Although we do not have any information on catalyst metal dispersions, it would not seem unreasonable to assume that dispersion increases with decreasing metal loading. If this is the case, as we will assume it is, then the lower polymer selectivities exhibited over catalyst of decreasing metal loading are due to the decreasing Pd crystallite size, if the polymerization reaction requires multiple neighboring Pd sites (as has been proposed (67, 70, 86, 109, 143, 543, 566, 567). The reasons for the higher initial surface polymer selectivities over low loaded catalysts are not so clear. We suggest that they may be caused simply by a greater retention of polymers on the catalyst surface on a Pd basis, which is how these selectivities are defined.

The actual pseudo-equilibrium concentration of lighter polymers will be approximately equal over all catalysts on a total catalyst basis. With decreasing metal loading, this translates into higher surface retention per unit Pd, and would increase the initial surface polymer selectivity in spite of the lower total polymer selectivities observed. While it is theoretically possible that this is due to some initial activity of the alumina support for polymer formation which is rapidly poisoned, experiments with alumina blanks, which exhibited little or no measurable weight gains, suggest that this is unlikely.
The discussion of the effects of catalyst surface area is complicated by the fact that reaction rate measurements and ethane selectivities suggest that the reaction was acetylene pore diffusion limited over both the 4 and 220 m²/g Al₂O₃ supported samples. Even if this were not the case, there are no clear trends among all four of the samples. Values observed over the 220 m²/g sample were particularly uncooperative in establishing any easily interpreted results.

It is not at all clear why the limiting polymer loading should increase with increasing surface area, except for the 220 m²/g sample (figure 51). If we ignore that sample, the increase with surface area between the other three could be due to different metal deposition profiles, assuming that the depth of impregnation increases with decreasing surface area. Polymer in pores near the catalyst surface would then choke off the reaction at lower polymer loadings than if the metal is deposited in a thin eggshell layer on or near the surface. Gas phase polymer selectivities appear to be relatively unaffected by changes in surface area (figure 52), the same as with changes in metal loading and/or reaction temperature.

Surface polymer selectivities on a polymer loading basis also increase with surface area, except for the 220 m²/g sample (figure 54). Again ignoring that sample, we might conclude that this is due to an assumed increase in the alumina acidity with increasing surface area, or perhaps to electronic and/or structural modifications of the Pd by the different supports. As surface polymer selectivities decrease with metal loading, which is almost surely due to changes in metal dispersion, increasing dispersion with increasing surface area, which
might be expected, cannot explain this trend. Support polymerization activity would also appear unlikely in light of the relatively high metal loadings (no such support effect is observed even with 0.02 wt% Pd sample) and the results of alumina blank experiments.

We can summarize our conclusions on the effects of catalyst surface area by stating that in light of the small amount of information we have, including the small number of reactions and the lack of catalyst characterization values (metal dispersions, impregnation profiles, and support acidities), we cannot conclude very much. We suggest that further studies on this behavior be conducted in the future.

We should note that as we predicted earlier (pp. 72-73), the oxygen-hydrogen treatment which Moses, et al (136) observed could prevent a decrease in ethylene selectivities during batch reactions is not sufficient to remove all of the surface polymer species (figure 58). In fact, this treatment only removes about 54% of the total polymer. In contrast, hydrogen treatment alone, which they found was not sufficient to prevent ethylene selectivity decline, removed 84% of the polymer on the surface. The effects which these treatments had on catalyst activity and product selectivities will be considered in later sections (IV C, Catalyst Activation and Deactivation, p. 333, and IV D, Ethylene Selectivity Decline, p. 394).
B. The Polymer Composition

1. Results

a. Gas Phase Polymer

The composition of the C₄ fraction and the total amount of gas
phase polymers of carbon number 6 and higher were measured throughout
the duration of every experiment. The composition of the C₆⁺ fraction
was not studied in such detail because the amounts of each species,
other than perhaps 1-hexene, were very small and their short, broad GC
peaks could not be integrated accurately.

The relative amount of C₆⁺ products was generally between 40 and
50%. At 40°C, there is an initial increase in this value, the duration
of which increases with decreasing metal loading (figure 75). Compared
at equal polymer loadings, however, the initial increase appears to be
unaffected by changes in metal loading, although the limiting value
decreases with decreasing loading (figure 76).

Figure 75. The percentage of C₆⁺ products in the gas phase polymers
observed during operation at 40°C on catalysts of different metal
loading supported on 90 m²/g Al₂O₃. (Experiments 8, 21, and 27).
Figure 76. The percentage of C₆+ products in the gas phase polymers compared at equal polymer loadings during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Λ₂O₃.

During initial operation 1,3-butadiene was always the major C₄ species. Its percentage decreased fairly quickly, while the amounts of the various butenes increased. At 40°C, these changes occurred more rapidly on catalysts of higher metal loadings (figures 77 and 78). Comparison at equal polymer loadings, however, shows that initially the changes occur at higher polymer loadings ("slower" on a polymer loading basis) over the 5 wt% Pd catalyst (figures 79 and 80), although this trend does not continue with increasing polymer loadings. During the relatively steady behavior at polymer loadings above about 300 mg/ml pore volume, the C₄ fraction is typically 50-55% 1-butene and about 10% 1,3-butadiene. The remaining 35-40% is composed largely of 2-butenes, as n-butane percentages were rarely higher than 2-3%. No multiply unsaturated species other than 1,3-butadiene (1,2-butadiene or
vinylacetylene) and no branched species (isobutane or isobutylene) were observed in the C₄ fraction under any conditions.

Figure 77. The 1,3-butadiene percentage in the C₄ fraction observed during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 78. The 1-butene percentage in the C₄ fraction observed during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.
Figure 79. The 1,3-butadiene percentage in the C4 fraction compared at equal polymer loadings during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 80. The 1-butene percentage in the C4 fraction compared at equal polymer loadings during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

No trends are apparent in the 1/2-butene ratio, while the trans/cis-2-butene ratios appears to decrease with catalyst metal loadings (figures 81 and 82). The behavior at equal polymer loadings
(figures 83 and 84) is essentially the same. Except for the values observed with the 0.1 wt% catalyst at polymer loadings lower than about

![Graph 1: 1/2-butene ratio vs. time (hours)]

Figure 81. 1/2-butene ratios observed during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃

![Graph 2: trans/cis-2-butene ratio vs. time (hours)]

Figure 82. Trans/cis-2-butene ratios observed during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃
Figure 83. 1/2-butene ratios compared at equal polymer loadings during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 84. Trans/cis-2-butene ratios compared at equal polymer loadings during operation at 40°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

250 mg/ml pore volume, the trans/cis ratio still appears to decrease with metal loading (figure 84). At low polymer loadings the 1/2-butene ratio appears to decrease with increasing metal loading. However, at
polymer loadings greater than about 500 mg/ml pore volume, it increases with further polymer formation over the 0.5 wt% Pd catalyst and decreases over the 0.1 wt% sample. Unfortunately, the 0.02 wt% catalyst was not operated long enough to achieve such high polymer loadings.

At 80°C the percentage of C₆₉ species is initially somewhat lower over a 0.02 wt% sample and decreases with operating time over both 0.1 and 0.02 wt% catalysts (figure 85). Compared at equal polymer loadings it decreases with decreasing metal loadings (figure 86), in agreement with experiments at 40°C (figure 76). Changes in the relative amounts of 1,3-butadiene and 1-butene occur faster and at lower polymer loadings over the 0.1 wt% sample (figures 87 and 88), also in agreement with trends observed at 40°C (figures 77-80).

Figure 85. The percentage of C₆₉ products in the gas phase polymers observed during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃. (Experiments 12 and 25).
Figure 86. The percentage of C₄ products in the gas phase polymers compared at equal polymer loadings during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 87. The 1,3-butadiene and 1-butene percentages in the C₄ fraction observed during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

The 1/2-butene ratio is significantly higher over the 0.1% sample (figure 89), in agreement with the trends observed over these same catalysts at 40°C. The 0.5 wt% Pd catalyst, which behaved very
differently at 40°C, was not used at 80°C due to strong pore diffusion limitations at this temperature.

![Graph showing composition vs. mg polymer/ml pore volume.](image)

Figure 88. The 1,3-butadiene and 1-butene percentages in the C₄ fraction compared at equal polymer loadings during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

![Graph showing 1/2-butene ratio vs. mg polymer/ml pore volume.](image)

Figure 89. 1/2-butene ratios compared at equal polymer loadings during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Compared at equal polymer loadings, the trans/cis-2-butene ratio is always higher over the 0.1 wt% sample (figure 90) in agreement with
results at 40°C (figure 84), although the difference is much smaller in this case.

![Graph showing trans/cis-2-butene ratio vs. mg polymer/ml pore volume.

Figure 90. Trans/cis-2-butene ratios compared at equal polymer loadings during operation at 80°C on catalysts of different metal loading supported on 90 m²/g Al₂O₃.

During experiments using 0.1 wt% Pd on 90 m²/g Al₂O₃ catalysts at temperatures between 40 and 80°C, the percentage of C₆, species at any given time does not appear to be affected by changes in the reaction temperature (figure 91). Compared at equal polymer loadings, there appears to be a slight trend toward decreasing C₆, values with increasing temperature between 60 and 80°C (figure 92), but the magnitude of these changes is slight, and the values observed at 40°C are the lowest of all four temperatures.
Figure 91. The percentage of C₆+ products in the gas phase polymers observed during operation over 0.1 wt% Pd on 90 m²/g Al₂O₃ catalysts at different temperatures. (Experiments 8, 10, 11, and 12).

Figure 92. The percentage of C₆+ products in the gas phase polymers compared at equal polymer loadings during operation over 0.1 wt% Pd on 90 m²/g Al₂O₃ catalysts at different temperatures.

The percentage of gas phase polymers of carbon number 6 and higher observed during reaction at 40°C over 0.5 wt% Pd catalysts was not
greatly affected by changing the support surface area from 4 to 220 m²/g; it is initially around 50% and decreases to about 40% during operation over each catalyst sample. The composition of the C₄ fraction, however, does differ over these different catalyst samples. The percentage 1,3-butadiene was highest over a 0.5 wt% Pd on 90 m²/g Al₂O₃ sample, although there was little or no difference between the other three (figure 93 and 94). The butadiene percentage decreased during the initial stages of operation over each catalyst, as observed previously (figures 79 and 87).

![Graph](image)

Figure 93. The percentage of 1,3-butadiene in the C₄ fraction observed during operation at 40°C over 0.5 wt% Pd catalysts on Al₂O₃ supports of different surface areas. (Experiments 3, 6, 7, and 28).

1/2-butene ratios observed over these catalysts were also strongly affected by the support surface area. These increase with increasing surface area, except for the 220 m²/g sample, while the direction of the changes observed during operation varied greatly (figure 95). Over the 90 m²/g sample, the 1/2-butene ratio increased during operation. On the
Figure 94. The percentage of 1,3-butadiene in the C₄ fraction compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd catalysts on Al₂O₃ supports of different surface areas.

Figure 95. 1/2-butene ratios observed during operation at 40°C over 0.5 wt% Pd catalysts on Al₂O₃ supports of different surface areas.

4 and 33 m²/g samples it remained essentially constant; over the 220 m²/g sample it decreased. Compared at equal polymer loadings (figure 96), the results are substantially the same, except that the values observed
Figure 96. 1/2-butene ratios compared at equal polymer loadings during operation at 40ºC over 0.5 wt% Pd catalysts on Al₂O₃ supports of different surface areas.

Over the 90 m²/g sample are very similar to those over the 4 and 33 m²/g samples up to polymer loadings of about 500 mg/ml pore volume. Values observed over the 220 m²/g sample are substantially lower than the others, except at polymer loadings less than 100 mg/ml pore volume.

Trans/cis-2-butene ratios, on an operation time basis, show no trends of any kind with changes in support surface area. Comparison at equal polymer loadings, however, does show some relationships (figure 97). Over both the 4 and 220 m²/g samples, this ratio decreases almost linearly, and the values are almost identical. Over the 33 and 90 m²/g samples, on the other hand, it goes through a broad maximum with polymer loading. Although the shape of these two curves are different, the maximum ratio observed over each catalyst sample is approximately the same (about 1.75).
Figure 97. Trans/cis-2-butene ratios compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd catalysts on Al₂O₃ supports of different surface areas.

Because acetylene conversions change throughout the duration of each experiment, we have also investigated the effects of the inlet acetylene concentration in order to clarify which of these effects are caused only by changes in the acetylene partial pressure in the reactor. During experiments using 1.05 and 0.35% inlet acetylene over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst at 40°C, the percentage of gas phase polymers of C₆ and higher is perhaps slightly lower with 0.35% acetylene, but the difference is small (figure 98). Comparison at equal polymer loadings (figure 99) shows that the value with 0.35% inlet acetylene is always lower than that with 1.05%, but the difference is not very large (on the order of 10% relative) considering both the three fold difference in inlet acetylene concentrations, and the two fold difference in acetylene partial pressures at the maximum conversions observed in each experiment.
(1.54 and 3.1 torr). The percentage of $C_6^+$ species drops sharply at high polymer loadings, but decreases only gradually before that point.

Figure 98. The percentage of $C_6^+$ products in the gas phase polymers observed during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations. (Experiments 3 and 4).

Figure 99. The percentage of $C_6^+$ products in the gas phase polymers compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.
The composition of the C₄ fraction, particularly the relative amounts of 1,3-butadiene and 1-butene, are only slightly affected by changes in the inlet acetylene concentration on both a time (figure 100) and polymer loading (figure 101) basis. On a polymer loading basis it

![Figure 100](image)

**Figure 100.** The percentages of 1,3-butadiene and 1-butene observed during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.

![Figure 101](image)

**Figure 101.** The percentages of 1,3-butadiene and 1-butene compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.
appears that the decrease in 1,3-butadiene and the increase in 1-butene occur at slightly higher polymer loadings with 1.05% inlet acetylene, but this difference is not large.

1/2-butene ratios, though initially similar, increase during operation with 1.05% inlet acetylene and remain fairly constant with 0.35% (figure 102). The steady values are about 1.5 and 1.4, respectively. Comparison at equal polymer loadings (figure 103) shows that the increase with 1.05% inlet acetylene occurs at a polymer loading of about 300 mg/ml pore volume. In both cases the ratio drops sharply at very high polymer loadings.

![Graph showing 1/2-butene ratio vs time (hours)](image)

Figure 102. 1/2-butene ratios observed during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.

Trans/cis-2-butene ratios increase sharply during the initial stages of each experiment (figure 104). With 1.05% inlet acetylene they reach a higher maximum, but then decrease faster, than with 0.35%. Compared at equal polymer loadings, they both increase rapidly, go
Figure 103. 1/2-butene ratios compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.

Figure 104. Trans/cis-2-butene ratios observed during operation at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ catalysts with different inlet acetylene concentrations.

through broad maximums, and then decrease sharply at high polymer loadings (figure 105). The maximum with 1.05% inlet acetylene is again
somewhat higher than with 0.35% (1.73 versus 1.62).

We have also investigated the effects of different catalyst treatments on the subsequent distributions of the various gas phase polymer species at 40°C over a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. The details of these treatments are given on pages 227–228. The percentage of C₆₆ products in the gas phase polymers increased during initial operation after each treatment (figure 106). Comparison at equal polymer loadings shows that regardless of the polymer loading after any treatment, the subsequent C₆₆ percentage is greatly decreased compared to values at similar polymer loadings without any treatment (figure 107). The extent of this decrease is smaller over the evacuated sample and increases at a lower rate than the others, all of which exhibit approximately the same behavior.
Figure 106. The percentage of C₆⁺ products in the gas phase polymers observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 21). 2. Same sample after 90 hours evacuation at 40°C (Exp. 22). 3. Same sample after hydrogen treatment (Exp. 23). 4. Same sample after oxygen-hydrogen treatment (Exp. 24).

Figure 107. The percentage of C₆⁺ products in the gas phase polymers compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 106 for symbol definition.

The percentage of 1,3-butadiene in the C₄ fraction decreases continuously during the initial experiment (figure 108). After both
hydrogen and oxygen-hydrogen treatments, the initial rate of this
decrease is much faster than the initial one. Following evacuation,
however, the 1,3-butadiene percentage is initially much lower, and then
actually increases during subsequent operation.

Comparison at equal polymer loadings (figure 109) shows that the
1,3-butadiene percentage is dramatically increased by oxygen-hydrogen
treatment, while hydrogen treatment alone actually decreases it, both
compared to values at similar polymer loadings during the initial
experiment. The rate of decrease after operation begins is higher on
both the hydrogen and oxygen-hydrogen treated samples than on the
initial sample. Evacuation is qualitatively different, as the 1,3-
butadiene percentage actually increases during subsequent operation.

The percentage of 1-butene in the C₄ fraction was initially higher
after each treatment compared to the initial experiment (figure 110).
Figure 109. The 1,3-butadiene percentage in the C₄ fraction compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 106 for symbol definition.

Figure 110. The 1-butene percentage in the C₄ fraction observed during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 106 for symbol definition.

The subsequent rate of increase was highest over the oxygen-hydrogen treated sample, followed by the sample treated in hydrogen alone, the initial sample, and finally the evacuated one, over which little or no
subsequent changes were observed. Final, steady values were all approximately equal (48%). Comparison at equal polymer loadings (figure 111) shows that oxygen-hydrogen treatment greatly decreased the 1-butene percentage relative to values observed at similar polymer loading during the initial experiment. Hydrogen treatment and evacuation actually increased in comparison with the same, although the extent over the evacuated sample was not large.

Figure 111. The 1-butene percentage in the C4 fraction compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 106 for symbol definition.

1/2-butene ratios observed during these experiments varied quite a bit. Comparisons during operation show little or no obvious trends in any direction. Comparison at equal polymer loadings (figure 112) suggest that the ratio is increased by hydrogen and oxygen-hydrogen treatments relative to the values observed at similar polymer loadings during the initial experiment. In contrast evacuation causes a decrease during subsequent operation.
Figure 112. 1/2-butene ratios compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 106 for symbol definition.

Changes in the trans/cis-2-butene ratios were also fairly small and difficult to resolve on a time basis. Comparison at equal polymer loadings (figure 113) shows that while hydrogen treatment has little or
no effect, oxygen-hydrogen treatment increases the subsequent value and evacuation decreases it. The steady values observed were essentially equal in all four cases.

We have also investigated the effects of evacuation on a sample with a much higher polymer loading than those used above (700 versus 200 mg/ml pore volume). These experiments were conducted at 40°C on a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. After evacuation the percentage of C₆⁺ in the gas phase polymers is decreased relative to values observed during the initial experiment (figure 114), but comparison at equal polymer loadings show no difference at all between the two operations (figure 115).

![Graph showing Gas Phase Polymer % C6⁺ vs. time (hours)]

Figure 114. The percentage of C₆⁺ products in the gas phase polymers observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27).
2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

The initial 1,3-butadiene percentage is decreased by evacuation, while the initial 1-butene percentage is increased (figure 116).

Compared at equal polymer loadings these differences are largely removed
Figure 115. The percentage of C₆⁺ products in the gas phase polymers compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

Figure 116. The percentages of 1,3-butadiene and 1-butene in the C₄ fraction observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

(figure 117). The only apparent change is that the very first point after evacuation seems slightly higher for 1,3-butadiene and slightly
lower for 1-butene, but these differences are rather small and are the result of only one data point each.

1/2-butene ratios after evacuation do not exhibit the initial decrease and are subsequently higher than those observed during the initial experiment (figure 118). Comparison at equal polymer loadings again shows very little change caused by evacuation (figure 119).

Evacuation appears to have little effect on the trans/cis-2-butene ratio during subsequent operation (figure 120). Comparison at equal polymer loadings, however, show that it has decreased it relative to the values observed at similar polymer loadings during the initial experiment (figure 121).

We have considerably less information on the composition of the C₆ gas phase species. Attempts to separate and identify them using the BMEA column employed for C₄ analyses were complicated by two different
Figure 118. 1/2-butene ratios observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

Figure 119. 1/2-butene ratios compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

considerations. Isothermal column operation, as employed for C₄ separation, eluted peaks that were so broad that in combination with the small total amount of each species present they could not be integrated
Figure 120. Trans/cis-2-butene ratios observed during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

Figure 121. Trans/cis-2-butene ratios compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 114 for symbol definition.

accurately. Temperature programmed GC operation yielded sharper peaks, but baseline shifts caused by the increasing GC oven temperature overwhelmed the relatively small peaks.
During several of the later experiments we employed the Dexsil column (usually used for surface polymer analysis) in a somewhat more successful attempt to identify and quantify the various gas phase polymer species present. However these analyses were also plagued by problems involving the small amounts of most of these species present and severe baseline shifts during temperature programming. The only data we obtained that were useful and at least fairly accurate were taken during the first 48 hours of operation over a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst at 80°C (Experiment 25).

We have previously shown that during the initial stages of this experiment the total polymer selectivity increased slightly (figures 37 and 38, p. 217), while the surface polymer selectivity decreased sharply (figure 39 and 40, p. 218). The gas phase polymer selectivity therefore increased sharply during this same time span. The percentage C₆, in the gas phase polymer fraction increased slightly during initial operation (figures 85 and 86). As the acetylene conversion also increased during this period, the actual amount of both the total gas phase polymers and the amount of those of C₆ and higher increased. During the first analysis (after about 1 hour operation), only C₆ species were observed. With each successive analysis, species of higher molecular weight were observed, and the amounts of those previously observed increased.

From about 7 to 48 hours operation time the 10 analyses we performed suggested that the total amount of each species was relatively constant. Severe baseline shifts and incorrect integrator parameter settings ruined half of these, leaving five of any use at all. The variations in these five analyses were still rather high (table 27). We
have neglected the highest and lowest integrated areas observed at each carbon number and averaged the remaining three values. The percentage distribution was calculated from these averages.

Table 27. GC integrated areas and percentage distribution of C₆⁺ species observed during operation at 80°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst

<table>
<thead>
<tr>
<th>Areas Measured</th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
<th>C₁₂</th>
<th>C₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1151</td>
<td>746</td>
<td>(683)</td>
<td>(32)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1080</td>
<td>775</td>
<td>394</td>
<td>239</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1033</td>
<td>(140)</td>
<td>252</td>
<td>(305)</td>
<td>(78)</td>
<td></td>
</tr>
<tr>
<td>(886)</td>
<td>228</td>
<td>(123)</td>
<td>95</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>(1273)</td>
<td>(800)</td>
<td>214</td>
<td>196</td>
<td>(-)</td>
<td></td>
</tr>
</tbody>
</table>

Average Area | 1088 | 583 | 287 | 176 | 8 |
Composition (mol%) | 51 | 27 | 13.4 | 8.2 | 0.37 |

During the time period these analyses were conducted we also measured the C₂, C₄, and total C₆⁺ products as usual. We have defined the total gas phase selectivity, S_{C₄⁺}, as \(\frac{(2R_C+3R_{C₆})}{(-R_{C₂H₂})}\). The percentage C₆⁺ in the gas phase polymers is defined as \(\frac{3R_{C₆}}{(2R_C+3R_{C₆})}\); both are defined in terms of the number of moles of acetylene forming the various species. We know the values of S_{C₄⁺} and C₆⁺ during the time period the C₆⁺ fraction analyses were conducted. Combining the two expressions above, we find \(R_{C₆}/(-R_{C₂H₂})=(\%_{C₆⁺})(S_{C₄⁺})/3\) and \(R_C/(-R_{C₂H₂})=(S_{C₄⁺}-3R_{C₆}/(-R_{C₂H₂}))/2\). These two values are true molar selectivities - the number of moles formed divided by the molar rate of acetylene consumption (the C₆⁺ value does not have to be corrected for
the actual molecular weight distribution because the molar GC response
factor was essentially constant for all species of carbon number six and
higher).

We have averaged the C₄⁺ selectivities and %C₆⁺ values observed
between 7 and 48 hours operation time (33.6 and 45.5%, respectively).
From these values and the equations described above we can calculate the
molar selectivities to C₄ and C₆⁺ species (9.14 and 5.10%, respectively).
Applying the molar analysis of the C₆⁺ species (table 27) to the latter
value (5.10%) yields the molar selectivity to each carbon number (table
28).

Table 28. Molar selectivities to different gas phase polymer species
during operation at 80°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

<table>
<thead>
<tr>
<th></th>
<th>C₄</th>
<th>C₆</th>
<th>C₈</th>
<th>C₁₀</th>
<th>C₁₂</th>
<th>C₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.14</td>
<td>2.60</td>
<td>1.38</td>
<td>0.68</td>
<td>0.42</td>
<td>0.019</td>
</tr>
</tbody>
</table>

We can define an apparent probability of further C₂ addition to
any species Cₙ as $\alpha_n = (S_{C_{n+2}}/S_{C_n})$. Taking the natural logarithm of both
sides yields $\ln(\alpha_n) = \ln(S_{C_{n+2}}/S_{C_n}) = \ln(S_{C_{n+2}}) - \ln(S_{C_n})$. The slope of a plot
of $\ln(S_{C_n})$ versus carbon number (n) will yield a slope (m) equivalent to
$m = (1/2)\ln(\alpha)$ (figure 122), where $\alpha$ is the overall probability of
further addition. We have also conducted a similar analysis of this
data based on relative acetylene selectivities (based on the number of
moles of acetylene forming each species), which are simply one half the
carbon number times the molar selectivities in table 28 above.
The slope of the molar selectivity data points is $-0.53$ ($R^2 = 0.891$), which corresponds to an addition probability of $\alpha = 0.35$.

Figure 122. The probability of acetylene addition to gas phase polymer species during operation at 80°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

However it is clear that the value at C₂₄ does not fit the line describing the other data points. Without this value, the slope is $-0.37$ ($R^2 = 0.968$), which corresponds to $\alpha = 0.48$. Similar values based on acetylene selectivities are $-0.41$ ($R^2 = 0.811$), $\alpha = 0.44$, and $-0.24$ ($R^2 = 0.963$), $\alpha = 0.62$, respectively.

Because we were not able to employ the MS we have very little information about the actual species present at each carbon number. In addition the dextril column did not separate individual species at any given carbon number very well. The C₆ fraction was the only one which was resolved into definitely more than one measurable peak. The retention times of the single peaks for all other species were consistent with both linear $\alpha$-olefins and normal parafins (the
retention times of these were very close and the run-to-run variation was larger than the difference between them), although we can not rule out other possibilities. The C₆ fraction was resolved into three separate peaks, accounting for approximately 45, 10, and 45% of the total, respectively. The first is almost certainly 1-hexene. The second appeared to be n-hexane, while the retention time of the third was consistent with that of benzene.
B. The Polymer Composition

1. Results

b. Surface Polymer

We have conducted solvent extractions, primarily with 2-methyl pentane, on a number of spent catalyst samples. GC analysis on a Dexsil 300 packed column yields a large number of partially resolved peaks (see figure 26, p. 185). Retention times of even carbon numbered linear \( \alpha \)-olefins and \( \eta \)-paraffins from \( C_6 \) to \( C_{44} \) have been measured with both pure and dilute mixture calibration standards (Alltech "NP" series). From these calibrations we have assigned carbon numbers to the species observed during GC analyses of solvent-surface polymer samples. Mole fraction distributions show an increase in concentration at the lower carbon numbers (8 to 10, 12, or 14), followed by a maximum and then a decrease to trace amounts at carbon number 20 or higher (table 29).

We should note that because of the design of our apparatus and the small amounts of catalyst usually employed it was not possible to remove catalyst pellets at different times during an experiment; these extraction were conducted using the total catalyst sample after the experiment had been terminated.

In addition, the GC baseline increased by a much greater amount than the heights of most eluting peaks, and there are many questions regarding the proper baseline correction methods. Degradation of the injection port septum also produced peaks corresponding to compounds of carbon numbers greater than 20 (both even and odd numbered). While this situation could be minimized by a fairly complicated sequence of injection port and oven temperature programs, it introduced an
Table 29. Molar distributions (mol%) of soluble surface polymer species extracted from spent catalyst samples in 2-methyl pentane.

<table>
<thead>
<tr>
<th>C_8</th>
<th>C_10</th>
<th>C_12</th>
<th>C_14</th>
<th>C_16</th>
<th>C_18</th>
<th>C_20</th>
<th>C_22</th>
<th>C_24</th>
<th>C_26</th>
<th>C_28</th>
<th>C_30</th>
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<tr>
<td>0.00</td>
<td>1.6</td>
<td>7.8</td>
<td>17.1</td>
<td>20.1</td>
<td>20.0</td>
<td>12.7</td>
<td>10.3</td>
<td>5.63</td>
<td>2.94</td>
<td>1.47</td>
<td>0.38</td>
</tr>
<tr>
<td>0.00</td>
<td>11.4</td>
<td>7.4</td>
<td>13.4</td>
<td>15.6</td>
<td>19.3</td>
<td>12.4</td>
<td>7.4</td>
<td>5.21</td>
<td>3.36</td>
<td>3.19</td>
<td>1.18</td>
</tr>
<tr>
<td>0.00</td>
<td>8.7</td>
<td>7.3</td>
<td>34.7</td>
<td>12.4</td>
<td>16.4</td>
<td>8.9</td>
<td>4.4</td>
<td>5.67</td>
<td>1.51</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>2.74</td>
<td>18.2</td>
<td>8.0</td>
<td>20.3</td>
<td>21.3</td>
<td>12.4</td>
<td>9.0</td>
<td>4.8</td>
<td>3.36</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.00</td>
<td>31.9</td>
<td>5.1</td>
<td>12.1</td>
<td>15.8</td>
<td>10.8</td>
<td>8.7</td>
<td>6.9</td>
<td>3.53</td>
<td>2.67</td>
<td>1.85</td>
<td>0.58</td>
</tr>
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<td>17.0</td>
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<td>10.5</td>
<td>6.5</td>
<td>5.32</td>
<td>4.58</td>
<td>2.90</td>
<td>1.14</td>
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<td>10.6</td>
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<td>33.3</td>
<td>29.0</td>
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<td>0.00</td>
<td>0.00</td>
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<td>54.0</td>
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<td>0.0</td>
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<td>0.00</td>
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<td>11.3</td>
<td>24.1</td>
<td>40.6</td>
<td>16.2</td>
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<td>2.8</td>
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<td>36.4</td>
<td>34.6</td>
<td>14.5</td>
<td>4.4</td>
<td>0.9</td>
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<td>1.26</td>
<td>7.6</td>
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<td>16.5</td>
<td>10.0</td>
<td>5.8</td>
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<td>0.96</td>
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<td>8.0</td>
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<td>18.0</td>
<td>11.3</td>
<td>2.0</td>
<td>1.8</td>
<td>0.4</td>
<td>0.00</td>
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<tr>
<td>0.00</td>
<td>8.7</td>
<td>34.0</td>
<td>34.9</td>
<td>11.7</td>
<td>5.9</td>
<td>3.2</td>
<td>1.5</td>
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<td>4.3</td>
<td>11.5</td>
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<td>21.9</td>
<td>13.5</td>
<td>11.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

^a0.22 13.6 24.2 23.0 16.1 9.3 6.1 3.8 1.94 1.11 0.52 0.18
^b0.17 1.6 4.6 2.3 1.3 1.7 1.2 0.9 0.57 0.40 0.26 0.09
^c 76 12 19 10 8 18 20 24 29 36 49 52

a. Mathematical average of all values in column above.
b. RMS deviation from average. c. %RMS deviation from average.

Additional possible source of error to these measurements.

All solvent-polymer solutions were very dilute. A spent pellet of 0.5 wt% Pd (about 45 mg initially) contained about 12 mg total surface polymer. Normally 1 ml solvent was employed in this case. If all of
the polymer had been soluble, the total concentration would be 12 mg/ml. Material balance calculations from the GC analyses, however, suggest that only about 30% of the total polymer sample is soluble, decreasing the total concentration to 3.6 mg/ml solvent. The highest mole fractions of any carbon number were generally on the order of 30-40%, decreasing the concentration of that group of compounds to 1-1.5 mg/ml. GC/MS analyses conducted by Mike Bulawa (Exxon Basic Chemicals, Baytown) have shown that the major species at any given carbon number never accounts for more than 50% of the total, decreasing the concentration of that species to a maximum of 0.5-0.75 mg/ml. Of course the concentration of most of the polymer species are significantly lower than this maximum.

The problem of such dilute concentrations can be theoretically overcome by using very large samples. In practice, however, the sample size is limited by the available volume in the GC column. We did not flood the column with the sample sizes typically used (1-100 µl), but samples larger than 10 µl did smother the FID flame at normal detector conditions. When injecting the more usual sample size of 100 µl it was necessary to turn the FID air supply almost completely off while the solvent peak eluted in order to keep the flame lit. The air flow was increased to the standard value after the solvent peak had eluted. In addition the baseline shift during temperature programming increased almost linearly with the amount of solution injected, negating most, if not all, of the expected gain from increasing the sample size.

Although it may seem that we have been belaboring the topic of experimental error in the measurement of the surface polymer
composition, we feel this is justified. We have not included a
description of the catalyst samples (metal loading, support surface
area, temperature and length of operation) in table 29 for the same
reason. We feel that one might be tempted to interpret differences
between the analyses of different surface polymer samples, caused by one
or more of these possible sources of experimental error, as due to
something more than random error. In fact they might be, but the data
do not support such an interpretation at this time.

With all of this in mind, we shall use the average values
calculated from the data in table 29 as representative of a sort of
average soluble surface polymer composition. We can construct a plot of
the natural logarithm of the mole fraction versus carbon number, similar
to the one for the gas phase polymer in the previous section (figure
140, p. 293). While the amounts of each gas phase species decrease with
increasing carbon number due to both the apparent reaction behavior and
the decrease in volatility with increasing molecular weight, in this
surface polymer solution they increase initially because of the
increasing surface retention due to the decreasing volatility with
increasing molecular weight (figure 123). The nearly linear portion of
this graph (from carbon numbers 14 to 28) has a slope of \(-0.27\) \((R^2
=0.991)\) corresponding to an addition probability of 0.58.

It would be desirable to construct a similar plot for the entire
polymer product spectrum, both the gas phase and surface species.
Unfortunately there are several serious problems in carrying out this
procedure. The very small amount of data we have in both cases is of
course one of them, as is the high degree of experimental error involved
Figure 123. Mole fraction distribution of the average soluble surface polymer species from GC analyses of the solvent extraction solution from spent catalysts (table 29).

in the surface polymer composition measurements. The most serious problem, however, arises from the distinctly different behavior of the two polymer phases.

During initial operation, the rate of and selectivity to surface polymer formation are high. During further operation both values decrease sharply. The gas phase polymer rate of formation and selectivity, on the other hand, are initially very low, but increase sharply during the initial stages of reaction. As discussed in the previous section (The Formation of Polymer, p. 211), most of these changes are probably due to the initial formation of lower molecular weight polymers, which must build-up on the catalyst surface to a extent sufficient to allow desorption to the gas phase. As the surface becomes "saturated" with these low molecular weight species, the rate of weight gain decreases sharply; further weight gain is due almost entirely to
the formation and build-up of higher molecular weight products, as the lower weight species which do not undergo further addition simply desorb (rather than remain on the surface and contribute to the weight gain). The average molecular weight of the surface species is most likely increasing throughout this period of operation.

The problem lies in choosing an adequate, and hopefully accurate, basis on which to compare the molecular weight distributions in the gas phase and on the surface. The total amount of each species is one such basis we might choose. However, because the average rate of polymer formation decreases continuously throughout operation, while the total gas phase selectivity is reasonably constant, there will be a sharp discontinuity in the molecular weight distribution at the boundary of the two phases (carbon numbers 8, 10, and 12). The results will also be strongly dependent on the overall duration of any given experiment.

Because we have only the gas phase polymer carbon number distribution from a single experiment, we have chosen it as the basis for comparison. In addition, because these data were taken during the first 48 hours of this experiment, we shall use this time period only. We should note that although the actual surface polymer molecular weight distribution on the catalyst during this time period was probably not the one we are going to use here, because C_{12} and C_{14} species were observed in the gas phase it seems reasonable to assume that they, at least, were present on the catalyst surface. In spite of these restrictions we have already placed on this calculational procedure, we must also define the specific time of comparison, as the surface polymer selectivity decreased markedly during this time period. Instead of one
time only, we have chosen four and calculated the total molecular weight distributions at all four surface polymer selectivities. These are; after seven hours operation where the surface polymer selectivity is 10.4%, after 15 hours (5.7%), 26 hours (3.3%), and 48 hours (1.6%). As these surface polymer selectivities are calculated from weight gains on the TGA, we must transform the mole fraction distribution of the surface polymer to weight fraction, then to molar selectivities from the surface polymer selectivity value and the molecular weight of the species in question. The reaction time chosen for this calculation, and hence the surface polymer selectivity, has a large effect on the resulting distribution (figure 124).

![Graph showing the relationship between Carbon Number (i) and ln (s_i) in mol%]

Figure 124. Total polymer distribution, expressed as molar selectivities, calculated for different operation times (surface polymer selectivities) from data from experiment 25.

The slope of the distribution calculated for 7 hours operation time is $-0.335 \ (R^2 = 0.989)$ which corresponds to $\alpha = 0.51$. The values calculated for 15 hours are $-0.364 \ (R^2 = 0.986)$ and 0.48; for 26 hours
they are -0.391 (R² =0.979) and 0.46; for 48 hours, -0.428 (R² =0.971)
and 0.42.

Because of constraints on our present GC system and our research
budget, we were not able to completely separate or identify the species
present in the solvent-surface polymer solutions. Three of these
samples, however, were analyzed with an integrated GC/MS system for us.
Unfortunately, the system was not previously calibrated for the specific
species present in these samples. The resulting chromatograms clearly
illustrate the amount of work which would be necessary to achieve
complete calibrations (figure 125a-b). In principle this is not a great
problem, because unknowns may be identified by MS analysis. Because of
the very dilute solutions resulting from our solvent extraction,
however, many of the peaks which yielded a measurable GC response
resulted in mass spectra which could not be adequately matched to any
spectra in the MS library file.

Because GC response factors for even the identifiable species were
also not measured, we cannot calculate the molecular weight distribution
from these results. In principle the response for compounds in this
molecular weight range should be fairly uniform, and we have toyed with
the idea of manually measuring the GC areas (height times width at 1/2
height), but the sheer number of peaks quickly banished that idea. In
any case, these chromatograms do not appear to differ from our
previously calculated carbon number distributions to any great extent.

Most of the largest peaks have been positively identified (see
Appendix H, p. 614 for details). At almost every even carbon number,
the largest peak is clearly that of the normal paraffin. The glaring
Figure 125a. Capillary gas chromatogram of a solvent extracted surface polymer sample.
Figure 12.5c: Capillary gas chromatogram of a solvent extracted polymer sample.

- 2-methyl pentane
- Solvent

Peaks at:
- n-C_{10}
- C_{12}
- C_{14}
- C_{16}
- n-C_{16}
- n-C_{18}
exception occurs at carbon number 12, where no normal paraffin was
detected at all. Many different branched paraffins of undetermined
structure were also detected. Other prevalent peaks at all even carbon
number are various linear and/or branched mono-olefins. Some of these
species are shown in table 30.

Table 30. Mono-olefins detected by GC/MS in extracted surface polymer
solutions (from data in figures 142-144).

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Mono-olefins Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2-decene  5-decene  4-decene  2,6-dimethyl-1-octene 2,6-dimethyl-4-octene 4-ethyl-2-octene 5-methyl-nonene</td>
</tr>
<tr>
<td>12</td>
<td>6-dodecane  4-dodecane  5-dodecane  2-methyl-5-undecene</td>
</tr>
<tr>
<td>14</td>
<td>3-tetradecane  7-tetradecane  5-tetradecane</td>
</tr>
</tbody>
</table>

A number of di-olefins were detected; 5,7-dodecadiene was
identified. Other mass spectra suggested the presence of mono-alkynes
of carbon number 12 and 14, but the GC peaks were very small and the MS
match was poor. Perhaps more surprising is the presence of several
aromatic compounds, such as alkyl-benzenes of carbon numbers 12, 14, 16,
and 18, biphenyl, and various naphthalenes. No species of odd carbon
numbers were detected, although they could be present in small amounts.

Comparison of these GC/MS results and the GC analyses conducted on
our Dexsil column at least show no serious contradictions. The major
peaks are normal paraffins and α-olefins, as we suspected from
retention time calibrations. There are obviously a large number of
poorly resolved species between the major peaks we have identified as
normal paraffins and/or α-olefins. Even the lack of a major normal paraffin peak at carbon number 12 is consistent with some of our GC analyses (such as the one appearing in figure 26, p. 185), which show a qualitative difference between the major peak at C_{12} and those at all other carbon numbers. Specifically this peak was often short, broad, and partially resolved into two or more peaks. All other major peaks were much sharper.

As we have mentioned several times earlier, material balance calculations from the total surface polymer on a catalyst sample, the amount of solvent used in extraction, and the composition of the solvent–polymer solution suggest that only about 30% (20-40% actually, the methods used were not very accurate) of the total surface polymer present was dissolved during extraction (alternatively we could say that only 30% was detected during GC analysis). Evacuation of a 0.5 wt% Pd sample with 700 mg/ml polymer loadings at 40°C for 72 hours resulted in a weight loss of 28.3%. Evacuation of a 0.02 wt% Pd sample with 200 mg/ml polymer loading at 40°C for 90 hours resulted in a weight loss of 26.8%. We believe there is a real correspondence between the species removed by long term evacuation and solvent extraction; we would expect all of the extracted species identified by GC/MS to be removed by this evacuation. We suspect both treatments remove the same species.

In contrast treatment of a 0.02 wt% Pd sample also with a polymer loading of 200 mg/ml for 2 hours at in hydrogen at 300°C resulted in a weight loss of 84%. Treatment of a similar 0.02 wt% sample in oxygen at 200°C for 1/2 hour followed by hydrogen at 300°C for 2 hours removed 53.6% of the surface polymer initially present. Evacuation of a 0.5 wt%
Pd sample with 700 mg/ml polymer loading for 2 hours at 200°C followed by 3 hours at 300°C removed 78.5% of the polymer.

During the 300°C hydrogen treatment of the 0.02 wt% Pd sample, a thin layer of semi-opaque (pale yellow) liquid was observed on the inside of the TGA hangdown tube beginning at about 200°C. The catalyst sample, which was initially black, was essentially the same color as a fresh sample (off white) after this treatment, but had an "oily" sheen. At temperatures between 100 and 300°C, a large number of hydrocarbon species, including small amounts of methane, ethane, ethylene, and acetylene, traces of 2-butenes and n-butane, and much larger amounts of 1-butene, benzene, and other unidentified C₆, species were detected in the reactor outlet stream. Unfortunately, most of this material was produced in such a short time (the rate of temperature increase was about 10°C/min) that only three analyses detected more than trace amounts of these species, and only one detected large amounts (at 295°C). For this reason we could not calculate the total amount of material which left the reactor (not enough data points, and the ones we had changed very rapidly with time), nor set-up the GC to run a Dexsil column chromatogram (for C₆, analysis) before only traces of hydrocarbons were leaving the reactor. Oxygen-hydrogen treatment removed much less of the surface polymer (53.6 versus 84%) and left the catalyst sample dark brown in color.

After solvent extractions catalyst pellets remained dark brown/black. We were not able to dissolve the species causing this discoloration in any solvent we used. In exasperation we placed several such samples in hydrofluoric acid (at room temperature). The acid
dissolved the alumina support in a matter of 5-10 minutes, and presumably dissolved the Pd too. After the alumina was completely dissolved, thin sheets of brown material were observed floating in the solution. These were collected, filtered with distilled water and dried. Mass balance calculations showed that they could account for at least 50% of the original surface polymer on the catalyst sample (62-83% of the polymer remaining after solvent extraction). We have no other information about their structure or composition.

We should note that this alumina digestion releases a substantial amount of heat, and if more than one or two catalyst pellets were placed in about 20 ml of acid at one time, the solution became hot enough to boil, and severely degraded the material otherwise left floating in solution. When this occurred, small globs of sticky, viscous brown "gunk" were left stuck to the acid container walls.
B. The Polymer Composition

2. Discussion

One might (and some probably will) argue that much of the polymer composition data presented in the previous sections should not be included in this report. We have given this idea a lot of thought, but have concluded to present this data anyway for several reasons. The first is that with only a small number of notable exceptions, the composition of both the gas phase and surface polymers has not been investigated in any detail in the past. Even in the small number of reports considering total C₄ and/or C₅, formation and selectivities, only LeViness (89), LeViness, et al (138) and Weiss, et al (139) have reported the composition of the C₄ fraction as more than just the results of one analysis (as in Bond and Wells (86)). Of the two literature reports we have located which consider surface polymer formation (Sarkany, et al (141) and Yajun, et al (194)), only Yajun, et al (194) report any results of the composition of these polymer species (see table 3, p. 53), and most of the details of their experimental procedure were not reported. In addition, we feel that much of the data presented here is probably not suitable for publication in peer review journals, but we maintain that it should be published in some form if only to serve as a starting point for future investigations. This report seems to be the most suitable format available.

The second reason for our decision is more intimately related to a better understanding of the acetylene hydrogenation reaction mechanism. As we shall demonstrate in the remaining two sections of experimental results and discussions, the surface polymer is directly related to
changes in catalyst activity (both activation and deactivation) and ethylene/ethane product selectivities. This fact alone explains the lack of success of previous authors who have attempted to synthesize the great body of published investigations of this reaction. We feel a complete understanding of the actual reaction mechanism is impossible without taking the surface polymer into consideration.

The composition of the gas phase polymers, particularly the $C_4$ fraction (which account for the majority of the experimental results in the preceding sections) has been included for a different, though equally important, reason. The previous investigations which measured the composition of the $C_4$ fraction have shown that under normal selective hydrogenation conditions (high ethylene/acetylene ratios and low (0.3–1%) acetylene concentrations) $1,3$-butadiene is the only $C_4$ species which can compete to any extent with acetylene and/or ethylene for surface Pd sites. The composition of the remaining $C_4$ species is therefore more indicative of the surface conditions under which the acetylene hydrogenation and polymerization reactions occur than the ethane and ethylene selectivities, which may be affected by the existence of a second type of surface site capable of adsorbing only ethylene (compared to acetylene). Of course any site capable of adsorbing ethylene is likely to be able to adsorb and hydrogenate butenes also, but the very high ethylene/butene ratios (> 100:1 in this work) characteristic of selective hydrogenation conditions are likely to prevent butene readsorption once initial formation and desorption have taken place.
With this background, let us first consider the composition of the C₄ fraction. We have shown in the previous sections that 1,3-butadiene is the major (50-60%) C₄ species formed during the initial stages of reaction. The percentage of 1,3-butadiene - and the absolute amount of it in the reactor - decreases to perhaps 10% of the total C₄ species during the time span up to 200-300 mg/ml polymer loading. This is the same range of polymer loadings values where, in the absence of acetylene pore diffusion limitations, the catalyst activity and the selectivity to ethane increase. It seems reasonable to suspect that these changes are related. However, because we are operating in a flow system, it is impossible to determine if the decrease in 1,3-butadiene pressure is due simply to a decrease in its rate of production (so that the observed decrease occurs only because of it leaving the reactor), or if it is also readsoorbing and reacting on the catalyst surface.

In the absence of labeled 1,3-butadiene experiments, the only method we could employ to determine if butadiene readsoption occurs is batch reactions, where any decrease in butadiene pressure must be caused by reaction. Since we have not conducted any batch reactions in this work, we shall have to look elsewhere for this information.

LeViness (89), LeViness, et al (138), and Weiss, et al (139) have investigated the formation and composition of C₄ species during batch selective acetylene hydrogenation reactions. Figure 126 shows the time dependent behavior of the various C₄ species during one such reaction. Here it is clear that 1,3-butadiene has readsobered and reacted. Butadiene consumption has definitely begun by 80 minutes reaction time (0.05 mol%), although the decreasing slope of the butadiene versus time
Figure 126. The production of C₄ species during a batch acetylene hydrogenation reaction at 23.5°C over 24.8 mg finely crushed 0.04 wt% Pd on 95 m²/g γ-Al₂O₃. Initial P = 670 torr. Reactant gas composition: 15.1% H₂, 1.03% C₂H₂, 35.5% C₂H₄, 0.29% C₂H₆, balance He (89,138).

curve suggests that it may have begun somewhat earlier (50 minutes, 0.04 mol%). Figures 127 and 128 show the acetylene-ethylene and acetylene-

Figure 127. Acetylene consumption and ethylene production/consumption during a batch acetylene hydrogenation reaction. See figure 126 for experimental conditions (89,138).
ethane compositions, while figure 129 shows the 1/2-butene and
trans/cis-2-butene ratios, all from same experiment.

Figure 127 or 128 shows that the acetylene concentration at which
butadiene reaction has definitely begun (at 80 minutes) is about 1.0%,
while it is about 1.5% after 50 minutes (where it appears that butadiene
may have begun to react). Ethylene consumption and large scale ethane
production, on the other hand, do not begin until after about 100
minutes reaction time, when the acetylene concentration is about 0.5%. Although ethylene reaction does not begin until the ethylene/acetylene
ratio exceeds about 140 (97/0.7), butadiene reaction definitely begins
at a butadiene/acetylene ratio of 0.5 (0.5/1.0) and may have begun at a
ratio as low as about 0.25 (0.4/1.5).

![Graph](image-url)

Figure 128. Acetylene consumption and ethane production during a batch
acetylene hydrogenation reaction. See figure 126 for experimental
conditions (89,138).
Figure 129. 1/2-butene and trans/cis-2-butene ratios observed during a batch acetylene hydrogenation reaction. See figure 126 for experiemtnal conditions (89,138).

1-butene hydrogenation, on the other hand, does not begin until after 120 minutes reaction time, when the 1-butene/acetylene ratio is about 0.7 (1.4/2.0) and 1,3-butadiene and ethylene hydrogenations are already in progress. We should note that the authors (89,138) concluded that: 1) ethylene hydrogenation begins when acetylene pore diffusion effects reduce the surface acetylene coverage to less than unity, so that ethylene can adsorb and react, and 2) the subsequent reaction of ethylene was ethylene diffusion controlled throughout because of the high hydrogen concentration (about 16% where the ethylene reaction begins), in spite of the high ethylene concentration (97% of the gas phase HC species - hydrogen/ethylene is about 0.39 (14/36)).

The highest acetylene conversions observed in this work occurred over the 0.1 wt% Pd catalyst at 40°C (88% maximum). Under these conditions the minimum reactor acetylene pressure was about 1.06 torr.
The maximum 1,3-butadiene pressure was 0.17 torr at an acetylene pressure of 2.21 torr (butadiene/acetylene ratio of 0.077), while the maximum 1-butene pressure was 0.37 torr at an acetylene pressure of 1.07 torr (1-butene/acetylene ratio of 0.35). These are the maximum butadiene/acetylene and 1-butene/acetylene ratios observed under any conditions in this work. Based upon these numbers, the results of LeViness (89) and LeViness, et al (138), (figures 126-129), and the much lower initial hydrogen/acetylene ratio used in our work (1.7 vs 15), we conclude that in the absence of acetylene pore diffusion effects 1-butene definitely does not adsorb and react (hydrogenate or isomerize) once it is initially formed and desorbs from the surface, and tentatively conclude that 1,3-butadiene does not adsorb and react under the same conditions.

We have now arrived at the conclusion that changes observed in the C₄ fraction composition in the absence of acetylene diffusion control are due only to changes on the catalyst surface, where they are initially formed, and are not due to subsequent readsorption and reaction. The absence of any major increases in n-butane production and 1-butene consumption, even in the presence of acetylene diffusion effects, suggests that at least the butenes still cannot adsorb and react due to the large excess of ethylene and the lack of ethylene pore diffusion control.

Bond and Wells (86) concluded that the formation of C₄ products during acetylene hydrogenation was due to formation of 1,3-butadiene as the initial acetylene dimerization product. They reported a C₄ fraction composition of 4% 1,3-butadiene, 54% 1-butene, 24% trans-2-butene, 14%
cis-2-butene (1/2-butene ratio 1.93, trans/cis-2-butene ratio 1.71), and 4% n-butane. This compares well with the results of Young, et al (120) for the hydrogenation of 1,3-butadiene over Pd (table 4, p. 56). However, the actual case is somewhat more complicated than this.

The C₄ product distribution reported by Bond and Wells (86) above was observed during reaction over a 5 mol% Pd/α-Al₂O₃ catalyst at 16°C and hydrogen/acetylene = 1.0. After the initial decrease in 1,3-butadiene and increase in the butenes, we have observed substantially identical C₄ distributions over a variety of catalysts of different metal loadings, support surface areas, and at temperatures of 40 - 120°C, all with initial hydrogen/acetylene ratios of 1.7. The C₄ distributions reported by LeViness (89) and LeViness, et al (138) above are also in substantial agreement with our results and those of Bond and Wells (86) - except for the 1/2-butene ratio, which is somewhat lower (figure 129) - despite the fact that the initial hydrogen/acetylene ratio was 15 in that work (89,138).

Recent work on selective 1,3-butadiene hydrogenation in excess 1-butene, conducted by Riley (658) in conjunction with this work, has shown that over 5.0 wt% Pd on alumina powder catalysts, 1/2-butene ratios are generally in the range 1.5-2 while the trans/cis-2-butene ratio may be anywhere from 1 to greater than 12. The trans/cis-2-butene ratios observed during acetylene hydrogenation therefore represent only a small part of the total range of values observed in 1,3-butadiene hydrogenation. We suspect that the relatively small range of 1/2-butene and trans/cis-2-butene ratios observed during acetylene hydrogenation is primarily due to presence of strongly adsorbed acetylene. In the
absence of acetylene pore diffusion control, large changes in the hydrogen/acetylene ratio will affect the catalytic surface environment to a much smaller degree than similar changes in the hydrogen/butadiene ratio in the absence of acetylene. In addition the huge excess of ethylene (compared to the butenes) is probably more effective in preventing the readsoption of butenes than is butadiene at the low butadiene/butene ratios characteristic of selective 1,3-butadiene hydrogenation (658).

We do, however, agree with Bond and Wells (86) that the initial C₄ species formed on the catalyst surface is probably 1,3-butadiene. The relatively high selectivities for 1-butene formation further support this conclusion, as 1-butene will result from the 1,2 hydrogen addition of one of the 1,3-butadiene C=C bonds. We could argue similarly that the formation of 2-butenes arises from the hydrogenation of 2-butyne or 1,2-butadiene, but this appears unlikely, as neither species is observed in the gas phase while 1,3-butadiene is. The formation of either species through the dimerization of acetylene would require a very large rearrangement of the original carbon-carbon bonds, which also seems unlikely. Even if 2-butyne did form on the surface, it would probably not desorb before undergoing hydrogenation to a 2-butene. 1,2-butadiene, being much less stable than 1,3-butadiene, would also tend to undergo further reaction before desorption occurred. Similarly, the formation of 1-butyne would lead to the high selectivity to 1-butene.

We feel it is more likely that the 2-butenes are formed both directly from 1,3-butadiene and by isomerization of 1-butene on the catalyst surface after it has formed from 1,3-butadiene hydrogenation.
2-butene formation from 1,3-butadiene can take place through 1,4 hydrogen addition to an adsorbed 1,3-butadiene molecule, particularly if the latter exists as a π-allylic or 2,3-di-σ-adsorbed species. Studies of the reaction between butadiene and deuterium (115) suggest that direct formation from 1,3-butadiene is the more prevalent route to 2-butene. While the 1-butene residence time on the catalyst surface is probably not very long - due to the comparatively large excess of acetylene and ethylene - isomerization to the more thermodynamically stable 2-butenes would be expected to take place fairly rapidly.

Trans/cis-2-butene ratios generally between 1 and 2 support this model, for the isomerization of 1-butene should produce the 2-butenes in amounts close to their equilibrium proportions under these conditions (trans/cis = 2). The fact that the trans/cis ratios are always slightly lower than the equilibrium value may be explained by the cis selective 1,4 hydrogen addition described above (115) and the observations of Margitfalvi, et al (134) that during acetylene hydrogenation over Pd black the initial trans/cis ratio is less than one. Our values would then represent a mixture of cis selective 2-butenes produced directly from 1,3-butadiene and trans selective 2-butenes produced by 1-butene isomerization.

The trans/cis ratio always increased during initial operation in the range of polymer loadings that the percentage 1,3-butadiene decreased and 1-butene increased. When little 1-butene is produced relatively more of the 2-butenes are formed directly from 1,3-butadiene and the trans/cis ratio is low. As 1,3-butadiene decreases and 1-butene increases, relatively more of the 2-butenes are formed from 1-butene,
and the trans/cis ratio increases towards equilibrium. The fact that
the percentage of n-butane is always low supports both the model of
initial 1,3-butadiene formation (Pd is a very selective 1,3-butadiene
hydrogenation catalyst (115,658)) and that 1-butene readsorption and
hydrogenation does not take place to any significant extent. 1-butene
isomerization to the 2-butenes must then occur more easily and/or
substantially faster then further hydrogenation to n-butane, which
appears reasonable.

Not all of our data, however, can be explained in such a simple
way. Compared at equal polymer loadings, trans/cis ratios over the 0.02
wt% Pd catalyst are significantly lower than those over 0.1 and 0.5 wt%
Pd samples (figures 84 and 90). Yet at the same polymer loadings, the
amount of 1-butene over the 0.5 wt% sample is smaller, while that of
1,3-butadiene is larger, than the values observed over the 0.02 wt%
sample (figures 79 and 80). At 80°C the amount of 1,3-butadiene is
larger over the 0.02 wt% sample than over the 0.1, but the amounts of 1-
butene are essentially identical (figure 88).

Similarly the 1-butene percentage observed during operation over
the 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with 0.35% inlet acetylene was
less than the value observed with 1.05% at low polymer loadings (less
than 300 mg/ml), while this relationship was reversed at higher loadings
(figure 101), yet the trans/cis ratio was lower with 0.35% at all but
the very lowest polymer loadings (figure 105).

There are similar problems in interpreting the results of the
various treatments we used on the 0.02 wt% catalyst. Evacuation had
little or no effect on the relative amounts of 1,3-butadiene (figure
109) and 1-butene (figure 111), yet decreased the trans/cis-2-butene ratio (figure 113). The trans/cis ratio is therefore affected by the physical presence of the volatile polymer fraction, while the relative amounts of 1,3-butadiene and 1-butene are not. Hydrogen treatment increased the 1,3-butadiene percentage and decreased that of 1-butene (figures 109 and 111), yet increased the trans/cis ratio (figure 113). These observations suggest that either the mechanism for 2-butene formation proposed above is incorrect or the conditions on the catalyst surface are considerably more complex than we had assumed. We conclude that the latter is definitely the case, while the former is a distinct possibility.

The reason for the initial decrease in 1,3-butadiene and increase in the butenes is perhaps more difficult to analyze. As we have discussed above, it appears unlikely that 1,3-butadiene adsorbs and reacts on the catalyst surface after it has initially formed and desorbed from the surface. The decrease must then be caused by changes in the environment on the Pd surface. The range of polymer loadings where this change occurs (0-200 mg/ml) is identical to that where significant increases in catalyst activity and ethane selectivity are observed. An increasing surface hydrogen concentration during this period would explain all of these results, but might also be expected to increase the relative formation of n-butane. The latter is not observed to any extent approaching the changes in 1,3-butadiene concentration, catalyst activity, or ethane selectivity. Changes in the actual nature of the catalytically active sites might also explain these results, but we have no direct information about what such changes might be.
The formation of a β-phase Pd-hydride (398) would explain all of these trends, but at the temperatures and hydrogen pressures used in this work, the β-phase probably cannot exist (figure 16, p. 126). In addition, if the β-phase did exist and was responsible for these changes, catalyst evacuation for 3-4 days should have decomposed it. After evacuation, however, the percentages of both 1,3-butadiene and 1-butene were essentially identical to the values observed prior to it (figures 126-130, 134, 135). Hydrogen and oxygen-hydrogen treatments did cause the initial behavior to be repeated (figures 126-130). We therefore tentatively conclude that alterations in the nature of the active sites cause all of these initial changes.

The actual nature of the active sites is presently unknown. The changes caused by hydrogen and/or oxygen-hydrogen treatment are most likely related to the removal of some type of surface species intimately related to the catalyst Pd. Whether this is a disordered (300) or ordered (103) carbonaceous layer, some sort of hydrogen transfer species (102, 115) or a supersaturated Pd-C phase (435) cannot be determined from our data. The changes upon hydrogen or oxygen-hydrogen treatments would be expected regardless of the actual species present. In particular, the Pd-C phase decomposes above 460 K in the presence of hydrogen (435); our hydrogen treatments were conducted at 573 K.

Major changes in the percentages of the various C₄ species other than n-butane occurred between polymer loadings of 0 and 200 mg/ml during all reactions except the one conducted over a 0.02 wt% Pd catalyst at 120°C. The trans/cis-2-butene ratios increased somewhat during the same period. The 1/2-butene ratio, however, generally did
not change in any similar manner during this same reaction stage. Changes in the 1/2-butene ratio were observed in almost every case, but the cause(s) of these changes are much less apparent. At high polymer loadings at 40°C, the 1/2-butene ratio increased over a 0.5 wt% catalyst and decreased over a 0.1 wt% sample (figure 83). The value observed over the 0.02 wt% catalyst at 40°C was higher than those observed over the 0.1 and 0.5 wt% samples at low polymer loadings (figure 83). At 80°C, the value observed over the 0.02 wt% was always lower than over the 0.1 wt% (figure 89). The behavior following the various treatments is perhaps even more confusing (figure 112).

Despite all of these different types of 1/2-butene and trans/cis-2-butene ratio behaviors, the results of experiments with different inlet acetylene concentrations suggest that values of these ratios are only slightly affected by a two fold change in the reactor acetylene pressure (figures 103 and 105). In addition, the trends observed with increasing polymer loadings are largely the same. Different amounts of 1,3-butadiene and 1-butene also cannot be ascribed to changes in the reactor acetylene pressure (figure 101). At the present time we have no real explanation for this behavior.

In order to continue this discussion of the mechanism of the surface polymerization reaction, we must first attempt to identify the nature of the insoluble polymer species, as they represent about 70% of the total polymer formed. The number of possibilities is actually not very large. Because these species are formed from hydrocarbons and are not soluble in any solvent we have used, we feel that they must be either coke or some type of conjugated polymer such as polyacetylene.
Hydrogen treatment at 300°C produced a large number of hydrocarbon species in the reactor outlet stream, including benzene, acetylene, ethylene and ethane. This product distribution is consistent with the products reported during the decomposition of polyacetylene (223), but since we have very little data on the amounts and total analysis of these decomposition products, we do not feel that this information alone proves the existence of polyacetylene.

Evacuation at 200 and 300°C removed 78.5% of the total polymer present on a sample of 0.5 wt% Pd catalyst. We would expect this treatment to remove all of the species that could be removed by lower temperature evacuation and/or solvent extraction; these should have amounted to about 30% of the total. The remaining 70% of the surface polymer must have lost about 48.5/70 = 69% of its initial weight. We do not feel that this is consistent with the existence of large amounts of coke prior to evacuation, for coke would not be expected to lose anywhere near this fraction of its total weight at these conditions. This procedure almost certainly caused coke formation, however, and the catalyst was subsequently completely inactive for further reactions. The appearance of the sheets of material left after hydrofluoric acid digestion of spent catalyst would also support the existence of a polymeric species relatively rich in hydrogen (compared to coke), as would the thick brown "gunk" remaining after the hydrofluoric acid/digested catalyst solution overheated (233).

The question of the nature of the unknown surface polymer is of crucial importance in elucidating the mechanism of polymer formation. Sheridan (67-70) proposed a free radical mechanism for the formation of
polymers during acetylene hydrogenation on Ni catalysts. Based upon the results of higher temperature homogeneous acetylene polymerization (41, 211,212), which almost certainly takes place by a free radical mechanism, we would expect a large amount of aromatic products if this reaction also proceeds by a free radical mechanism. This is not to imply that all of the surface polymers must be aromatic if the free radical mechanism is correct. It seems reasonable to suspect that a free radical bonded to a metal surface will be more "selective" than one at high temperatures in a gas phase. Nonetheless, we should expect some non-negligible aromatic formation. There are relatively low molecular weight aromatic species in the soluble polymer fraction (biphenyl, alkyl benzenes and naphthalenes) but the amount of these is small. The dominant species in this fraction are aliphatic (figure 125, or Appendix H, p. 614).

The unknown species accounts for 70% of the total surface polymer, and if it were mostly aromatic, such as coke, it would strongly support the free radical polymerization mechanism proposed by Sheridan (67-70). If, on the other hand, the unknown species are chiefly long chain conjugated polymers, the likelihood of this free radical mechanism will be greatly diminished. Based on both the decomposition products and the large weight loss observed during moderate temperature evacuation, we tentatively conclude that this fraction is largely composed of conjugated polymeric species which are mainly aliphatic in nature (the molecular weight need not be very high (41)). Assuming that this is the case, a number of features of the polymerization reaction are apparent.
The reaction almost certainly does not proceed through the formation of a surface free radical, as proposed by Sheridan (67). If it did, we would expect a much higher percentage of aromatic products, perhaps even a majority. If the insoluble fraction of the surface polymers is not aromatic, then the total percentage of aromatic species is much less than 1%. In addition, we have previously shown that the selectivity to polymer formation decreases regularly with decreasing metal loadings. This is almost surely due to an increase in metal loading with the same. It would be difficult to reconcile this decrease in polymer selectivity with metal loading if the reaction did proceed through a free radical. The radical, once formed, would be expected to react with whatever hydrocarbon it came in contact with, whether this molecule was adsorbed on the surface or in the gas phase. This would imply that changes in dispersion would only effect polymer selectivity to the extent that they favor or inhibit the formation of the radical.

In addition, we would expect this radical to react principally with ethylene. As this is by far the dominant species in the gas phase, the amount of acetylene in the polymers should be fairly small. We have no data indicating whether ethylene is incorporated into any of the gas phase or surface polymers. However, of all previous investigations considering polymer formation from ethylene (89, 109, 134, 135, 155, 194), only Yahun, et al (194) reported observing any, and the details of this observation (reaction conditions and the extent of ethylene incorporation) were not reported.

McGown, et al (109) observed that in the presence of gas phase CO two neighboring acetylene molecules were a necessary prerequisite for
dimerization to occur (table 10, p. 70). The C_{4} distributions produced in the presence of gas phase CO, reported by McGown, et al (109) and Weiss, et al (139), are in general agreement with those observed here in its absence. The only differences are the higher percentage of 1,3-butadiene and the absence of n-butane observed with CO, both of which are consistent with the proposed role of CO competing with hydrogen and lowering the surface hydrogen concentration (110-112,138,139). The otherwise close correspondence between the C_{4} distributions formed in the presence and absence of CO suggests that the same reaction mechanism is operating in each case. This in turn implies that two adjacent adsorbed acetylene molecules are necessary for dimerization to occur in its absence.

We believe that such a mechanism is more likely than the formation of a surface free radical, which we would expect to form a large amount of aromatic products, incorporate large amounts of ethylene, and be relatively unaffected by changes in catalyst metal loadings or dispersions.

The polymerization reaction could proceed through the insertion of a surface acetylene species into an existing Pd-C bond, or through the formation of a bond between neighboring adsorbed species. The difference between these mechanisms is rather small, but can be identified. Insertion into an existing Pd-C bond implies that it occurs during the adsorption of the second molecule or following transport across the Pd surface. The latter is unlikely due to the very high heat of acetylene adsorption on Pd. The former, like the free radical mechanism, would imply that the reaction should be unaffected by the
catalyst metal dispersion and might also be expected to incorporate ethylene. We therefore conclude that it occurs because of the geometry of adsorbed molecules on the surface.

The initial product is almost certainly adsorbed 1,3-butadiene. This species may desorb as butadiene, undergo hydrogen addition to form butene (which then desorbs), or add another acetylene molecule. Based upon the carbon number distribution of the volatile polymer fraction, the latter is about half as likely as the sum of the first two (figure 142, $\alpha = 0.5$), at least in the early stages of reaction. The probability of further addition decreases during continued operation ($\alpha$ decreases with increasing reaction time).

This relationship ($\alpha = 0.5$) apparently does not hold if we include the insoluble surface polymer species. Evacuation of a 0.02 wt% Pd sample with a polymer loadings of 200 mg/ml removed nearly 30% of the polymer initially present. Evacuation of a 0.5 wt% Pd sample with a polymer loading of 700 mg/ml also removed nearly 30% of the initial polymer present. If we assume that the fraction of removable polymer on the 0.02 wt% sample at a loading of 200 mg/ml is comparable to the conditions of the 0.5 wt% sample at an identical loading, and vice versa at a loading of 700 mg/ml, then the distribution between removable and insoluble surface polymer species remains essentially constant during this stage (200-700 mg/ml polymer loadings) of reaction.

The continued addition of acetylene occurs very quickly, or at least largely during one residence time on the surface, and must take place in the absence of hydrogenation. Once 1,3-butadiene hydrogenation occurs the resulting butene desorbs and cannot compete for surface
adsorption sites at a later time. Therefore we suspect that further acetylene addition to an adsorbed 1,3-butadiene molecule must take place rapidly, and probably forms adsorbed 1,3,5-hexatriene. Further additions without hydrogenation will lead to the formation of polyacetylene or polyacetylene precursors which will remain on the catalyst surface, although it is likely that they will be displaced to the support by the continued adsorption of acetylene.

Any adsorbed polymer species may also undergo hydrogenation. If this occurs first at the chain ends, further polymerization would be unlikely to occur and the molecule will desorb or be displaced onto the support. Which of these occurs will depend on the molecular weight of the species in question and the reaction temperature. Those that remain on the surface may undergo further hydrogen addition both before the initial desorption and from time to time later depending on the surface coverage of acetylene. After acetylene diffusion control begins (due to the build-up of polymers in the catalyst pores), we expect relatively more polymer hydrogenation will occur.

Polyacetylene is stable in molecular hydrogen at the reaction temperatures we have employed (430). We do not have any data concerning its stability to atomic hydrogen. It may be subject to atomic hydrogen attack and degradation if it is located on or near Pd sites, particularly under conditions of less than total acetylene surface coverage. If hydrogen spillover to the support occurs it might have a similar effect.

This reaction mechanism seems to explain most of the limited results we have obtained on the amount and structure of the surface
polymer. The amount of paraffinic species in the gas phase polymer is low due to the desorption of the olefins after they are formed. Under the conditions of full surface acetylene coverage and a large excess of ethylene, any olefin readsoption is unlikely. Surface polymers continue to grow until terminated by hydrogenation. Those that are terminated at relatively low molecular weights desorb into the gas phase as primarily olefins if the temperature is high enough. Those of higher molecular weights stay on the catalyst and may undergo further hydrogen addition from time to time.

Although we do not know the exact range of carbon numbers where polyacetylenes become insoluble, it must be between C_4 and C_{24}, as 1,3-butadiene (the lowest molecular weight polyacetylene) is soluble in hydrocarbon solvents while polyacetylenes containing 12-15 acetylene units are black and insoluble (41). We feel that this observation further supports the presence of polyacetylene on the catalyst surface, as very high degrees of polymerization are not required.

In order for the polymerization reaction to occur as we have proposed, the surface hydrogen concentration must be relatively low. Otherwise hydrogenation would terminate essentially all of the growing chains at very low molecular weights (C_4 and C_6). This is consistent with the strong adsorption of acetylene on Pd and the low selectivity to both butane, observed in this work, and ethane, as observed with labeled acetylene or ethylene (108,110-112,133-143). Increasing ethane selectivities may be observed under conditions where the acetylene reaction is not diffusion controlled, but this comes from the hydrogenation of ethylene, not acetylene (108,110-112,133-143).
The final observation which we must consider is the fact that relatively little (90,91,110-112,209) or no (194,210) acetylene polymerization is observed in the absence of hydrogen (compared to the amounts formed during hydrogenation). We propose that this is due to the rapid poisoning of the surface Pd sites by the formation of nonvolatile polymers. In the presence of hydrogen, a larger proportion of the Pd surface would be polyacetylene free due to hydrogen termination of the polymerization reaction. This is supported by our observation that only the volatile, removable polymer species cause deactivation (see the following section). To paraphrase Thomson and Webb (see p. 20, or (102)), we propose that although the polymerization of acetylene is self-poisoning, it remains continuous for a much longer period of time in the presence of hydrogen. It is also at least theoretically possible that there are distinctly different surface sites involved in polymerization and hydrogenation, as proposed by Berndt, et al (113) for acetylene hydrogenation on Ni catalysts.

The deactivation of Pd catalysts used for tail-end (low hydrogen/acetylene ratio) acetylene hydrogenation occurs because of the build-up of heavy oils, leading to mass transfer limitations after 1 to 6 months operation (659). Deactivation of front-end (high hydrogen/acetylene ratio) hydrogenation catalysts, on the other hand, is caused by the slow (5-10 year) sintering of the catalyst (659). We believe this further supports our mechanism of polymer formation. We have directly observed the conditions described for tail-end hydrogenations, while front end reactions should produce relatively
little surface polymer (because of termination by hydrogenation) based on this mechanism.

We realize, of course, that the development of this model depends very strongly on the nature of the insoluble species. In particular, if these are coke then the Sheridan free radical mechanism must be considered the most likely candidate. Although we have not positively identified this polymer species, we believe the limited data we have are more consistent with the existence of polyacetylene, as coke formation would not be expected at these experimental conditions. Nonetheless we strongly recommend that suitable analysis of this surface polymer be conducted in order to identify it completely.

Wells (116) has proposed a model for 1,3-butadiene hydrogenation whereby butane is formed near zones of high hydrogen content formed by the occlusion of hydrogen. Away from these hydrogen rich zones, butenes are formed almost exclusively. We propose a somewhat analogous explanation for the formation of polymeric species during acetylene hydrogenation. In this model polymerization occurs between adjacent adsorbed acetylene species in the absence of hydrogen. In zones of relatively higher hydrogen concentrations polymerization does not occur due to ethylene formation and desorption, or occurs to only a small extent before hydrogenation terminates it. Regions of higher hydrogen concentrations (β-phase hydrides and/or zones of occluded hydrogen) will catalyze ethane formation. Any conditions which geometrically isolate the adsorbed species, such as increasing metal dispersions, or increase the surface hydrogen concentration, such as the formation of a β-phase hydride or increasing hydrogen/acetylene ratios should decrease both the
extent of polymer formation and the polymer molecular weights achieved, but may also promote ethane formation.

We are faced with the paradox that the very characteristics that make Pd an attractive selective hydrogenation catalyst - strong alkyne/diolefin adsorption and low surface hydrogen concentrations - also make it an effective acetylene polymerization catalyst. The formation of polymer is undesirable both because of what it could have been - ethylene - and what it does to the catalyst activity and ethylene selectivity. We shall now consider the latter.
C. **Catalyst Activation and Deactivation**

1. Results

Acetylene conversions, measured at constant feed concentrations and flow rates and constant temperature, change markedly during operation. At 40°C, 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts reach a maximum conversion very quickly (15-20 hours) and deactivate to a fairly steady value by about 50 hours operation time (figure 130). A 0.1 wt% Pd sample reaches a maximum conversion after a somewhat longer period and takes up to 250 hours to deactivate to a fairly steady value. In contrast, a 0.02 wt% sample does not reach a maximum after more than 200 hours, and exhibits no deactivation prior to that time.

![Graph showing conversion vs. time](image)

**Figure 130.** Acetylene conversions observed during operation at 40°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 27, 1, 8, 21)

Because conversion is a fairly arbitrary way to compare the results of different experiments (it provides no information on catalyst loadings, feed concentrations, and flow rates) and because hydrogen
consumption is not only dependent on conversion but also on the product selectivity values, we have also presented the results of these experiments as first order (hydrogen) rate constants calculated from the experimental data (figure 131). Because the feed concentrations and flow rates and the total Pd charged to the reactor are very similar in all four of these experiments, in this comparison the conversion and rate constant behaviors are almost identical.

![Graph](image)

**Figure 131.** First order rate constants calculated during operation at 40°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 27, 1, 8, 21)

Because we have previously seen (figure 29, p. 211) that the polymer loadings on these catalysts at any given time are very different (except of course for the two 0.5 wt% samples), we have also compared conversions and rate constants at equal polymer loadings (figures 132 and 133, respectively). In both cases the behavior which appears very different on a time basis is remarkably similar on a polymer loading basis. The conversion/rate constant on all catalyst samples increases
Figure 132. Acetylene conversions compared at equal polymer loadings during operation at 40°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 27, 1, 8, 21)

Figure 133. First order rate constants compared at equal polymer loadings during operation at 40°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 27, 1, 8, 21)

up to polymer loadings of 100-200 mg/ml pore volume. As the amount of surface polymer increases, values over the 0.1 and 0.5 wt% samples remain fairly constant up to loadings of about 600 mg/ml, then drop off
sharply with further polymer formation. Unfortunately, we did not conduct the experiment over the 0.02 wt% sample for a long enough period of time to reach high polymer loadings in order to investigate if the catalyst activity would also decrease in the same way. The maximum value of the rate constant over the 0.1 wt% sample is much higher than those calculated for the other three samples.

At 80°C, the conversion over a 0.1 wt% sample decreases almost from the start of reaction, while it initially increases and then remains fairly constant over a 0.02 wt% catalyst (figure 134). First order rate constants behave in the same qualitative way, although the initial value over the 0.1 wt% sample is considerably higher than the maximum value observed over the 0.02 wt% sample (figure 135).

![Diagram](image_url)

**Figure 134.** Acetylene conversions observed during operation at 80°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 12 and 25)

Compared at equal polymer loadings (figures 136 and 137), the behavior of the 0.02 wt% sample is very similar to the behavior of all
Figure 135. First order rate constants calculated during operation at 80°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 12 and 25)

Figure 136. Acetylene conversions compared at equal polymer loadings during operation at 80°C with catalysts of different metal loadings supported on 90 m²/g Al₂O₃. (Experiments 12 and 25)

samples at 40°C (figures 132 and 133), while the 0.1 wt% sample deactivates almost linearly with increasing polymer loading. The initial rate constant over the 0.1 wt% sample is again much higher than
the maximum over the 0.02 wt% sample.

The conversion over 0.1 wt% catalysts decreases much more slowly at 40°C than when operated at higher temperatures (figure 138). The rate of decrease appears to be slightly lower at 60°C than at 70 or 80°C, where it is essentially equal. Because the rate of reaction increases with temperature the conversion data appearing in figure 137 was taken with very different amounts of catalyst in the reactor, the rate constants calculated at these different temperatures are very different, even though conversions are similar in each case (figure 139). Because of these large changes in $K$ over the temperature range in question, we have plotted $K$ values on a log scale; on a straight scale the details from the experiment at 40°C are lost. The rate constant at 40°C initially increases, then remains fairly constant up to about 100 hours
Figure 138. Acetylene conversions observed during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. (Experiments 8, 10, 11, and 12)

Figure 139. First order rate constants calculated during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

operation time after which it decreases, as we have seen before. At 60°C, however, there is only a small initial increase, followed by a sharp decrease to values lower than those calculated at 40°C after about 40 hours. At 70 and 80°C there is no initial increase and the rate
constant drops sharply throughout the duration of each experiment. The rate of this decrease is essentially identical at these two temperatures, as we might suspect from the conversion versus time behavior (figure 138).

Comparisons at equal polymer loadings again shows the initial increase in conversion at 40 and 60°C (figure 140), although in this case the conversions at 70 and 80°C are always equal to or higher than the values at 60°C; compared versus time (figure 141) they are always equal or lower.

Figure 140. Acetylene conversion compared at equal polymer loadings during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

Rate constants compared at equal polymer loadings, again on a log scale (figure 141), shows that although there is an initial increase, a steady period, and a subsequent decrease with increasing polymer loadings at 40°C, at 60°C there is no initial increase and the steady period only lasts up to polymer loadings of about 300 mg/ml (versus 600
at 40°C. At the two higher temperatures there is no initial increase or steady period; the rate constants decrease continuously from the start, although the rate decline seems to accelerate at polymer loadings above 500 mg/ml.

![Graph showing K (mole/mole Pd*min*torr) vs mg polymer/ml pore volume for different temperatures: 40, 60, 70, and 80°C.](image)

Figure 141. First order rate constants compared at equal polymer loadings during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

We have also investigated the effects of a larger range of temperatures over a 0.02 wt% Pd catalyst. The acetylene conversion increases initially at 40°C and has not reached a maximum after more than 200 hours operation (figure 142). At 80°C it also increases initially, reaching a maximum after about 70 hours operation time, and thereafter decreases. At 120°C the conversion decreases almost linearly throughout the experiment after an initial sharper decrease. First order rate constants behave in much the same way (figure 143), although here we can see the almost two orders of magnitude difference between the maximum rate constants at 40 and 120°C.
Figure 142. Acetylene conversions observed during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. (Experiments 21, 25, and 26).

Figure 143. First order rate constants calculated during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

Compared at equal polymer loadings the conversions at 40 and 80°C behave in much the same way, both increasing up to at least 200 mg/ml pore volume (figure 144). Unfortunately, since the experiment at 40°C was terminated at this polymer loading, we cannot say whether the
conversion would have reached a maximum and then decreased in the same way it did at 80°C. At 120°C the conversion decreases continuously with increasing polymer loadings, although the rate of this decrease is higher at very low (up to about 100 mg/ml) and high (above about 600 mg/ml) polymer loadings than it is at intermediate loadings.

![Conversion graph](image)

Figure 144. Acetylene conversions compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

First order rate constants compared at equal polymer loadings (figure 145) behave in much the same way as acetylene conversions, although the rate constant at 80°C is fairly steady at polymer loadings higher than 100 mg/ml, while the conversion decreases at loadings higher than 200 mg/ml at the same conditions. The reasons for this apparent discrepancy might not be immediately obvious, but the behavior is indeed consistent. As we have defined it, the rate constant depends not only on the rate of acetylene consumption (conversion at constant flow rates and inlet concentrations) but also on the hydrogen pressure in the
Figure 145. First order rate constants compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst.

The latter is in turn dependent on both the acetylene conversion and the various product selectivities, particularly the ethane selectivity. The rate constant is defined as the reaction rate divided by the hydrogen pressure (in torr). Therefore if the ethane selectivity increased at constant conversion, the rate constant would increase due to the resulting lower hydrogen pressure (increased hydrogen consumption to meet the stoichiometry of ethane formation). In this case although the conversion decreases, the ethane selectivity increases so that the higher rate of hydrogen consumption lowers the hydrogen pressure enough that the rate constant remains essentially constant.

The rate constant data from these experiments conducted over 0.1 and 0.02 wt% catalysts at different temperatures may be used to construct an Arrhenius plot and calculate apparent activation energies. This procedure is complicated by the changes in rate constant values
calculated during each experiment, and by the qualitatively different nature of these changes between experiments. We have chosen to use the maximum value of the rate constant calculated during each experiment. This will of course also be the initial value over catalysts that deactivated throughout. Perhaps surprisingly, plots constructed in this way are quite linear (figure 146), and the activation energies calculated over the two catalyst types are in good agreement (11.2 kcal/mole \( R^2 = 1.000 \) over the 0.02 wt% sample; 11.0 kcal/mole \( R^2 = 0.963 \) over the 0.1 wt% sample).

Figure 146. Arrhenius plot from experiments over 0.1 and 0.02 wt% Pd on 90 m\(^2\)/g Al\(_2\)O\(_3\) catalysts. (Experiments 8,10,11,12,21,25, and 26).

Experiments at 40°C over 0.5 wt% Pd catalysts supported on aluminas of different surface areas show that although the acetylene conversion increases initially over samples on 33 and 90 m\(^2\)/g supports, it decreases continuously on supports of 4 and 220 m\(^2\)/g (figure 147). The rate constant behavior (figure 148) is similar, except that after about 20 hours operation, the 33 and 90 m\(^2\)/g values are identical, while
Figure 147. Acetylene conversion observed during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas. (Experiments 1, 3, 6, and 7)

Figure 148. First order rate constants calculated during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas. Those on the 4 and 220 m²/g samples are identical throughout. Compared at equal polymer loadings (figures 149 and 150), these differences are amplified even more. The conversion on the 33 and 90 m²/g samples increases up to polymer loadings of about 100 and 150 mg/ml,
Figure 149. Acetylene conversions compared at equal polymer loadings during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

Figure 150. First order rate constants compared at equal polymer loadings during operation at 40°C with 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

respectively, while on the 4 and 220 m²/g it reaches a maximum at loadings of about 50 mg/ml (figure 150). In addition, the conversion on the 33 and 90 m²/g samples remains high and fairly steady up to polymer
loadings of 400 and 600 mg/ml, respectively, while on the other two samples it decreases rapidly at loadings of less than 100 mg/ml.

The rate constants behave in much the same way, except that on the 4 and 220 m²/g samples they are essentially identical at all polymer loadings (figure 150). At very high polymer loadings, the slopes of both the conversion and rate constant versus polymer loading over the 33 and 90 m²/g samples are practically infinite.

The acetylene conversion of a 0.5 wt% Pd on 33 m²/g alumina catalyst decreases faster with increasing acetylene inlet concentration (figure 151). Although the maximum conversion with 1.05% inlet

![Conversion vs Time Graph](image)

Figure 151. Acetylene conversions observed during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations. (Experiments 3 and 4).

acetylene is just over 60%, within 35-40 hours it has fallen below the conversion with 0.35% inlet acetylene, where the maximum conversion is about 45%. The first order rate constant also decreases much faster with 1.05% inlet acetylene, although it is always lower than the rate
constant with 0.35% (figure 152). The maximum values, however, are quite similar (0.27 and 0.32 moles/mole Pd*min*torr) in spite of the three fold difference in inlet acetylene concentrations.

![Graph showing first order rate constants](image)

Figure 152. First order rate constants calculated during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations.

Comparison of the conversions at equal polymer loadings (figure 153) shows quite similar behavior due to the different rates of polymer formation (the rate of polymer formation is higher with 1.05% acetylene (figure 55, p. 230). Rate constants compared at equal polymer loadings are even more similar (figure 154), although the values with 0.35% acetylene are somewhat higher at polymer loadings below 300 mg/ml, and are somewhat lower at higher loadings.

We have conducted a number of evacuation and hydrogen or oxygen-hydrogen treatments on a single sample of 0.02 wt% Pd on 90 m²/g alumina catalyst. The details of these procedures have been given previously
Figure 153. Acetylene conversions compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations.

Figure 154. First order rate constants compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with different inlet acetylene concentrations.

(p. 231). The acetylene conversion increases after all treatments except the evacuation at 40°C, although the data points for this experiment are admittedly not easy to see (figure 155). In this case
the conversion is fairly constant at about 55%. The conversion after the hydrogen and oxygen-hydrogen treatments is always higher than that observed during the initial experiment (after standard pretreatment).

Rate constants behave in much the same way (figure 156). Following evacuation at 40°C the rate constant initially decreases and then remains fairly constant at a value higher than those following the other treatments. The rate constants calculated during the initial experiment are always the lowest at any given time.

The treatments conducted on this catalyst sample removed different amounts of the total surface polymer (see p. 231). For this reason comparisons at equal polymer loadings are qualitatively different than those considered previously. The conversion after evacuation is slightly decreased relative to the values observed at similar polymer
Figure 156. First order rate constants calculated during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 155 for symbol definition.

loadings during the initial experiment (figure 157). Both hydrogen and oxygen-hydrogen treatments lowered the conversion dramatically.

Following these treatment, however, it increased rapidly, much more so

Figure 157. Acetylene conversions compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 155 for symbol definition.
than it increased during the initial experiment.

Because of changes in product selectivities following these treatments, the behavior of the rate constants at equal polymer loadings is somewhat different (figure 158). Evacuation, which caused a slight decrease in conversion, actually caused an increase in the rate constant because of the higher ethane selectivities observed following this treatment. The final rate constant after hydrogen and oxygen-hydrogen treatments are significantly higher than those in the initial experiment due to both a higher conversion and a higher ethane selectivity.

We have also investigated the effects of evacuation on a sample of 0.5 wt% Pd on 90 m²/g alumina which had been operated at 40°C until it contained about 700 mg polymer/ml pore volume, at which time the conversion and rate constant had decreased significantly (figures 159 and 160). Evacuation for 72 hours at 40°C removed 28.3% of the polymer.

![Figure 158. First order rate constants compared at equal polymer loadings during operation at 40°C with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 155 for symbol definition.](image)
initially present. The reaction was then restarted at identical conditions.

Figure 159. Acetylene conversions observed during operation at 40ºC with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40ºC (Exp. 28).

Figure 160. First order rate constants calculated during operation at 40ºC with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 159 for symbol definition.
This evacuation increased the acetylene conversion to almost the same value as the maximum observed during the initial experiment (figure 159), but it subsequently decreased at a higher rate than initially. The rate constant behaved in much the same way, although following evacuation it was actually higher than the previous maximum value (figure 160).

Comparison at equal polymer loadings shows that evacuation increases the conversion to essentially the same value that was observed at identical polymer loadings during the initial experiment (figure 161). During operation after evacuation, the polymer loading-conversion relationship remains identical. Evacuation increases the rate constant somewhat compared to the values calculated in the initial experiment (figure 162), but the difference is rather small and the subsequent behavior is again identical.

![Graph](image)

**Figure 161.** Acetylene conversions compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 159 for symbol definition.
Figure 162. First order rate constants compared at equal polymer loadings during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 159 for symbol definition.

After the evacuated sample had reached a polymer loading of about 700 mg/ml pore volume, the reaction was terminated and the sample was evacuated again. This time, however, the temperature was raised to 200°C for two hours, followed by 300°C for 3 hours. This removed 78.5% of the polymer present initially. The sample was cooled back to 40°C, and H₂ and He were introduced at identical flow rates. The sample had no measurable activity (conversion < 2%) and gained no measurable weight (< 0.1 mg) during operation following this treatment.

Ethane selectivities increased during operation of every catalyst sample we investigated. In order to test for possible acetylene diffusion limitations as the cause of this behavior (by allowing ethylene to adsorb and react on open surface sites), we conducted an experiment at 40°C over a sample of 0.1 wt% Pd on 90 m²/g alumina which had been crushed to 40-60 mesh. This would decrease the pore length
that acetylene must traverse to reach all surface Pd sites, and a
decrease in ethane selectivities following this particle size reduction
would indicate acetylene pore diffusion effects as a cause of the
increase in ethane selectivities observed over whole pellets.

The ethane selectivity was indeed affected, although it actually
increased sharply. This behavior will be presented in more detail in
the following section. However, the acetylene conversions observed and
the rate constants calculated were also affected (figures 163 and 164).
The maximum values of both are lower, and both subsequently decrease
much more rapidly over the crushed sample. Because the powdered sample
could not be placed in the TGA balance pan (it would be "blown away"),
but was instead placed between glass wool plugs in the TGA hangdown
tube, comparisons at equal polymer loadings cannot be made.

![Figure 163. Acetylene conversions observed during operation at 40°C with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Whole catalysts pellets (Exp. 8). 2. Pellets crushed to 40-60 mesh (Exp. 9).](image-url)
Based upon the previous results of this section, we might suspect that the behavior of both the acetylene conversion and the rate constant were similar, if not identical, at equal polymer loadings. This implies either that the rate of polymer formation was much higher over the crushed sample, or that the total pore volume was greatly decreased during the crushing operation.

![Graph](image)

**Figure 164.** First order rate constants calculated during operation at 40°C with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Whole catalysts pellets (Exp. 8). 2. Pellets crushed to 40–60 mesh (Exp. 9).
C. Catalyst Activation and Deactivation

2. Discussion

Both acetylene conversions and first order rate constants increased during initial operation over all three 90 m²/g Al₂O₃ supported catalysts at 40°C (figures 130 and 131). Similar increases were observed with the 0.02 wt% catalyst at 80°C, although both values decreased continuously over a 0.1 wt% sample (figures 134 and 135). This behavior was not repeated during operation after the long term (3-4 day) evacuation of either the 0.02 or 0.5 wt% Pd (figures 155,156,159, and 160). Therefore we conclude that it is not an artifact caused by the reaction system we employed, particularly diffusion to and/or from the TGA (see Section III C. Experimental Error, p. 195).

Experiments conducted at 40°C over 0.5 wt% Pd on 33 m²/g Al₂O₃ with different inlet acetylene concentrations exhibited similar behavior (figures 151 and 152). This strongly implies that no non-zero acetylene order is responsible. This is a particularly important consideration, because a negative order in acetylene, which has been observed during several previous investigations (70,72,86,89,134,138), would cause an increase in rate as the acetylene partial pressure decreased. In this case the reaction rate must be multiplied by the acetylene pressure (in addition to being divided by the hydrogen pressure) in order to yield the correct rate constant. A negative order with respect to acetylene pressure would largely remove the initial increase in the rate constant (increasing rate constants calculated assuming zero order acetylene would be multiplied by decreasing acetylene pressures), but the 2 fold difference in reactor acetylene pressures would make the maximum value
of the rate constant with 1.05% inlet acetylene twice that calculated with 0.35%. We conclude that zero order acetylene dependence is correct.

We must also consider the very different time dependence of the initial changes over the 90 m²/g catalysts (figures 130 and 131). The initial increase in conversion/first order rate constant occurs during the first 3-5 hours over the 0.5 wt% samples, during the first 8-12 hours over the 0.1% sample, and during practically the entire reaction (170⁺ hours) over the 0.02 wt% sample. These reactions were conducted at almost identical total flow rates, feed compositions, and total Pd loadings. Similar, though smaller, time dependent differences are apparent between reactions conducted at different inlet acetylene concentrations (figures 151 and 152). Diffusion into the TGA cannot be invoked in any way to explain this trend.

Comparison at equal polymer loadings, however, shows remarkably similar trends over all the 90 m²/g samples at 40°C (figures 132 and 133), and at the different inlet acetylene concentrations (figures 153 and 154). In each of these experiments, the conversion increases up to polymer loadings of about 100 mg/ml (figures 132 and 153), while the rate constant increases until almost 200 mg/ml (figures 133 and 154).

There are previous reports of this type of behavior in the literature. Inoue, et al (103) observed an induction period during the first batch acetylene hydrogenation reaction conducted on polycrystalline Pd-black surfaces. This effect was absent during subsequent reactions. They interpreted this as the formation of a surface template from strongly bound acetylenic species. Several of
these authors (107) also observed that a Pd foil, deactivated to less than 1/50 of its original activity by repeated ethylene hydrogenation reactions, could be reactivated to a steady state activity of about 1/5 of the initial value by adsorbed acetylene. This was interpreted as acetylene displacing dissociatively adsorbed ethylene from the surface and forming a "polymerizate" which could stabilize the active surface sites by fixing surrounding metal atoms. The authors were not able to identify the actual structure of the active sites, but suggested that they were closely correlated with surface irregularities such as lattice defects.

Nair (229) conducted continuous acetylene hydrogenation reactions in a CSTR system similar to the one employed in this work, except that he could not monitor the formation of surface polymer by catalyst weight gain. Acetylene conversions, reaction rates of the C_2 and total C_4 compounds, temperatures, catalyst types, and feed concentrations and flow rates are given in one of his appendices (229). Figure 165 shows the acetylene conversions reported for two of these experiments. The conversion in the first experiment is essentially constant, while in the second it appears to increase somewhat initially, then decrease more slowly. The author considered and discussed the results of both of these reactions in terms of constant catalyst activity. From the feed composition, the acetylene conversion, and the reaction rates of the C_2 and total C_4 compounds, we can calculate the hydrogen pressure at any given time and convert these results to rate constants (figure 166). Despite the nearly constant acetylene conversions observed during these two experiments, a concurrent increase in ethane selectivities causes
Figure 165. Acetylene conversions reported during CSTR operation at 25°C over 0.04 wt% Pd catalysts supported on 1) γ-Al₂O₃, 2) α-Al₂O₃. Feed composition: 1) 0.30% acetylene, 0.44% hydrogen. 2) 0.34% acetylene, 0.37% hydrogen. Both balance ethylene (229).

Figure 166. First order rate constants calculated from data in ref. (229). CSTR operation at 25°C over 0.04 wt% Pd catalysts supported on 1) γ-Al₂O₃, 2) α-Al₂O₃. Feed composition: 1) 0.30% acetylene, 0.44% hydrogen. 2) 0.34% acetylene, 0.37% hydrogen. Both balance ethylene. The hydrogen consumption rate to increase also. This in turn increases the calculated rate constants. Although we do not know the surface
polymer loadings on these catalysts, it is apparent that the overall
trends are very similar to our results over the 0.02 wt% sample (figure
130). Of course, the absolute values of the rate constants are
different, as these experiments were conducted at 25°C; 40°C was the
lowest temperature we employed.

We do not have such detailed data for any other examples of this
behavior in the literature. However, some meaningful comparisons can
still be made. Weiss, et al (132) report an essentially constant rate
of acetylene consumption during continuous PFR operation at 0°C and 3.04
atm over a 0.1 wt% Pd on γ-Al₂O₃ catalyst. At a conversion of
approximately 10%, the initial (65 hour) rates of both acetylene and
deuterium consumption were about 0.01 μmoles/gcat*sec. After 570 hours
operation, the rate of acetylene consumption was unchanged, while the
deuterium rate had increased to 0.035. These values correspond to an
increase of about 11% in first order rate constants.

Sarkany, et al (141) report that during CSTR operation over a
0.038 wt% Pd on γ-Al₂O₃ catalyst at 28°C, the acetylene conversion was
essentially constant (85%) while the ethane selectivity increased from
about 20% initially (0 hours) to a final, apparently steady value of 85%
(80 hours). The feed gas contained 0.29% acetylene and 0.44% hydrogen
(hydrogen/acetylene ratio = 1.52). These values correspond to a first
order rate constant increase of more than a factor of two. Similar
results may be found in other parts of (132) and (141). Clearly our
results are not without precedent.

Yahun, et al (194) also observed an initial increase in activity,
lasting about 120 hours, during acetylene hydrogenation over 0.035 wt%
Pd catalysts (see figure 10, p. 52). In this case, however, it is not clear whether the catalyst samples were reduced prior to reaction. If they were not, we would expect such an initial increase in activity as the surface is reduced by the reaction gas mixture.

Borodzinski, et al (398) observed that the formation of a β-phase Pd-hydride increases the activity and decreases the ethylene selectivity of Pd acetylene hydrogenation catalysts (see table 11, p. 101). As ethane selectivities increased (and ethylene selectivities decreased) during the same range of polymer loadings (0-200 mg/ml) that the activity of our catalyst samples increased, it is tempting to ascribe these changes to the formation of a β-phase hydride.

Our results are not that straightforward. At the temperature (40°C) and range of hydrogen pressures (1-14 torr, or 0.0013-0.018 atm) that these experiments were conducted, the β-phase is thermodynamically unlikely to form (see figure 16, p. 93). In addition, as conversions (acetylene reaction rates) and ethane selectivities increase, the hydrogen partial pressure in the reactor decreases. Therefore even if the β-phase formed at low conversions (hydrogen pressures of about 0.01 atm), which seems unlikely, we would not expect it to continue forming as the hydrogen pressure decreased to values where the β-phase certainly cannot exist. The almost identical maximum rate constants observed with 0.35 and 1.05% inlet acetylene feeds further supports this argument, as the hydrogen pressures at these conditions differed by a factor of almost two.

Evacuation for 3-4 days at 40°C would have certainly decomposed any β-phase hydride if it had previously existed on these catalyst
samples, yet the rate constant was nearly identical after this procedure was carried out (figure 158).

The time dependent behavior of the different 90 m²/g samples is even harder to reconcile with the formation of a β-phase hydride. Palcewska (117) reported that large metal crystals transform into hydrides slowly, while small crystallites form hydrides instantly. We observe an increasing duration of the initial catalyst activation with decreasing metal loading. We will not insist that the metal dispersion increases with decreasing metal loading, but we highly doubt that the dispersion of the 0.02 wt% catalyst is significantly lower than that of the 0.1 wt% sample, and that the 0.1 wt% sample is itself of lower dispersion than the 0.5 wt% sample. If the formation of a β-phase hydride is the cause of these increasing activities, then the Pd crystallite size must increase with decreasing metal loading in order to explain the different durations of the activation. We conclude that we have no evidence for the formation of a β-phase Pd-hydride, and a large amount against the conclusion that it plays any role at all in the observed initial catalyst activation.

Since the time that the β-phase hydride investigations of Borodzinski, et al (398) were published, Stachurski and Frackiewicz (435) have challenged their interpretation that the observed XRD peak deformations and displacements represent the formation of a β-phase hydride. They have instead observed the formation of a supersaturated solution of carbon in Pd of the composition PdC₀.₁₃. We have been unable to locate any investigations which discuss the parameters (temperature,
acetylene pressure, hydrogen pressure, metal particle size, etc.) that affect the formation of this phase (435,438-443,655).

If we accept the assertion of Stachurski and Frackiewicz (435) that Borodzinski, et al (398) actually observed the formation and decomposition of this PdC phase rather than a β-phase hydride, then the conclusion that our results are caused by this PdC phase suffers from the same problems that the β-phase hydride conclusion does. If we not only assume that Borodzinski, et al (398) really did observe a β-phase hydride, but also that a PdC phase such as that observed by Stachurski and Frackiewicz (435) can exist, we are left with no data on either the formation or subsequent effects of this phase. Because the number of interstitial sites for the β-phase hydride and/or PdC phase decrease with increasing dispersion (decreasing Pd crystallite size (356-358)), we would not expect the degree of activation to be the same over all three 90 m²/g catalyst samples, if either phase is the cause.

The degree of activation and the maximum activity reached over the 0.1 wt% catalyst do appear to be higher than over the other two catalysts. This is probably due to another cause, which we shall discuss later. In any case, it is hard to believe that the dispersion of the 0.1 wt% catalyst is significantly lower than that of both the 0.02 and the 0.5 wt% samples, as it would have to be if either of these phases are implicated in the initial activation. The increasing duration of catalyst activation with decreasing metal loading presents a severe problem whether we assume a β-phase hydride or a PdC phase as the cause of activation. We conclude that neither of these phases is responsible for our results.
The original low activity of the 0.02 wt% catalyst could be restored by either hydrogen or oxygen-hydrogen treatment (figures 173-176). Hydrogen treatment removed 84% of the surface polymer initially present; oxygen-hydrogen treatment removed only 53.6%. The rate constant after hydrogen treatment was essentially identical to the initial rate constant, while that following oxygen-hydrogen treatment was actually lower than the initial one (figure 158). Evacuation at 40°C removed 26.8% of the surface polymer and had only a small effect on the rate constant, which actually increased somewhat, while evacuation of a 0.5 wt% Pd sample at higher temperatures removed 78.5% of the surface polymer, yet completely poisoned the catalyst. Clearly the amount of polymer removed is less important than what part is removed and what condition the catalytic surface is in following the polymer removal.

We have previously shown that low temperature evacuation probably removes the volatile, soluble paraffins and olefins that are formed by acetylene polymerization; these do not cause the initial activation. We have also presented evidence that suggests the majority of the remaining nonvolatile, insoluble species are conjugated polyacetylenes. For the sake of this discussion we will accept the possibility that these may be coke. We do not believe that there is any plausible mechanism by which either polyacetylene or coke can cause an increase in catalyst activity. At least the majority of these polymers must exist on the support surface, away from the Pd. We make this conclusion for two reasons: 1) the polymers recovered after hydrofluoric acid digestion of spent catalysts consisted of sheets of material, while most of the Pd must be
located in the catalyst pores; and 2) there is simply too much polymer present on the catalyst for it to be intimately associated with the Pd and not completely poison (cover) it. The 0.02 wt% sample had a polymer loading of 200 mg/ml, which was about 70% polyacetylene or coke. This corresponds to a weight loading of 49 mg/g. The catalyst contains only 0.02 wt% Pd, or 0.2 mg/g (500 mg polymer/mg Pd). Much higher polymer loadings (600 mg/ml) were observed on the 0.1 and 0.5 wt% catalysts before deactivation began.

Similarly, although we might conceive of a mechanism whereby polyacetylene acts as the active hydrogen transfer species proposed by Thomson and Webb (102), this will not catalyze acetylene hydrogenation. In the absence of a suitable catalyst, acetylene addition to or reaction with polyacetylene will not occur; if it did, polyacetylene production would be trivial (it isn't). Polyacetylenes of high molecular weight can exist as free radicals because of there molecular size and because their unpaired electrons can be delocalized (41), but if anything these will catalyze further polymerization, with the same conclusion for polyacetylene production.

Coke has been implicated in literally thousands of catalyst deactivation mechanisms (see for example (199-206)), and it is difficult to imagine it increasing activity in this reaction. In fact, its formation appears unlikely under these reaction conditions (low temperatures, excess hydrogen). We therefore conclude that whatever the composition of the insoluble surface polymer fraction, polyacetylene or coke, it cannot be responsible for the observed initial catalyst activation.
With this background, we propose that a third type of surface hydrocarbon deposit is formed on the active Pd centers, and that it is this species which is responsible for the initial increase in activity. We do not have any evidence of what the nature or structure of this third type might be. A hydrogen transfer species, such as that proposed by Thomson and Webb (102) is certainly a candidate, as is the formation of a surface template which stabilizes the active sites, as proposed by Inoue, et al (103). Disordered carbonaceous deposits, particularly those capable of storing large amounts of hydrogen (as proposed by Davis, et al (295)), are another inviting candidate.

A different possibility is that during reaction, the Pd itself is somehow rearranged to yield a rougher, more irregular surface. There is considerable evidence that such a surface is more active than a smooth, regular one (246-250). If the original catalyst particles were fairly large, changes in the Pd lattice parameter caused by the formation of a 8-hydride or supersaturated PdC phase could conceivably cause such a surface roughening. This mechanism, however, would require that both the hydrogen and oxygen-hydrogen treatments caused the surface to revert to its original smooth state. At the temperatures that these treatments were conducted (200-300°C), such an effect is unlikely (247,248,252).

Whatever the actual nature of this species, we can conceive of three possible ways in which it causes the initial catalyst activation. The first is by somehow increasing the surface hydrogen concentration, as a hydrogen transfer species or disordered carbonaceous species might be expected to do. This looks particularly attractive in light of the simultaneous decrease in 1,3-butadiene and increase in 1-butene in the
C₄ fraction, and the increase in ethane selectivity, which are all observed in the same range of polymer loadings. This, however, cannot account for either the fact that essentially all of the increase in ethane comes from ethylene, not acetylene (108,110-112,136-143). The lack of any similar increase in n-butane production could, of course, be caused by the high ethylene/butene ratio preventing butene adsorption and hydrogenation.

The second possibility lies in electronic modification of the Pd, so that acetylene is less strongly adsorbed, or the formation of a species which acts as the actual catalytic site on which acetylene adsorbs and to which it is bound less strongly than to Pd. Because of the very high adsorption strength of acetylene on Pd, any decrease in the strength of adsorption will increase its rate of reaction. This effect has been observed by Abon, et al (571) upon alloying Pd with Ni. The formation of a species having this effect would satisfactorily explain the increased rate of acetylene reaction, and the subsequent hydrogenation of ethylene to ethane (by allowing ethylene to compete with acetylene), provided of course that the strength of ethylene adsorption is not similarly decreased and the strength of acetylene adsorption is decreased enormously. In the case of Abon, et al (571), the formation of a PdNi alloy actually reduced the adsorption strength of ethylene more than acetylene.

The third possibility is that this hypothetical species actually creates, or activates previously existing, sites as it is formed, and that more than one type of site is created or activated in the process. The second site would of course be for only ethylene adsorption and
reaction. A species which simultaneously increases the surface hydrogen concentration around acetylene and provides spillover hydrogen to support sites, where ethylene adsorption and hydrogenation can occur, would fit this model. Anything which caused an increase in the roughness of the Pd surface would in effect create more catalytic sites. Whether some of these would be active only for ethylene adsorption and hydrogenation is unknown.

We believe that the support must be intimately involved in this activation process, regardless of the possibility of hydrogen spillover and alumina catalyzed ethylene hydrogenation. The time necessary for activation over the 0.02 wt% catalyst is some 35 times longer than that over the 0.5 wt% sample (3-5 vs. 170' hours, figure 130). Although we do not know the actual dispersions of the catalyst samples, it would be remarkable - though not impossible - if particle size differences (structure sensitivity) were alone responsible for this large difference in activation time. The maximum rate constants over these two samples are almost identical, and unless a much lower turnover frequency (TOF) on the 0.02 wt% sample has almost completely cancelled out a much larger number of active sites, we would assume that the dispersions are not vastly different.

We have no real idea of what type of support effect might be present. Experiments over 0.5 wt% catalysts supported on a number of aluminas of different surface areas (figure 147-150) do not differ in any pattern that suggests an answer to this question. The activation of a relatively small number of support sites near the Pd-support interface, as has been proposed in a number of different reaction-
catalyst systems (510,511,513,602,603), may be involved somehow, but we do not have the information about Pd dispersions, degrees of metal-support interaction, and/or support acidities that we would need to resolve this support effect.

The rates of activation over our samples of different metal loadings can be compared based on the amount of polymer on the total catalyst pellet in spite of the large changes in Pd/support ratio (a factor of 25 between the 0.5 and 0.2 wt% catalysts). This cannot be explained by any significant support activity, as the rate constants on a per Pd basis are identical at equal polymer loadings, and reach very similar maxima. At equal polymer loadings, where rate constants on a per Pd basis are essentially identical, the total polymer/Pd ratio is much higher on the 0.02 wt% catalyst. The total polymer likewise cannot have any significant activity (which isn't surprising). The paradox is that hydrogenation and polymerization almost certainly depend on the Pd content of a catalyst (they occur on sites that are, or are associated with, Pd). The polymer loading depends on the amount of polymer per total catalyst, which is mostly support (the amount of Pd is not considered in calculating the polymer loading). Yet the rates of polymerization and hydrogenation are dependent on the polymer loading. Something very strange is occurring.

Evacuation at 40°C does not affect the active species to any significant degree; it merely removes volatile paraffinic and olefinic polymers on the support surface. Hydrogen treatment at 300°C for 2 hours removes essentially all of this species (as shown by the low initial activity following this treatment). It is likely that it also
drives off the volatile polymers and removes up to 77% of the insoluble polymeric species (84% total polymer removed, 30% is volatile so 54 out of 70 - 77% - of the insoluble fraction). During subsequent operation, however, both the conversion and the rate constant are significantly higher than during the first reaction at all times and polymer loadings other than the very earliest (figures 155-158). This effect could be related to previously reported activity increases involving β-phase Pd hydride formation-decomposition cycles (see p. 104, or (147,402-407)).

Oxygen-hydrogen treatment must also remove both the active surface species and the volatile polymers. It does not appear to remove very much of the insoluble species on a weight basis (perhaps 34%), although if this species is polyacetylene it is likely that oxygen treatment dehydrogenates it to coke, particularly the polymer molecules that are located on the support, away from Pd. Those near or on the Pd are likely to undergo complete combustion due to attack by atomic oxygen dissociated on the Pd. If the former (degradation of support polymers) did not occur, then we should expect the subsequent hydrogen treatment to remove most of the insoluble polymers, as it did without previous oxygen treatment. Curiously, this oxygen-hydrogen treatment, which must have significantly altered the structure of the hydrocarbons remaining on the catalyst results in conversions and rate constants which are essentially identical to those observed at equal polymer loadings during the initial experiment (figure 158).

The paradox here is that conversions and rate constants appear to depend on the total amount of hydrocarbonaceous species on the surface (figures 157 and 158), even though the structure and composition of
those species must have been radically affected by this treatment. In
the case of hydrogen treatment alone, most, though not all, of the
polymers are removed and the subsequent catalyst activity is enhanced
compared to the initial experiment.

We can also compare these results based on the amount of polymer
formed after the treatments are conducted (figure 167). Using this
diagram, we can see that polymer loading definition, the rate constants following hydrogen and
oxygen-hydrogen treatments are nearly identical, and both are higher
than those observed during the initial experiment. This would suggest
that the active surface is essentially the same after these two
treatments, while the treatments themselves (as in the case of B-phase
hydride formation-induced roughness, p. 369), or the remaining polymer
species (the amount, and probably structure, of which are different
after the two treatments) causes the increase in activity relative to

Figure 167. First order rate constants compared at differential polymer
loadings on a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst following different
treatments. See figure 155, p. 351, for symbol definition.
the first experiment. Of these two possibilities, we conclude the former (increased surface roughness), although such an effect would require relatively large Pd particles initially in order for Pd \rightarrow PdO and/or Pd \rightarrow \beta\text{-phase PdH} transitions to induce lattice deformations capable of significantly increasing the roughness/dispersion. The fact that the different amounts of surface polymer remaining after these two treatments has no effect on the catalyst activity is consistent with the idea that the active surface species is removed by these treatments, while the insoluble polymer (or more correctly, the insoluble polymer residue created by these treatments) located on the support, away from the Pd, plays no real role in the reaction after it is formed.

A similar increase in activity, from an initial rate constant of 0.00169 to 0.00672 mole/mole Pd*min*torr after six batch reactions with oxygen-deuterium treatments (identical to our oxygen-hydrogen treatments) between each reaction, has been reported by Moses, et al (136). After this point, however, they conducted only deuterium treatments between the next 7 reactions and the rate constant decreased to 0.00067 mol/mole Pd*min*torr.

Evacuation at 200-300°C is thankfully easier to interpret. It must remove the volatile species removed by evacuation at 40°C. It probably decomposes and dehydrogenates the insoluble polymers to some form of surface coke. This coke and/or other forms created by thermal dehydrogenation of the active surface species poison(s) the catalyst for all further reactions.

We shall therefore conclude this portion of the discussion with the proposal that catalyst activation is due to the formation of some
surface hydrocarbonaceous species of unknown structure and composition which increases catalyst activity by increasing the surface hydrogen concentration and/or reducing the adsorption strength of acetylene and/or creating/activating new sites over which the reaction takes place, possibly by increasing the roughness of the surface through hydride or carbon phase formation induced Pd lattice deformations. In addition, this species must be intimately related with the catalyst support in order to explain the results we have observed over catalysts of different metal loadings.

We suspect that the total amount of this active species cannot be large compared to the amounts of polyacetylene or volatile polymers. We base this on both the small amount of Pd present (compared to the total polymer), which would be completely covered and poisoned by any significant fraction of the total polymer, and by material balance calculations that show that the volatile and insoluble polymer fractions can account for at least 70-90% of the total. We shall now leave this vexing problem of catalyst activation behind.

We have not yet considered the unusually high activity of the 0.1 wt% catalyst. We might argue that it is higher than the 0.5 wt% sample because of some significantly higher dispersion or to some support activity for the reaction. The apparently low activity of the 0.02 wt% catalyst at 40°C could then be due to our terminating the reaction before complete activation took place. However at 80°C this conclusion is unwarranted (figures 134-137). The 0.02 wt% catalyst was operated until polymer loadings of 400 mg/ml were attained (twice those reached at 40°C) and at this temperature (figure 137) it behaves much as the 0.5
and 0.1 wt% samples did at 40°C (figure 133). In addition, the initial rate constant over the 0.1 wt% catalyst at 80°C is still significantly higher than the maximum observed over the 0.02 wt% sample (3 versus about 2 mole/mole Pd*min*torr).

Experiments conducted with different inlet acetylene concentrations (figures 151-154) indicate that the assumption of first order hydrogen, zero order acetylene is fairly accurate. Therefore the high conversion over the 0.1 wt% sample at 40°C cannot explain the difference in rate constants at that temperature. The Arrhenius plot constructed from experiments over both the 0.1 and 0.02 wt% catalysts at a range of temperatures (figure 146) shows that the 0.1 wt% sample is always more active than the 0.02 wt% while conversions over the 0.1 wt% sample at temperatures higher than 40°C were not unusually high (figures 148 and 150). This is unlikely to be caused by changes in catalyst dispersion, as the 0.1 wt% is also more active than the 0.5 wt% sample (figures 130-133).

We suspect that this difference in rate constants, calculated on a per mole Pd basis, is due to the metal loading of at least one of the catalyst samples differing from the nominal, vendor supplied value. Because the activities of the 0.2 and 0.5 wt% sample appear to be nearly identical (figures 132 and 133), we conclude that it is the 0.1 wt% sample which is in error. In order to correct the rate constant to a value comparable to the other two samples, the actual metal loading of this catalyst must be about 1.5 times higher than reported, or 0.15 wt%. While we have no independent measurements of any of the catalyst metal
loadings, we do not feel that this is an unreasonable correction to assume.

We do not have catalyst dispersions with which to calculate turnover frequencies for comparison with previously published values. We have corrected TOF's reported by Sarkany, et al (143) and Gigola, et al (192) to 1 torr hydrogen pressure (see Appendix C, p. 520). These values range from 0.00384 to 0.0218 at 27°C (143) to 0.000146 to 0.00149 at 25°C (192). The hydrogen pressures used in these two investigations were very different (2 torr in (143), 3420 torr in (192)), and may have contributed to the large spread observed. Assuming an activation energy of 11 kcal/mole, as observed here (figure 146), yields TOF's at 40°C between 0.00826 and 0.047 from (141) and 0.000356 and 0.00363 from (192). Assuming 50% dispersion, TOF's for the 90 m²/g catalysts at 40°C are 0.0127 (k=0.38) over the 0.1 wt% sample and 0.00833 (k=0.25) over the 0.1 and 0.5 wt% samples. Unless the metal dispersions of the catalysts used in this work are very low (< 1%), our rate constants are clearly within the reported range. Comparison with other reported rate constants (table 23, p. 159) leads to an identical conclusion.

Continued operation at 40°C over the 0.5 catalyst leads to a fairly sharp decrease in conversion and rate constant after about 20 hours (figures 130 and 131). With further operation the rate of decrease slows and the catalyst activity appears to be approaching a low, steady value. The 0.1 wt% sample exhibits similar behavior, except that the changes take place after longer periods of time and occur much slower.
Comparison on polymer loading basis shows that the conversions and rate constants of both catalysts decrease sharply at polymer loadings higher than about 600 mg/ml (figure 132). With increasing temperature over the 0.1 wt% catalyst this decrease begins at lower polymer loadings (figure 140). Deactivation is reversible over the 0.5 wt% sample at 40°C upon removing the volatile polymer fraction by evacuation (figures 159-162). This observation rules out the formation of coke, or other nonvolatile reaction sideproducts or poisons as the cause of deactivation (at least at this temperature). Deactivation is not strictly temperature dependent either, as the 0.02 wt% sample does not deactivate immediately at 80°C, while the 0.1 wt% does (figures 134-137).

We propose that deactivation is caused by the build-up of liquid polymer sufficient to cause acetylene pore diffusion limitations. The polymer loading at which diffusion control, and hence deactivation, begins will be determined by a complex set of parameters. These include the rate of the surface reaction (which is temperature, hydrogen pressure, and degree of activation dependent), catalyst metal loading (which in conjunction with the rate of reaction per Pd determines how fast acetylene must be transported into the catalyst pellet), the metal impregnation profile (which determines the length that acetylene must be transported into the pellet and probably effects the polymer location), the mean pore size of the support (which determines the mean free path of acetylene diffusion and the relative effect of adding a unit amount of additional polymer), the actual acetylene pressure in the reactor (which determines the maximum concentration gradient and hence the
maximum rate of diffusion), and the total composition of the gas phase (which may effect the diffusivity of acetylene).

The polymer loading in turn will be dependent on the rate of surface reaction (which is temperature, hydrogen pressure, metal loading, and metal dispersion dependent), the polymer selectivity (which is probably temperature, acetylene pressure, hydrogen/acetylene ratio, metal dispersion, and perhaps support surface area and acidity dependent), the catalyst porosity (which determines the maximum pore volume for polymer accumulation), and the duration of the reaction.

Diffusion should also be dependent on the polymer composition (the distribution between gas phase and surface polymers, and perhaps the distribution of the surface polymer between liquid and solid fractions). At the present time it is unclear if and how this is affected by changes in the various reaction parameters.

Based upon the fact that hydrofluoric acid digestion produced sheets of polymer, rather than the thin chains or small particles that we would expect if they resided in the catalyst pores, and that the removal of only the volatile portion of the surface polymers is sufficient to restore catalyst activity, we conclude that the insoluble polymer does not contribute to pore diffusion effects or deactivation. This is probably because the polymer sheets are porous, or at least not continuous, allowing the smaller reactant acetylene molecules to pass through them in spite of the fact that they apparently reside on the outside of the catalyst pellets. Examination of broken, spent catalysts shows a dark brown polymer layer around the pellet, while the central portions are stained a light greenish-yellow from oil build-up.
The fact that deactivation at 40°C begins at polymer loadings of 600-800 mg/ml over the 0.5 and 0.1 wt% samples (suggesting that the pores are entirely full of a typical hydrocarbon liquid with a density of 0.8 g/ml) is just a coincidence, as deactivation occurs at this temperature at lower loadings over 0.5 wt% samples on different supports (figures 149 and 150), and begins at lower polymer loadings over the 0.1 and 0.02 wt% catalysts at higher temperatures (figures 140 and 141, and 144 and 145, respectively). Evacuation of the 0.5 and 0.02 wt% catalysts shows that the volatile surface polymer accounts for only 30% of the total, and it appears that it is this fraction which causes diffusion limitations. Deactivation would be more accurately related to the catalyst loading of only this polymer fraction. However, we have very little data about the distribution of volatile and solid surface polymer, and no data on how this distribution might change during operation or be affected by changing other reaction parameters (support type, metal loading, hydrogen/acetylene ratio, etc.). Diffusion is likely to begin long before the catalyst pores are completely full of liquid polymer.

We believe that this is a very reasonable, and the most likely, explanation for the deactivation behavior presented in the previous result section. However, this does not guarantee that it is the actual mechanism of deactivation. Because we have no information about catalyst impregnation profiles and only the nominal, vendor supplied values of the other catalyst characteristics (metal loading, support surface area, mean pore size), it is probably impossible for us to completely prove the validity of this proposal. In particular, the
location of the polymer may strongly depend on the Pd distribution in the catalyst pores, and the location of both the polymer and the Pd will greatly affect the calculated acetylene concentration profiles through the catalyst pellets.

We can, however, investigate the internal consistency of it based on experiments conducted on the same catalyst samples under different conditions. During operation over the 0.1 wt% sample at both 70 and 80°C, deactivation appears to begin at the very beginning of the reaction. The rate at these conditions cannot be severely diffusion limited, because the Arrhenius plot for this catalyst (figure 148) fit a fairly straight line ($R^2 = 0.963$) and the slope corresponds to an activation energy of 11.2 kcal/mole. This value is almost identical to the one calculated for reactions over the 0.02 wt% sample (11.2 kcal/mole), and both are well within the previously reported range of generally 10-13 kcal/mole (see table 21, p. 154). At 60°C the rate constant begins to decrease sharply at a polymer loading of about 250 mg/ml, while at 40°C it does not begin until polymer loadings of almost 700 mg/ml.

As mentioned previously, ethane selectivities increased during the period of operation corresponding to polymer loadings up to about 200 mg/ml. Over catalysts where the rate constant remained essentially constant with increasing loadings, ethane selectivities did more or less the same thing. However, they rose sharply at polymer loadings where the rate constant began to decrease. This would be entirely expected if acetylene pore diffusion caused the decrease in activity, for it would allow ethylene to adsorb and react on free surface sites. Deactivation
by any irreversible mechanism would not be expected to increase the ethane selectivity unless the poisoning was itself selective, and would not, of course, be reversible upon evacuation.

Deactivation is also not strictly temperature dependent, at least up to 80°C. 0.1 wt% catalysts deactivate from the very beginning at this temperature, while the 0.02 wt% sample behaves much as the 0.1 and 0.5 wt% catalysts did at 40°C. We only used one catalyst (the 0.02 wt%) at temperatures higher than 80°C. At 120°C this catalyst also deactivated from the beginning of operation. However the ethane selectivity did not increase markedly with this deactivation, as all other samples did at all other conditions. It is therefore possible that some other mechanism of deactivation operates at this temperature. Unfortunately, we did not attempt catalyst evacuation after this experiment to verify if this was the case. At 120°C, coke formation is a more likely, though still not probable, occurrence. The alternative is that acetylene pore diffusion also caused this deactivation, but for some unknown reason the catalysts activity for ethylene hydrogenation was poisoned (ethane selectivities were lower at 120°C than at lower temperatures). We tend to favor the former hypothesis, although we have little data with which to support this choice.

The nearly identical behavior of the two experiments using different inlet acetylene concentrations (figure 154) is also explained very well by diffusion induced deactivation. At the polymer loading where deactivation begins (300 mg/ml) the surface reaction rate will differ by the ratio of hydrogen pressures, while the rate of acetylene diffusion will differ by the ratio of acetylene pressures. As the feed
in both experiments had an identical hydrogen/acetylene ratio, the observed behavior would be expected if our deactivation model is correct. In addition, ethane selectivities increased sharply during both experiments as deactivation began.

The results over 0.5 wt% catalysts supported on different surface area aluminas (figures 147-150) are more difficult to analyze due to the absence of catalyst characterization. Specifically, we have no information about the depth of metal impregnation in each case. We feel it is reasonable to assume that the depth of impregnation on the 4 m²/g sample is higher than on the others, if only because of its low surface area. In this case, the longer distance that acetylene must travel to completely cover the Pd sites would explain the relatively early (on a polymer loading basis) deactivation observed on this catalyst.

The almost identical behavior over the 220 m²/g sample is more difficult to justify. We suspect that it may be due to a combination of a higher metal dispersion, which would increase the total rate of reaction per pellet, and the small pore size, which would cause diffusion at much lower polymer loadings than would larger pores. The difference in pore size between this sample and the 90 m²/g sample, however, is not large (average radius 22 vs. 30 Å, see table 25, p. 174). We also cannot discount the possible effects of different surface polymer distributions (liquid vs. solid) between catalysts on different surface areas aluminas.

We also conducted a reaction over a crushed sample of 0.1 wt% Pd (figures 163 and 164). This crushed catalyst deactivated much more rapidly than the corresponding experiment on whole catalyst pellets.
Ethane selectivities increased much faster as well. We conclude that the crushing operation destroyed most of the catalyst pore volume. One industrial supplier of high surface area alumina has confirmed that this treatment probably did have such an effect (79). As the initial rate of polymer formation was apparently identical (at least judging by gas phase polymer selectivities), we suspect that liquid polymer quickly filled the small amount of available pores and caused the rapid deactivation and ethane selectivity increase.

The models of catalyst activation and deactivation that we have developed fit our data and seem to explain most, if not all of our experimental observations. However, probably the largest single factor preventing a thorough understanding of the acetylene hydrogenation reaction mechanism has been the fact that most researchers have proposed models that satisfactorily explain their own data, but at the same time are only cursorily compared to other investigations. Very often models proposed based on the results of one investigation are practically incompatible with previously published results. We shall now attempt to avoid falling in this trap.

As we have mentioned previously, there are precedents in the literature for our initial catalyst activation. There are more examples which demonstrate a similar activation at constant conversion and increasing ethane selectivities (table 23, p. 159). We are not aware of any investigations conducted over low (≤ 0.5 wt%) Pd loaded catalysts in the absence of CO where at least the rate constant did not increase during operation. The general absence of deactivation over most of these catalysts may be explained by the polymer-deactivation
relationship we have observed here. Table 23 shows the amounts of acetylene reacted per gram catalyst for a series of low loaded samples. The lowest amount reacted where deactivation occurred is about 5 moles; those catalysts which reacted less than 0.2 moles acetylene showed no deactivation.

We can integrate the conversion versus time curves for our experiments (as we did for others to generate table 23), and in conjunction with the acetylene feed rate and reactor catalyst loading, calculate similar values for our experiments. Considering the 90 m²/g alumina supported catalysts at 40°C, the 0.02 wt% sample converted 0.029 moles of acetylene and did not deactivate. Over the 0.1 and 0.5 wt% samples, 0.15 and 0.08 moles had been converted, respectively, when deactivation began. These numbers do not exactly fit the trend of the other data in table 23, but this is not really surprising. The values of moles converted per gram catalyst do not consider the effects of the hydrogen/acetylene ratio (which may increase or decrease surface polymer selectivities and/or change the polymer composition), metal impregnation profiles, pore size distributions, or catalyst pellet porosities. We believe that in light of the number of variables which will affect the final results of a catalyst polymer loading versus activity comparison, the correspondence between our results and those over other low loaded catalysts in table 23 is surprisingly good.

The behavior reported over catalysts of higher metal loadings (≥ 1%) is not so easily compared to our results. Sheridan (70) observed a continuous deactivation and an associated increase in ethane
selectivities during repeated batch reactions over a 9 wt% Pd on pumice catalyst. This can easily be explained by our results.

Bond and Wells (89), however, report an initial increase in ethylene selectivity (from 85 to 95% of the total ethylene and ethane produced) over a 5 mol% Pd on $\alpha$-Al$_2$O$_3$ catalyst, and make no mention of deactivation. Bond, et al (77) had previously observed deactivation to 0.4 times the initial activity during operation on an identical catalyst, but made no mention of changes in product selectivities. After deactivation, ethylene selectivities were constant and high.

Al-Ammar and Webb (110-112) observed continuous catalyst deactivation during batch reactions over 5 wt% Pd on alumina and silica catalysts (see figure 6, p. 30). The ethylene selectivities that they reported during these experiments are almost certainly incorrect (see Appendix B, p. 510), but they do not appear to have decreased as much as we would expect based on our results and those of others conducted over catalysts of lower molecular weight.

One problem is that the catalysts used by Bond and Wells (77,86) and Al-Ammar and Webb (110-112) appear to have deactivated after far too little acetylene had been converted (table 23, p. 159). We might explain this by assuming a much higher polymer selectivity on these catalysts. However, the real problem is if this deactivation had been caused by polymer induced acetylene pore diffusion effects, we would expect ethylene selectivities to have decreased as we have observed them to here. Apparently they did not.

We have not conducted any experiments over catalysts of such high metal loadings; the highest we used were 0.5 wt%. Therefore we do not
know if we could reproduce their results if we tried. However, they may be explained by looking in an entirely different direction.

Sarkany, et al (141) also used Pd-black catalysts for continuous CSTR operation. The feed gas used in this work was 0.29% acetylene, 0.44% hydrogen, balance ethylene. The results that they observed were very different from those they reported during operation with low loaded, supported Pd catalysts. Over 0.04 wt% supported Pd catalysts, they observed nearly constant conversions and increasing ethene selectivities. Deactivation of these supported catalysts was observed only after 120 hours operation at 93°C. Approximately 0.22 moles of acetylene per gram catalyst had been converted at that time.

Pd-black, on the other hand, exhibited low initial ethylene selectivities (20%) which increased during further operation, approaching 40% after 60 hours operation. Product selectivities are not reported after that time, but they do mention that the acetylene conversion had dropped from an initial value of about 75% to 52% after 329 hours operation. 0.15 moles of acetylene per gram Pd-black had been converted during the time that the ethylene selectivity increased, while something like 0.30 moles/g had been converted after 329 hours. The Pd dispersion of this black was estimated (from the BET surface area) as 2.2%.

Margitfalvi, et al (134,135) also studied acetylene hydrogenation over Pd-black. With a feed gas containing 0.29% acetylene and 1.9% hydrogen, they observed a fast initial deactivation. During the first 20 minutes of operation, the rate of acetylene consumption decreased from about $1.6 \times 10^{-5}$ to a steady value of about $2 \times 10^{-6}$ mole/g_cat*sec.
During this period of operation, approximately 0.0108 moles of acetylene per gram Pd-black were converted. At the same time, the selectivity to ethylene, defined as the ratio of ethylene produced over the sum of ethylene plus ethane, increased from an initial value of about 0% to a steady value somewhat higher than 90%. The authors proposed that deactivation was caused by the build-up of carbonaceous residue on the surface, but did not investigate the amounts or composition of the species involved.

We cannot explain the large difference in the time required for deactivation between the investigations of Margitfalvi, et al (134,135) and Sarkany, et al (141). From the data of Sarkany, et al (141) we calculate a reaction rate of about $1.45 \times 10^{-7}$ mole/g-cat*sec at 299 K; this corresponds to a rate constant of 0.00108 mole/mole Pd*min*torr. We cannot calculate the rate constant from the deactivation data of Margitfalvi, et al (134,135), because acetylene and hydrogen pressures are not given. After deactivation, however, rates corresponding to rate constants of 0.000283 mole/mole Pd*min*torr at 273 K are reported; correcting this value to 299 K yields 0.00194. This is somewhat higher than the initial value (0.00108) calculated from the data of Sarkany, et al (141). However, we also have no information about the dispersion of the Pd-black catalyst employed by Margitfalvi, et al (134,135). We conclude that the reason(s) for the very different deactivation behavior between the results of these two investigations is unknown.

The Pd dispersions of the 5 mol or wt% Pd catalysts used by Bond and Wells (86) and Al-Ammar and Webb (110-112) are also unknown. However, as these catalysts have a very high metal loading and are
supported on $\alpha$-Al$_2$O$_3$ (surface area also unknown, but probably fairly low), we believe it would be correct to assume that their dispersions are not very high. Under these conditions, we believe that the apparent correspondence between the behavior observed by these authors over 5 wt% Pd supported catalysts (high and constant, or increasing ethylene selectivities, fairly rapid deactivation compared to low loaded supported catalysts) and the results of at least Margitfalvi, et al (134,135) over Pd-black is meaningful.

If the results of Bond and Wells (86) and Al-Ammar and Webb (110-112) can be explained by the reaction occurring over their catalysts in the same manner as it does over Pd-black, then there are several predictions that we can make about what that behavior must be. Deactivation does not occur by liquid polymers building-up in the catalyst pores. If it did, it would cause acetylene pore diffusion limitations and the selectivity to ethylene would decrease. Similarly, there are no pores as such for polymer to fill and deactivate Pd-black. The deactivation must be caused by some other mechanism. This is not to suggest that liquid polymers cannot be produced by these catalysts. None of the 0.5 wt% Pd catalysts we have found in the literature have been operated long enough to deactivate by this type of polymer build-up (see table 23, p. 159).

Sites which are capable of adsorbing and hydrogenating only ethylene initially exist on Pd-black (141). During continuous operation, these sites are poisoned first, so that the observed selectivity increases. Supported Pd particles this large are very unlikely to undergo any type of electronic or geometric alterations due
to the nature of the support. There seems to be no reason to assume
that they (supported Pd particles of approximately the same dispersion
(< 2%)) should behave any differently.

The cause of Pd-black deactivation is currently unknown. It
obviously cannot be due to polymer induced acetylene pore diffusion
effects, as there are no pores as such. Sarkany, et al (141) concluded
that the deactivation they observed was due to "self-poisoning by
polymer formation". Margitfalvi, et al (134,135) made similar
conclusions. Neither group investigated or speculated about the
composition of this surface species. We might speculate that it differs
from the liquid polymers we have observed, specifically that it is
immobile and not volatile. A similar species will then be responsible
for deactivation of supported Pd catalysts of rather large Pd
crystallite size. Liquid polymer induced transport limitations would
only occur if these catalysts had been used to convert much more
acetylene (table 23, p. 159).

The type of surface species formed, and their subsequent effects
on catalyst activity and selectivity, would therefore be dependent on
the size of the Pd crystallites. During this work, we have used
catalysts of relatively low Pd loadings, which we assume consist of
small Pd particles. Our results are quite compatible with the results
of other investigations on similar, low Pd loaded catalysts. Apparently
the nonvolatile carbonaceous species which poisons Pd-black and
supported catalysts with very large Pd crystallites does not form, or
forms only very slowly, on low loaded, relatively highly dispersed
supported catalysts. Supported catalysts of much higher Pd loadings and
Pd-blacks are assumed to have much larger Pd crystallite sizes, over which this carbonaceous species forms much more rapidly, exhibit very different behavior.

We have little proof for these speculations, but they lead to predictions about the nature of the reaction, particularly the type(s) of polymer species formed, on large Pd particles that can be tested. We suggest that such testing be conducted in the future. In addition, as it is unlikely that the different behaviors that have been reported change abruptly at some specific Pd particle size, investigation of catalysts with intermediate Pd particle sizes (or perhaps intermediate loadings - what is the effect of the support?) should exhibit behavior somewhere between the extremes we have been considering. We believe we may have observed such behavior (see part D. Ethylene Selectivity Decline).

In closing this section we should point out what we believe is a rather important result of this work which some may find surprising. Boudart (155) has championed the use of TOF's to compare catalyst activities observed by different investigators at different conditions. We heartily agree with this idea. However, in a later work Boudart and Djega-Mariadassou (660) perhaps oversimplify the relationship between TOF and the reaction controlling regime. They report that for most catalytic reactions, the TOF is about 1 sec\(^{-1}\). With much lower values, the rate is too slow to be measured or useful, and with much higher values, the rate is too large and becomes influenced by transport limitations (660).
This appears to be the case in almost every conventional reaction. However, we have observed transport limitations on fresh catalysts at rate constants on the order of 0.15 mole/mole Pd$\cdot$min$\cdot$torr. Assuming that the catalyst dispersion is about 50%, this corresponds to a TOF of 0.005 sec$^{-1}$ at 1 torr hydrogen. The hydrogen pressure at this point of operation was about 4 torr. The TOF was therefore about 0.02 sec$^{-1}$. We suggest that those investigating this reaction in the future keep this in mind.
D. Ethylene Selectivity Decline

1. Results

\( \text{SC}_2\text{H}_6 \) (the selectivity to ethane) increased while \( \text{SC}_2\text{H}_4 \) (the selectivity to ethylene) decreased during the course of almost every experiment conducted in this investigation. At 40°C over catalysts supported on 90 m²/g \( \text{Al}_2\text{O}_3 \), the rate of change of both is dependent on the catalyst metal loading (figures 168 and 169). The rate of \( \text{SC}_2\text{H}_6 \) increase over a 0.02 wt% catalyst is very slow, increasing from an initial value of about 5% to only 18% after 150 hours operation (figure 168). There is a rapid initial rise in \( \text{SC}_2\text{H}_6 \) over a 0.1 wt% catalyst which is followed by a period of almost constant values up to about 150 hours time. After this point the rate of increase accelerates somewhat. The behavior of a 0.5 wt% catalyst is considerably more complex. There is an initial rise in \( \text{SC}_2\text{H}_6 \) to values approaching 55%. However, it then

![Graph: Ethane Selectivity vs Time (Hours)]
drops sharply to about 30%. After this minimum it accelerates upward at a rate approaching the initial increase.

\( \text{SC}_2\text{H}_4 \) follows much the same trends (figure 169), although its values are also affected by changes in the total polymer selectivity occurring during the same time periods.

As we have come to expect, the results compared at equal polymer loadings are considerably different (figures 170 and 171). \( \text{SC}_2\text{H}_6 \) increases at low polymer loadings over all catalyst samples. Over the 0.02 wt% sample, this increase continues up to a polymer loading of at least 200 mg/ml, when the experiment was terminated. Over the 0.1 wt% sample, it only continues to a loading of 100 mg/ml. It then remains fairly constant to a loading of about 500 mg/ml, after which it increases almost linearly with additional surface polymer. The 0.5 wt% samples behave much differently. Over this catalyst \( \text{SC}_2\text{H}_6 \) increases steadily at low polymer loadings, going through a broad maximum at about
Figure 170. Ethane selectivities compared at equal polymer loadings during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

Figure 171. Ethylene selectivities compared at equal polymer loadings during operation at 40°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.

300 mg/ml. It then decreases with increasing polymer loading up to 600-700 mg/ml, after which it accelerates upward almost vertically.

Once again, S₉C₂H₄ behaves in much the same way (figure 171),
except that over the 0.02 wt% catalyst it seems to also go through a minimum and maximum. The actual values at these inflection points are more similar (35 and 50%) than those observed over the 0.5 wt% samples (0 and 30%). Over the 0.02 wt% sample these inflections occur at much lower polymer loadings than over the 0.5 wt% catalyst (40 and 100 mg/ml vs. 300 and 600 mg/ml).

During operation at 80°C over the 0.02 wt% catalyst, SC₂H₄ again increases gradually throughout the duration of the experiment (figure 172). Over the 0.1 wt% sample, however, it increases sharply during the first few (8-12) hours time, then increases much more slowly.

![Graph showing ethane selectivity over time for 0.02 and 0.1 wt% catalysts.](image)

Figure 172. Ethane selectivities observed during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃. (Experiments 12 and 25).

SC₂H₄ remains fairly constant over the 0.02 wt% sample, although there is a slight indication that it may have increased somewhat initially (figure 173). Over the 0.1 wt% sample it decreases in a
Figure 173. Ethylene selectivities observed during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃. The mirror image of the increase in SC₂H₆.

Compared at equal polymer loadings, SC₂H₆ increases more gradually over the 0.1 wt% catalyst than it does on a time basis (figure 174).

Figure 174. Ethane selectivities compared at equal polymer loadings during operation at 80°C with catalysts of different metal loading supported on 90 m²/g Al₂O₃.
After this gradual increase up to a polymer loading of about 300 mg/ml, it remains fairly constant to about 500 mg/ml, after which it begins to accelerate upward, very sharply at polymer loadings above 700 mg/ml. Over the 0.02 wt% sample the increase is almost linear up to a polymer loading of 400 mg/ml, where the reaction was terminated.

\( \text{SC}_2\text{H}_4 \) behaves in much the same way, although on a polymer basis the initial increase and maximum over the 0.02 wt% catalyst are more clearly visible than they were on a time basis (figure 175). This catalyst is much more ethylene selective than the 0.1 wt% sample at all polymer loadings other than the very lowest (about 40 mg/ml).

![Ethylene Selectivity Graph]

Figure 175. Ethylene selectivities compared at equal polymer loadings during operation at 80°C with catalysts of different metal loading supported on 90 m²/g \( \text{Al}_2\text{O}_3 \).

The 0.1 wt% catalyst is much less ethane selective at 40°C than at higher temperature (figure 176). \( \text{SC}_2\text{H}_6 \) values are essentially identical at 60, 70, and 80°C until after about 50 hours of operation, when the value at 60°C reaches a fairly steady plateau, while those at the higher
temperatures continue to increase quickly. \( \text{SC}_2\text{H}_4 \) values behave in largely the same way (figure 177).

Figure 176. Ethane selectivities observed during operation at different temperatures with a 0.1 wt% Pd on 90 m\(^2\)/g \( \text{Al}_2\text{O}_3 \) catalysts. (Experiments 8, 10, 11, and 12).

Figure 177. Ethylene selectivities observed during operation at different temperatures with a 0.1 wt% Pd on 90 m\(^2\)/g \( \text{Al}_2\text{O}_3 \) catalysts.

On a polymer loading basis \( \text{SC}_2\text{H}_4 \) behaves somewhat different manner (figure 178).
Ethane Selectivity (%) vs. mg polymer/ml pore volume

40 C
+ 60 C
* 70 C
* 80 C

Figure 178. Ethane selectivities compared at equal polymer loadings during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalysts.

C₂H₄ behaves in much the same way except at loadings less than about 150 mg/ml, where the values at the three lower temperatures are essentially equal and somewhat higher than those at 80°C (figure 179).

Ethylene Selectivity (%) vs. mg polymer/ml pore volume

40 C
+ 60 C
* 70 C
* 80 C

Figure 179. Ethylene selectivities compared at equal polymer loadings during operation at different temperatures with a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalysts.
Over the 0.02 wt% catalyst, $\text{SC}_2\text{H}_6$ behaves very similarly at 40 and 80°C, increasing fairly steadily throughout operation, although the value at 40°C is always lower than at 80°C (figure 180). At 120°C, it begins considerably higher than at the lower temperatures (15-20% vs. about 5%). During further operation, however, it passes through a broad minimum, when it is lower than even the value at 40°C. After about 300 hours operation it accelerates upward.

$\text{SC}_2\text{H}_4$ mirrors these changes in $\text{SC}_2\text{H}_6$ fairly well (figure 181) except at 40°C, where it goes through the early minimum and maximum that we have seen previously (figure 179). Values at 120°C are always higher than at the lower temperatures due to the considerably lower values of the total polymer selectivity observed at this temperature (figures 45 and 46, pp. 221-222).

![Graph](image)

Figure 180. Ethane selectivities observed during operation at different temperatures with a 0.02 wt% Pd on 90 m$^2$/g $\text{Al}_2\text{O}_3$ catalysts. (Experiments 21, 25, and 26).
Figure 181. Ethylene selectivities observed during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalysts.

Comparison at equal polymer loadings shows much the same behavior, although at 80°C SC₂H₆ is always lower (figure 182) while SC₂H₄ is always higher (figure 183) than at 60°C. The sharp increase in SC₂H₆ and decrease in SC₂H₄ at 120°C take place at a loading of about 750 mg/ml.

Figure 182. Ethane selectivities compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalysts.
Figure 183. Ethylene selectivities compared at equal polymer loadings during operation at different temperatures with a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalysts.

The time dependent behavior of both Sc₂H₆ and Sc₂H₄ over 0.5 wt% catalysts at 40°C is strongly affected by the surface area of the alumina support (figures 184 and 185). Both selectivities behave very

Figure 184. Ethane selectivities observed during operation at 40°C over 0.5 wt% Pd on Al₂O₃ supports of different surface areas. (Experiments 1, 3, 6, and 7).
Figure 185. Ethylene selectivities observed during operation at 40°C over 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

Similarly over the 33 and 90 m²/g catalysts (we have previously seen the latter, figures 168 and 169). Over the 4 and 220 m²/g samples, however, S₃C₂H₂ increases sharply and S₃C₂H₄ decreases sharply until after about 15-20 hours time, when values over the 4 m²/g catalyst change much slower, while those over the 220 m²/g sample continue their rapid changes.

Compared at equal polymer loadings, S₃C₂H₂ over the 90 m²/g sample is always less than or equal to the values over the 33 m²/g catalyst (figure 186). In addition, over the 33 m²/g sample it increases rapidly at lower polymer loadings (650 mg/ml) than over the 90 m²/g catalyst (700 mg/ml). The values over the 4 and 220 m²/g samples are always lower than over the other two samples, although unlike the comparison on a time basis, the 220 m²/g catalyst is less ethane selective at low polymer loadings and the difference at high polymer loadings is not as great as the difference on a time basis after about 20 hours operation (figure 184).
Figure 186. Ethane selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on Al₂O₃ supports of different surface areas.

Sc₂H₄ values (figure 187) again generally mirror the behavior of Sc₂H₆, except at very low polymer loadings (less than 100 mg/ml).

A 0.5 wt% Pd on 33 m²/g Al₂O₃ with an inlet acetylene concentration

Figure 187. Ethylene selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on Al₂O₃ supports of different surface areas.
of 1.05% is initially much less ethane selective than an identical catalyst sample with 0.35% acetylene (figure 188). However after 30 hours continuous operation, $\text{SC}_2\text{H}_4$ with 1.05% acetylene increases rapidly to values higher than with 0.35%, where the increase is more gradual.

![Ethane Selectivity Graph](image)

**Figure 188.** Ethane selectivities observed during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ supports catalyst with different inlet acetylene concentrations. (Experiments 3 and 4).

Values of $\text{SC}_2\text{H}_4$ behave in much the same way (figure 189). They are also always negative (net ethylene consumption) during operation with 0.35% inlet acetylene.

On a polymer loading basis (figures 190 and 191), both $\text{SC}_2\text{H}_6$ and $\text{SC}_2\text{H}_4$ behave in almost exactly the same way in each case, despite the different inlet acetylene concentrations, although $\text{SC}_2\text{H}_6$ is always higher and $\text{SC}_2\text{H}_4$ always lower with the lower feed concentration (0.35%).

$\text{SC}_2\text{H}_6$ values over a 0.02 wt% on 90 m²/g Al₂O₃ are identical during the very early stages of reaction on the initial sample and after both
Figure 189. Ethylene selectivities observed during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ supports catalyst with different inlet acetylene concentrations.

Figure 190. Ethane selectivities compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ supports catalyst with different inlet acetylene concentrations.

hydrogen and oxygen-hydrogen treatments (figure 192). Values following the hydrogen and oxygen-hydrogen treatments, however, increase much more rapidly than during the initial experiment. Evacuation actually
increases $S_{C_2H_4}$ compared to its value when the initial reaction was terminated (for the details of these treatments see p. 231).

Figure 191. Ethylene selectivities compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ supports catalyst with different inlet acetylene concentrations.

Figure 192. Ethane selectivities observed during operation at 40°C over a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 21). 2. Same sample after 90 hours evacuation (Exp. 22). 3. Same sample after hydrogen treatment (Exp. 23). 4. Same sample after oxygen-hydrogen treatment (Exp. 24).
$\text{SC}_2\text{H}_4$ values (figure 193) behave somewhat differently after these treatments due to changes in the total polymer selectivity that differed from treatment to treatment. These differences occurred largely during the first 25 hours of operation, and after this point $\text{SC}_2\text{H}_4$ behaves in much the same way as $\text{SC}_2\text{H}_6$, except that the slope of subsequent changes is somewhat reduced compared to changes in $\text{SC}_2\text{H}_6$. This difference is again largely due to changes in the total polymer selectivity.

![Figure 193. Ethylene selectivities observed during operation at 40°C over a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 192 for symbol definition.](image)

As we have previously seen with catalyst activity, and polymer selectivities and compositions, comparison of these experiments at equal polymer loadings is somewhat different from the previous ones in this section. Both hydrogen and oxygen-hydrogen treatments reduce $\text{SC}_2\text{H}_6$ to essentially the same value initially observed during the first experiment (figure 194). Compared at equal polymer loadings, $\text{SC}_2\text{H}_6$ immediately after hydrogen treatment is exactly equal to the value
observed during the first run. Immediately after oxygen-hydrogen treatment it is actually lower than the value observed at the same loading in the first experiment. The first increments of added surface polymer increase \( \text{SC}_{2}\text{H}_6 \) following hydrogen treatment much more than during the first experiment or after oxygen-hydrogen treatment, and the value after hydrogen treatment remains higher than these two at all higher polymer loadings. Evacuation causes an increase in \( \text{SC}_{2}\text{H}_6 \) compared to equal polymer loadings during the initial experiment.

![Graph](Image)

**Figure 194.** Ethane selectivities compared at equal polymer loadings during operation at 40°C over a 0.02 wt% Pd on 90 m²/g \( \text{Al}_2\text{O}_3 \) catalyst. See figure 192 for symbol definition.

\( \text{SC}_{2}\text{H}_4 \) values after these treatments are considerably more complicated (figure 195). Although oxygen treatment sharply lowers \( \text{SC}_{2}\text{H}_4 \), \( \text{SC}_{2}\text{H}_4 \) is also decreased due to the high rate of polymer formation following this treatment. Hydrogen treatment, which also lowered \( \text{SC}_{2}\text{H}_6 \), increases \( \text{SC}_{2}\text{H}_4 \) relative to equal polymer loadings during the initial experiment. During continued surface polymer accumulation, \( \text{SC}_{2}\text{H}_4 \) is
always higher during the first experiment, although the initial behavior during the first run and following hydrogen treatment look very similar. Evacuation causes a large decrease in $\text{Sc}_2\text{H}_4$; the values observed immediately following this treatment are the lowest observed at any time during this series of experiments.

![Graph](image)

Figure 195. Ethylene selectivities compared at equal polymer loadings during operation at $40^\circ\text{C}$ over a 0.02 wt% Pd on 90 m$^2$/g Al$_2$O$_3$ catalyst. See figure 192 for symbol definition.

Evacuation of a 0.5 wt% Pd on 90 m$^2$/g Al$_2$O$_3$ catalyst which had a polymer loading of about 700 mg/ml (the details of this treatment are given on p. 238) lowers $\text{Sc}_2\text{H}_4$ relative to the final value observed before evacuation (figure 196), but not relative to the initial value during the first experiment. During continued operation after this evacuation, $\text{Sc}_2\text{H}_4$ increases continuously, while it went through a broad maximum and minimum during the first run. $\text{Sc}_2\text{H}_4$ behaves in much the same way (figure 197), although initial values are essentially equal in this case.
Figure 196. Ethane selectivities observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2. Same sample after 72 hours evacuation at 40°C (Exp. 28).

Figure 197. Ethylene selectivities observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 196 for symbol definition.

Comparison on a polymer loading basis shows that this evacuation has actually lowered SC₂H₆ relative to equal polymer loadings during the initial experiment (figure 198). Further polymer addition, however,
causes $\text{SC}_2\text{H}_4$ to increase sharply at lower polymer loadings after evacuation than during the first run. The polymer loadings at which this sharp increase occurs are, however, fairly similar in each case.

![Graph showing Ethane Selectivity (%) vs. mg polymer/ml pore volume](image)

**Figure 198.** Ethane selectivities compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 196 for symbol definition.

$\text{SC}_2\text{H}_4$ values behave in almost the exact opposite way (figure 199). Evacuation increases $\text{SC}_2\text{H}_4$ to a value somewhat higher than that observed at equal polymer loadings during the initial experiment. It then decreases with additional surface polymer at lower polymer loadings than it did during the first run.

As mentioned previously, we also conducted an experiment on a sample of 0.1 wt% Pd on 90 m²/g Al₂O₃ which had been crushed to 40-60 mesh. We did this in order to test for possible pore diffusion effects as the cause for the observed selectivity changes. In traditional catalysis, the selectivity to the intermediate species $B$ in a reaction scheme $A \rightarrow B \rightarrow C$ will be markedly decreased by pore diffusion...
limitations on the rate of reaction of species A.

Over this crushed sample $\text{SC}_2\text{H}_6$ increased much more rapidly then it did over the whole catalyst pellets (figure 200). In addition, it reached a maximum value of about 90% and then decreased with further operation. The final values over each catalyst sample appear to be approaching the same limit, even though it takes much longer to increase to that value over the whole pellets, while over the crushed sample it actually decreases to get there.

$\text{SC}_2\text{H}_6$ behaved in an exactly mirror image way (figure 201), as over the whole pellets it took 200 hours to decrease to a limiting value of about 0% (no net change in ethylene), while over the crushed sample it decreased rapidly to about -30% and then increased slowly to an apparent limit of nearly 0%. Because of the small particle size of the crushed sample, it was not placed in the TGA balance pan, so comparisons
on a polymer loading basis cannot be made. We should note that because surface polymer formation was not measured during the experiment on the crushed samples, $S_{C_2H_4}$ values shown here are actually the sum of the
surface polymer selectivity and $\text{SC}_2\text{H}_4$. Initial ethylene selectivities are therefore somewhat lower than they appear in figure 201. However, by the time the catalyst approaches the limiting value of $\text{SC}_2\text{H}_4$, the polymer selectivity is probably less than 1–2%, so these later values are essentially correct.
D. Ethylene Selectivity Decline

2. Discussion

In a previous section (IV A, the Formation of Polymer, p. 211), we demonstrated that at the reaction conditions employed (40-120°C, 1 atm total pressure, 1% inlet acetylene, and inlet hydrogen/acetylene = 1.7), neither surface nor gas phase polymer selectivities are negligible. We concluded that had we ignored the formation of either polymer phase, the calculated ethylene selectivities would have been incorrect. Figures 202-205 show values of $S_{C_2H_4}$ as: 1) we have calculated them, 2) what we would have calculated ignoring surface polymer, and 3) what we would have calculated ignoring all polymer formation.

Most previous investigations of acetylene hydrogenation that have observed a decrease in $S_{C_2H_4}$ have been conducted over 0.04 wt% Pd on various alumina supports generally with about 0.3% inlet acetylene and hydrogen/acetylene ratios close to 1.5 (89,108,132,136-144,190,229). In addition, most of these were conducted with ethylene/acetylene ratios so high that the rate of ethylene production and/or consumption could not be accurately measured; $S_{C_2H_4}$ was calculated as the difference of 100% and the sum of all other product selectivities, as we have done in this work. These catalysts have rarely been operated long enough to deactivate; the reaction was usually terminated after $S_{C_2H_4}$ and $S_{C_2H_6}$ reached apparent steady states.

While we did not test any catalysts with 0.04 wt% Pd loadings, we feel that our 0.02 wt% catalyst operated with 0.91% inlet acetylene (experiment 21) should be a fairly close approximation. $S_{C_2H_4}$ values calculated ignoring surface polymer formation are not very different
Figure 202. Ethylene selectivities calculated during operation at 40°C over a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. As we have defined them. 2. Ignoring surface polymer formation. 3. Ignoring all polymer formation. (Experiment 21).

from those including it after about 50 hours of operation (figure 220). Prior to this time, however, values calculated ignoring surface polymers decrease from an initial value of about 80% to 60% in a very short time. Values calculated including surface polymers also drop sharply initially, but the magnitude of this change is less (50 to 38%) and they then rise to about the initial value. $S_{C_2H_4}$ values calculated ignoring all polymer formation bear very little resemblance to the actual case. Figure 203 shows these same $S_{C_2H_4}$ values on a polymer loading basis, where the initial changes have been expanded and are clearer.

We do not maintain that surface polymer selectivities are always this high. The reaction variables that affect surface polymer formation are poorly understood. However, only one investigation that observed a decline in $S_{C_2H_4}$ investigated the formation of surface polymer in any way (141), and although they concluded that it was negligible, it is
conceivable that it really was higher than they believed it to be (p. 80). It is certainly possible that polymer formation was significant during other investigations that did not consider it, so the \( S_{\text{C}_2\text{H}_4} \) values that were reported in these works should be considered suspect (89,108,136-140,142-144,229). \( S_{\text{C}_2\text{H}_4} \) values reported during one of these investigations (132), which failed to include even the gas phase polymers, must be considered completely wrong.

The 0.02 wt% catalyst was only operated to polymer loadings of about 200 mg/ml at this temperature. We therefore also include identical values calculated for operation at 40°C over the 0.1 wt% catalyst, which was operated to the higher polymer loadings where catalyst deactivation occurred (figures 204 and 205). These show that at high polymer loadings, ignoring the surface polymer selectivity, which decreases throughout operation, does not result in a very large error in
Figure 204. Ethylene selectivities calculated during operation at 40°C over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. As we have defined them. 2. Ignoring surface polymer formation. 3. Ignoring all polymer formation. (Experiment 8).

Figure 205. Ethylene selectivities calculated at equal polymer loadings during operation at 40°C over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. As we have defined them. 2. Ignoring surface polymer formation. 3. Ignoring all polymer formation. (Experiment 8).

$\text{SC}_2\text{H}_4$. Ignoring gas phase polymer selectivities, however, will continue to yield $\text{SC}_2\text{H}_4$ values that are far higher than the actual ones. Gas
phase polymer selectivities decrease very slowly, if at all, and must always be included.

With this comparison completed, we now turn to a discussion of our results, and the reaction mechanisms which might explain them. Because \( S_{\text{C}_2\text{H}_4} \) values are defined as the difference of 100% and the sum of all other product selectivities, we shall mainly focus on the behavior of \( S_{\text{C}_2\text{H}_6} \). This was chosen for several reasons. The first is that although we are confident that all other product selectivities have been included in this calculation, values of \( S_{\text{C}_2\text{H}_4} \) include the sum of the experimental error from the measurement and calculation of all other product selectivities. This means that although each of the other selectivities may display only small deviations from linear or smoothly curving behavior, the sum of these deviations may impart seriously inaccurate fluctuations to the calculated values of \( S_{\text{C}_2\text{H}_4} \). Of course there are many instances where the apparent deviations in the behavior of other product selectivities are not minor. This makes interpreting the trends in \( S_{\text{C}_2\text{H}_4} \) that much harder.

The second reason relates more fundamentally to the reaction mechanism that we are attempting to understand. Previous investigations which used carbon 13 and/or 14 labeled species have shown that, at least in the lack of acetylene pore diffusion effects, observed increases in \( S_{\text{C}_2\text{H}_6} \) come only from an increase in the reaction rate of ethylene \((89,108,110-112,133-143)\). This is a very important factor in considering the actual reaction mechanism. In the absence of labeling, we can be confident that ethylene reaction has occurred only in cases where the value of \( S_{\text{C}_2\text{H}_4} \) is negative (net ethylene consumption). Under
any other circumstances, a decrease in $\text{SC}_2\text{H}_4$, and the associated increase in $\text{SC}_2\text{H}_6$, could arise simply from a higher percentage of acetylene being converted to ethane.

As explained previously (p. 172), we planned to conduct experiments with $^{12}\text{C}$ labeled ethylene in order to measure the relative amounts of ethane that were produced directly from acetylene and from the adsorption and hydrogenation of ethylene. For reasons beyond our control, some of the equipment necessary to do this was not available. In absence of the data from such experiments, we must decide how best to treat our data.

The highest selectivity value for ethane produced directly from acetylene (the so-called intrinsic selectivity to ethane) at full surface acetylene coverage over supported Pd catalysts that we have been able to locate in the literature is 17.5% (143). More typical values are 2-5% (89,108,110-112,133-143). Under conditions where the surface acetylene coverage is less than complete, higher intrinsic ethane selectivities have been observed (133-135). We should point out that in these cases, the authors did not conclude that the acetylene surface coverage was low because the rate of reaction was acetylene pore diffusion controlled. These experiments were conducted on Pd-black catalysts and at very low acetylene pressures. They concluded that at these pressures, the ethylene/acetylene ratio was high enough, and the absolute pressure of acetylene low enough, that the thermodynamics of the adsorption process controlled the acetylene surface coverage. We know of no such observations on supported Pd catalysts, as it appears
that acetylene pore diffusion limitations always occur before such low acetylene pressures are reached.

This difference is crucial. In the absence of pore diffusion effects, we shall assume an intrinsic ethane selectivity of 5% at all times over all catalysts. Sarkany, et al (143) have observed a decrease in the intrinsic ethane selectivity with decreasing Pd particle size (increasing dispersion), and that of course may have occurred in some of our experiments. However, this decrease is not large (from 17.5% at d = about 6%, to 8.2% at d = about 45%, to 3.8% at d = about 60%), and we have no information about our catalyst dispersions anyway. We believe that when acetylene pore diffusion control begins, only a limited number of surface sites will be at less than full acetylene coverage. Before diffusion control begins, the acetylene pressure must be high enough to ensure complete coverage on every site. As diffusion limitations increase, sites furthest from the pellet surface will be first available for ethylene adsorption, as the acetylene concentration will decrease into the pellet. All sites closer to the surface than the point where the acetylene pressure has dropped below the critical value will still experience full acetylene coverage. Therefore, although we suspect that the intrinsic ethane selectivity increases when diffusion effects become rate controlling, we do not believe this increase will be large, and we shall use a value of 5% as an approximation at all times.

Further support for this conclusion can be found in the behavior of the polymer selectivities under diffusion limited conditions (see IV A, the Formation of Polymer, p. 211). Values of the total polymer selectivity do not decrease markedly when diffusion control begins, as
we would expect if most of the surface sites are less than completely covered by acetylene.

With these background assumptions clearly described, let us now consider the changes in ethane and ethylene selectivities.

We have proposed in the previous discussion that some type of surface species, which is responsible for the observed catalyst activation, is formed during the initial stages of operation lasting up to polymer loadings of about 200 mg/ml. We have also proposed that on a polymer loading basis, \( \text{SC}_2\text{H}_4 \) decreases sharply and \( \text{SC}_2\text{H}_6 \) increases sharply at the point where acetylene pore diffusion limitations begin.

Over the 0.02 wt% Pd catalysts supported on 90 m²/g Al₂O₃ at 40°C, \( \text{SC}_2\text{H}_6 \) increases steadily throughout the duration of the experiment (figure 168). Over the 0.1 wt% catalyst it increased sharply for the first 15–20 hours of operation, and then increased more gradually until the reaction was terminated. The behavior of \( \text{SC}_2\text{H}_6 \) over the 0.5 wt% catalyst is very different. It also increases very sharply during initial operation (the first 8–10 hours). After this point, however, it begins to decrease at nearly the same rate as the previously increase. After about 30 hours there is another inflection point, and \( \text{SC}_2\text{H}_4 \) increases very sharply again. The values of \( \text{SC}_2\text{H}_4 \) observed over the three catalyst types are always 0.5 > 0.1 > 0.02.

Compared on a polymer loading basis, a very different picture emerges (figure 170). At low polymer loadings (up to about 200 mg/ml), \( \text{SC}_2\text{H}_6 \) increases over all three catalyst types, and is essentially equal over the 0.1 and 0.5 wt% samples, while over the 0.02 wt% catalyst it is slightly lower. With increasing polymer loadings, however, the value
over the 0.1 wt% catalyst levels off and remains fairly constant up to polymer loadings of about 500 mg/ml, after which it begins increasing again. Over the 0.02 wt% sample, it appears that it was increasing to higher values than over the 0.1 wt% when the experiment was terminated; we do not know if this trend would have continued. The 0.5 wt% catalyst behaves very differently. Here $SC_2H_4$ increases at loadings higher than 200 mg/ml and passes through a broad maximum at around 300 mg/ml. With increasing polymer loadings, it decreases substantially until a rapid, nearly vertical increase begins at around 700 mg/ml.

From these data alone, we can conclude that ethylene hydrogenation does not occur on any large fraction of the alumina support. If it did, $SC_2H_6$ should increase with decreasing metal loading - as the alumina/Pd ratio increases. It is very hard to justify a mechanism of hydrogen spillover induced alumina activity when ethane selectivitys are generally highest over the sample of the highest metal loading (lowest alumina/Pd ratio). Further support for this conclusion may be found from a comparison of $SC_2H_4$ values over 0.5 wt% Pd catalysts on the 33 and 90 m²/g aluminas (figures 184 and 186). Here, $SC_2H_4$ over the 90 m²/g sample is always lower than over the 33 m²/g sample, on both a time and polymer loading basis.

This does not necessarily rule out the existence of some small number of active alumina sites located in the region of the alumina-Pd interface. However, the number of these sites must be small, and probably cannot account for the increase in ethane production.

Assuming that the intrinsic ethane selectivity is about 5% at all times on the 90 m²/g catalysts, we can compare the relative rates of
both acetylene and ethylene during these experiments. If the intrinsic ethane selectivity is 5%, then the rate of ethylene hydrogenation over the rate of acetylene consumption is \( SC_2H_6 \) minus five. \( SC_2H_6 \) is defined as the rate of ethane production over the rate of acetylene consumption, and we have assumed that the rate of ethane production from acetylene only over the rate of acetylene consumption is 5%. Since the remaining ethane must come from ethylene, the rate of ethylene hydrogenation over the rate of acetylene consumption is that given above: \( SC_2H_6 \) minus five.

We can also compare the actual rates of ethylene and acetylene consumption through the use of a modified ethylene conversion. Let us define this conversion as the rate of ethylene production over the rate of acetylene into the reactor. As the acetylene conversion is defined as the rate of acetylene consumption over the inlet rate of acetylene, this ethylene conversion is simply the product of the ratio of rates (\( SC_2H_6 \) minus five) and the acetylene conversion. In other terms this is \( (\frac{rC_2H_6}{r_0})(\frac{rC_2H_4}{rC_2H_2}) = \frac{rC_2H_4}{r_0} \), where \( r_0 \) is the inlet acetylene rate.

From this comparison, several interesting features emerge. Over the 0.5 wt% sample, the acetylene conversion increases initially, as previously seen (figure 206). The relative rate of ethylene reaction (defined as % \( C_2H_4 \) reaction in figure 206), which is simply the observed \( SC_2H_6 \) minus five, behaves exactly as \( SC_2H_6 \) does, except that it begins to increase at somewhat higher polymer loadings than does \( SC_2H_6 \) (\( SC_2H_6 \) is initially about 5%). The ethylene conversion also increases initially, as we would suspect from the increasing values of \( SC_2H_6 \).

The surprising thing is that the modified conversion of ethylene, which is a measure of the absolute rate of ethylene hydrogenation,
Figure 206. Acetylene and ethylene conversions as functions of surface polymer loadings during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst.

begins to decrease at lower polymer loadings than does the acetylene conversion; it actually continues to decrease even after the acetylene decrease has begun. Sc₂H₆ only increases at polymer loadings above 700 mg/ml because up to that point, the rate of ethylene hydrogenation is decreasing faster than the rate of acetylene, and even after that point it only increases because the rate of acetylene is decreasing faster than the rate of ethylene. The important point is that if our assumptions are correct, something quite different from acetylene pore diffusion limitations is also occurring here.

There are a number of possible explanations for this behavior, ranging from the trivial to the profound. The most obvious solution to this surprising result is that our assumption of a constant intrinsic selectivity is wrong, or if it is constant, we have chosen the wrong value. First let us consider the case of a constant value other that
5%. If the correct value is 0% (no ethane from acetylene), then the % \( \text{C}_2\text{H}_4 \) reaction curve in figure 224 will be identical to the \( \text{SC}_2\text{H}_6 \) curve in figure 170. As these two curves are already almost identical (they differ only by the subtracted 5%), the \( \text{C}_2\text{H}_4 \) conversion will be changed only slightly. This will raise the entire curve, but will not change the initial increase or the subsequent decrease. The lowest \( \text{SC}_2\text{H}_6 \) values observed during this experiment were about 5%. As \( \text{SC}_2\text{H}_6 \) cannot be negative (ethane consumption does not occur), a constant intrinsic \( \text{SC}_2\text{H}_6 \) cannot be higher than 5%. Therefore, if the intrinsic ethane selectivity is constant, we will have the same \( \text{C}_2\text{H}_4 \) conversion behavior.

Next we consider a constant intrinsic ethane selectivity up to the point that acetylene pore diffusion control occurs, after which time it increases. This is equivalent to less than surface coverage of acetylene caused by diffusional limitations, and to some extent it is probably correct. In this case, the % \( \text{C}_2\text{H}_4 \) reaction curve will be identical up to polymer loadings of about 600-700 mg/ml (depending on where we choose to say diffusion control begins). As relatively more ethane will be produced from acetylene after this point, less must come from ethylene. The result is that both the % \( \text{C}_2\text{H}_4 \) reaction and the \( \text{C}_2\text{H}_4 \) conversion will be lower than they are in figure 206. This in turn implies that the catalyst activity for ethylene has decreased even more than the rather surprisingly large amount we have previously calculated.

Suppose now that the intrinsic ethane selectivity changes throughout the experiment. Based on the results of previous investigations, it most likely decreases during opération. As the initial ethane selectivity is 5%, it could not be any higher than this
initially, and unless there is an inflection point (increase then decrease), this will yield similar results. $C_2H_4$ conversion will decrease at polymer loadings higher than 400–450 mg/ml.

Over a series of alumina supported 0.04 wt% Pd catalysts, Sarkany, et al (141) reported changes in intrinsic ethane selectivities during operation. These ranged from 4.7% at 9.5 hours to 3.3% after 92 hours with a $\gamma$-Al$_2$O$_3$ support, through 1.9% at 6.5 hours, 4.8% at 43 hours, to 2.9% at 95 hours with an ICI-38-1 catalyst, to a fairly constant value of about 1.3% with an $\alpha$-Al$_2$O$_3$ support. These results suggest that large changes in intrinsic ethane selectivities do not occur. However, we could eliminate this ethylene conversion behavior by assuming that all ethane comes from acetylene prior to diffusion control, but mostly from ethylene once surface sites become available. While we cannot disprove this suggestion with our own data, it does appear highly unlikely in light of previous investigations (108,110–112,134–143). We conclude that this behavior is real and not an artifact of our previous assumptions.

The next possibility is one we have not considered previously. It is also more subtle and, on the surface at least, more difficult to disprove. This hypothesis is that deactivation is caused not by pore diffusion effects, but by liquid diffusion effects. By this we mean that the rate decreases when the entire catalytic surface becomes covered with a layer of liquid polymers. The decrease in rate would be caused by the much lower diffusivities in liquids as opposed to gasses. The rate of ethylene hydrogenation would decrease before the rate of acetylene because acetylene can compete with the liquid more effectively.
(due to its higher adsorption strength). Once even acetylene could not compete anymore, and both acetylene and ethylene have to diffuse through the liquid layer, the rate of ethylene hydrogenation will be much higher than the rate of acetylene due to ethylene's much larger concentration gradient. This in turn could cause the observed increase in ethane selectivities.

On the surface, this is a very reasonable hypothesis, and would explain almost all of our deactivation behavior at least as well as would pore diffusion. We can begin to test the likelihood that this is occurring by considering the amount of liquid polymer present in relation to the catalyst surface area. The ethane selectivity increases markedly at a polymer loading of about 700 mg/ml. We have previously shown that the surface polymer was composed of about 30% volatile liquids. The loading of these liquids is therefore 210 mg/ml. Assuming a liquid density of 0.75 g/ml, we have about 0.28 ml polymer/ml pore volume. The catalyst porosity is 0.35 ml/g. The polymer loading is then about 0.1 ml/g. One gram of catalyst has a surface area of 90 m². This is equivalent to 9 X 10⁵ cm²/g. 0.1 ml is 0.1 cm², the average thickness of the liquid polymer film would be 0.1/(9 X 10⁵) = 1.1 X 10⁻⁷ cm (11 Å) if the liquid were distributed evenly across the surface.

This is not enough liquid to completely choke off the catalyst pores (mean radius = 30 Å), although we might still expect some strong pore diffusion limitations. Because we do not have any information about the location of the Pd or the liquid polymer in the catalyst pellets, it does not appear that we can decide which of these possible mechanisms of deactivation is actually occurring from these data alone.
This point is important because diffusion through a liquid layer removes the apparently anomalous behavior of the ethylene conversion just prior to deactivation; pore diffusion does not.

Sarkany, et al (141) observed no changes in catalyst activity or product selectivities after the addition of squalane or hexadecane up to loadings of 185 mg/gcat. Assuming that their unreported catalyst porosity is about 0.35 ml/g, this represents a loading of about 0.69 ml/ml catalyst pore volume. They too did not have any information about the location of this liquid in the catalyst pellets, but concluded that no liquid film diffusional effects occurred. We cannot completely explain why this loading of perhaps 0.69 ml/ml had no effect on their catalyst activity, while a loading of 0.28 ml/ml did cause deactivation of ours. We suspect it is related to the large difference in metal loadings (0.04 vs. 0.5 wt%). Over our higher Pd loaded catalyst, the depth of impregnation may be greater and the total reaction rate per pellet will definitely be higher. The former will causes a larger distance for diffusion, while the latter increases the rate at which acetylene must diffuse into the pellets. In addition, our operation was conducted at a higher temperature (40 vs. 26°C).

After the reaction over the 0.5 wt% catalyst (figure 206) was terminated, the reactor system was evacuated until no further weight loss was observed in a 24 hour period. This required 72 hours and removed 28.6% of the surface polymer initially present. We have previously shown that this evacuation caused an increase in both the acetylene conversion and the first order rate constant (figures 161 and 162, pp. 355 and 356). In this section we have shown that this
treatment also decreased $\text{SC}_2\text{H}_6$ to a value somewhat lower than that observed before diffusion began (figures 198), while it increased $\text{SC}_2\text{H}_4$ to a value somewhat higher than before (figure 199).

We have calculated modified ethylene conversions (as defined earlier) from the data in this experiment, again assuming that the intrinsic ethane selectivity is constant at 5% (figure 207). It is apparent that only the acetylene conversion deactivation is reversible upon removal of the liquid polymer; immediately after evacuation the ethylene conversion is actually slightly lower than it was when the first reaction was terminated. We have also presented the results from these two experiments as a function of total reaction time (figure 208). In this scheme, evacuation was conducted at 40 hours and the second reaction begins immediately afterwards (at 40 hours reaction time).

Here the disparate effects of evacuation are more clearly visible. While
evacuation causes very little change in the ethylene conversion, the
acetylene conversion is increased to essentially the same values
observed before deactivation.

Figure 208. Acetylene and ethylene conversions as functions of total
reaction time during operation at 40°C with a 0.5 wt% Pd on 90 m²/g Al₂O₃
catalyst. 1. Initial sample after standard pretreatment (Exp. 27). 2.
Same sample after 72 hours evacuation at 40°C (Exp. 28).

Acetylene conversion deactivation is reversible. This must be
cased by the physical presence of the liquid polymer which is removed
by evacuation. Because of the absence of catalyst characterization and
information about the location of the polymer we cannot completely
determine whether this deactivation is caused by pore diffusion
limitations or liquid film diffusion limitations. Either case will
explain the data we have observed. The deactivation of ethylene
hydrogenation sites is fundamentally different. It cannot be caused by
the presence of the liquid polymer fraction, as the presence or absence
of this liquid has no effect on it.
From our data alone, we can make no firm hypothesis about the cause of this ethylene hydrogenation deactivation. However, based upon the results of other investigations on Pd-black (134,135,141) and 5 wt% Pd supported catalysts (77,86,110-112), we propose that this deactivation is identical to the early increase in ethylene selectivity that is often observed on these large Pd particles. This has been proposed as due to carbonaceous deposit formation on the "ethylene only" sites that are present initially on Pd-black. While our acetylene conversion is not greatly affected by the cause of the ethylene deactivation, we believe deactivation would have occurred had this catalyst were operated for longer periods of time. Of course, we would not see it because the liquid polymer has already caused severe transport limitations long before this point. On large Pd particles, irreversible deactivation takes place much faster compared to the buildup of liquid polymer. This appears to be some demented form of structure sensitivity. We predict that if these catalysts with large Pd particle sizes (5 wt% Pd or Pd-black) were operated for much longer periods of time after the activity and selectivity had reached an apparent steady state, further deactivation by liquid polymer-induced transport limitations would be observed.

Over the 0.1 wt% catalyst, which probably has a higher metal dispersion than the 0.5 wt% we have been considering, deactivation of the acetylene conversion occurs in the same way - by liquid polymer buildup (figure 209). In this case, ethylene conversions actually increase somewhat as acetylene deactivation begins (as we would expect in the absence of special ethylene site poisoning) and later decrease to
a much smaller extent. We suspect that the absence of the non-diffusion ethylene deactivation is due to a smaller Pd particle size distribution on this catalyst (compared to the 0.5 wt% sample).

![Diagram](image)

Figure 209. Acetylene and ethylene conversions as functions of surface polymer loadings during operation at 40°C over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst.

A similar comparison between the reaction over whole catalyst pellets and a crushed sample illustrates the difference in behavior between acetylene and ethylene conversions (figures 210 and 211). It is apparent that although the catalyst crushing operation has greatly reduced the time necessary for acetylene deactivation to occur, ethylene conversions are relatively unaffected. This seems to be clear evidence that at least on this catalyst type at this temperature (40°C), acetylene conversion deactivation occurs by pore diffusion limitations.

If diffusion through a liquid film caused the decrease in acetylene conversion, it should have also caused a decrease in ethylene conversion. This arises because of the large difference in pressure between ethylene and acetylene (>10:1). When acetylene is pore
Figure 210. Acetylene and ethylene conversions observed during operation at 40°C over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Whole catalyst pellets (Exp. 8). 2. Crushed pellets (Exp 9).

Figure 211. Acetylene and ethylene conversions observed during operation at 40°C over a 0.1 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Whole catalyst pellets (Exp. 8). 2. Crushed pellets (Exp 9).

diffusion limited, a much greater concentration gradient allows ethylene to continue reacting at the same rate (or even at an increased rate as more surface sites become available). The greater concentration
gradient of ethylene would also allow it to react faster than acetylene under liquid film diffusion controlling conditions, but its rate would be much smaller than if there was no polymer film.

Here too we can observe the difference between this catalyst and the 0.5 wt% sample. Over the latter, ethylene activity is irreversibly poisoned (it decreases during operation and cannot be restored by evacuation), while no decrease is observed on the former. Again, we suspect this is due to different particle size distributions.

The role that acetylene pressure plays in this behavior has been investigated over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with inlet acetylene concentrations of 0.35 and 1.05% (figure 212 and 213).

![Conversion (%)](image)

**Figure 212.** Acetylene and ethylene conversions compared at equal polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g Al₂O₃ catalyst with 1.05% inlet acetylene. (Experiment 3).

Although the overall trends are nearly identical, comparison of the actual values of acetylene and ethylene conversions shows that with the lower acetylene pressure, substantially more ethylene conversion occurs than with the higher pressure. Assuming that the intrinsic ethane
selectivity has not changed, which prior investigations would support
(138,141), this may be due to competition between acetylene and ethylene
for surface sites.

![Conversion Graph]

Figure 213. Acetylene and ethylene conversions compared at equal
polymer loadings during operation at 40°C over a 0.5 wt% Pd on 33 m²/g
Al₂O₃ catalyst with 0.35% inlet acetylene. (Experiment 4).

"Acetylene only" sites appear to be just - only acetylene adsorbs
and reacts in the absence of acetylene pore diffusion control (full
surface acetylene coverage). "Ethylene only" sites, however, may simply
be sites on which the relative strengths of acetylene and ethylene
adsorption are similar. The large excess of ethylene over acetylene
would then make them de facto "ethylene only" sites. We believe that
this is the most likely explanation for the increase in ethylene
conversion relative to acetylene conversion with decreasing acetylene
pressure. Sarkany, et al (141) measured intrinsic selectivities with a
feed gas of 0.29% acetylene (compared to 0.35% in our low pressure
experiment) and observed intrinsic ethane selectivities on the order of
1-5%. We do not believe an increase in the amount of acetylene forming ethane explains the difference in overall selectivities between these experiments.

There seems to be a slight decrease in the % C₂H₄ reaction with 1.05% inlet acetylene (figure 212) which may be related to the larger one observed over the 90 m²/g sample, above. This difference is rather small, though, and is absent at 0.35% (figure 213). It is not clear if a similar poisoning of ethylene hydrogenation sites is occurring on these catalysts. Unlike the 90 m²/g catalyst, the acetylene conversion decreases gradually between 400 and 600 mg/ml polymer loading, before ethane selectivities increase sharply and deactivation by pore diffusion limitations has definitely begun. In principle, we could compare the relative acetylene and ethylene activities using rate constants. In order to do this, however, we must have a suitable form for the ethylene rate expression, and it is not at all clear that we do.

The acetylene conversion activity using these different acetylene concentrations is modeled fairly well by a zero order acetylene, first order hydrogen rate expression (figure 154, p. 350). The close correspondence between ethane selectivities observed with 0.35 and 1.05% acetylene (figure 190, p. 408) would suggest that the ethylene reaction is also first order in hydrogen. If ethane selectivities are somewhat higher with 0.35% acetylene (vs. 1.05%) because of competition between ethylene and acetylene for "ethylene only" sites, this implies a negative acetylene dependence for the rate of ethylene hydrogenation. While we do not feel that this is unreasonable, we do not have enough data to accurately calculate what that dependence is.
In contrast with evacuation of a 0.5 wt% catalyst with a polymer loading of 700 mg/ml (figures 196–199, 204, and 205), evacuation of a 0.02 wt% sample with only 200 mg/ml polymer has very little effect (figures 192–195). We have seen previously that this causes no real change in the catalyst activity for acetylene consumption (figures 155–158). A similar situation is observed here. \( \text{SC}_2\text{H}_6 \) at the end of the initial experiment was about 25%. Immediately after evacuation a value of about 34% was observed, and it quickly increased to about 38%. This is very different than evacuation at high polymer loadings, after deactivation has begun. It is possible that on this catalyst, the liquid polymer actually poisons some ethylene only sites long before high polymer loadings are achieved, but this is the only example of such an effect that we have.

The important point here is that it is not the presence of a specific type of liquid polymer which causes the increase in ethane selectivities or the deactivation observed at high polymer loadings. Instead it is the physical presence of enough liquid to cause diffusional limitations on the rate of acetylene transport to the active sites.

Hydrogen and oxygen-hydrogen treatments both initially restore ethane selectivities to their original low values. During further operation, \( \text{SC}_2\text{H}_6 \) over the hydrogen treated sample increases faster than over the oxygen-hydrogen treated one. After about 50 hours of operation, however, this order is reversed. Ethylene selectivities are increased by hydrogen treatment. After oxygen-hydrogen treatment they
are perhaps surprisingly low. This is caused by the high polymer selectivities observed after this treatment (figures 62, p. 235).

Both McGown, et al (108) and Moses, et al (136) observed that hydrogen treatments (of the kind we have used here) had no effect on product selectivities during batch reactions where ethylene selectivities decreased from reaction to reaction. Moses, et al (136), however, observed that oxygen-hydrogen treatments (also of the kind we have used here) did restore the ethylene selectivity to its original high value. The discrepancy between their work and our results is quite puzzling.

We have previously calculated (table 23, p. 159) that these catalysts were used to convert no more than 0.00012 (108) and 0.0040 (136) moles of acetylene per gram of catalyst. Under our operating conditions, the catalyst had converted about 0.029 moles per gram catalyst. The hydrogen/acetylene ratios used in these works were 2:1 (108,136); we used 1.7. We would not expect their catalysts to have a higher polymer loading than ours (200 mg/ml) under these conditions. If they did, this might explain the differences observed, as perhaps our hydrogen treatment would not have restored the selectivities if we had started at a higher polymer loading. In the absence of any other data about the polymer loadings of their samples, we must conclude that we cannot explain this difference: with our catalyst, hydrogen treatment was at least as effective as oxygen-hydrogen treatment in restoring the catalyst to its original form, if not more so. McGown, et al (108) and Moses, et al (136) observed no effect of hydrogen treatment, while the
latter group observed a beneficial effect with oxygen-hydrogen treatment ($\text{SC}_2\text{H}_4$ increased).

The differences that we observed between these treatments can be more easily seen when we compare them at equal differential polymer loadings (only considering polymer formed after the treatment, see figure 167, p. 374). Here it is clear that although the ethane selectivity is initially lower after oxygen-hydrogen treatment (figure 214), at differential polymer loadings higher than about 50 mg/ml, they are lower on the hydrogen treated sample. Ethylene selectivities, meanwhile, are lower after oxygen treatment (figure 215) due to the high polymer selectivity observed after it.

Selectivity changes on the 0.5 wt% Pd catalysts of different surface areas (figures 184-187) can be easily explained by acetylene pore diffusion limitations in conjunction with their activity behavior.
Figure 215. Ethylene selectivities compared at equal differential polymer loadings during operation at 40°C on a 0.02 wt% Pd on 90 m²/g Al₂O₃ catalyst. See figure 192, p. 409, for symbol definition.

In the absence of any catalyst characterization, these will not be considered further here. Similarly, changes in selectivity with temperature over the 0.1 wt% catalyst (figures 176-179) are complicated by diffusion control throughout the reactions at 70 and 80°C.

Temperature dependent selectivity changes over the 0.02 wt% are not so easy to explain or dismiss (figures 180-184). At 120°C the ethane selectivity hardly changed at all up to polymer loadings of almost 800 mg/ml (figure 182). At the lower temperatures they increased from initially lower values to sharply higher ones. These trends cannot be explained by diffusion, which at higher temperatures (increased surface reaction rates) should cause changes at lower polymer loadings. Because the behavior at 40 and 80°C is rather similar, we suspect some temperature related phenomenon caused the difference at 120°C. Specifically, this catalyst deactivated throughout operation (figures
142-145, p. 342), yet the ethane selectivity did not increase until after almost 250 hours operation (figure 180). We will only suggest that perhaps this case is indicative of both irreversible deactivation by carbonaceous deposits, and, after a much longer time, deactivation by volatile liquid polymers (which would cause the increase in $S_{C_2H_6}$ observed at loadings above 700 mg/ml (figure 182)), as we have suggested might occur over larger Pd particles at lower temperatures. It is conceivable that some nonnegligible amount of coke formed at this temperature, causing the continual deactivation at constant ethane selectivity. This too should be investigated in the future.

In closing this section, we should note that in light of the nearly constant total polymer selectivities during operation described previously (see the Formation of Polymer, p. 211), if previous observations that the intrinsic selectivity to ethane remains fairly constant (and low) is correct, then intrinsic ethylene selectivities (the percentage of acetylene reacting to form ethylene, regardless of whether that ethylene subsequently readsorbs and hydrogenates) also remains essentially constant throughout the duration of an experiment.

This suggests that the product distribution from the reaction between acetylene and hydrogen hardly changes during continuous operation. Had we ignored surface polymer formation, we would have calculated an initial decrease in the intrinsic ethylene selectivity (due to the actual decrease in surface polymer selectivity). In at least one previous investigation (141), initially increasing values of $S_{C_4}$, led to exactly this conclusion. We would instead propose that the total polymer selectivity was essentially constant and the increase in
SC₄⁺ was a result of the decreasing surface polymer selectivity. The intrinsic ethylene selectivity therefore probably did not change. Despite these nearly constant acetylene selectivities, very large changes in the total (overall) ethylene and ethane selectivities may be observed due to the simultaneous hydrogenation of ethylene.
V. CONCLUSIONS

We have shown that surface polymer formation during acetylene hydrogenation is not negligible; initially it can account for more than 20-30% of the acetylene consumed and is composed of two fractions. One is removed by long term (3-4 days) evacuation or solvent extraction in hydrocarbon solvents. The other is solid and insoluble, and can be largely removed by higher temperature evacuation, hydrogen treatment, or oxygen-hydrogen treatment. The liquid fraction accounts for about 30% of the total, and is largely composed of normal paraffins, branched paraffins and linear and branched mono- and di-olefins of even carbon number. Most are C_{10} to C_{16}. The solid, insoluble surface polymer phase has not been completely identified, but the information we do have is consistent with the existence of polyacetylenes of carbon number somewhat greater than 24.

When the liquid portion of this polymer accumulates to a sufficient extent in the catalyst pores, it causes diffusion limitations on the rate of acetylene arrival at the catalyst active sites. Under these conditions, the acetylene reaction rate decreases and the selectivity to ethane increases due to ethylene hydrogenation on the vacant sites. This deactivation is reversible upon removal of the liquid polymer fraction while the solid polymer phase appears to have no effect on the catalyst activity or selectivity.

The catalyst activity increases during initial operation, and during the same period the catalyst selectivity to ethane increases. This occurs independent of the increase in ethane selectivity observed during deactivation and is only reversible by higher temperature (200-
300°C) hydrogen or oxygen-hydrogen treatments, which do not remove all of the surface polymer present but do restore both the catalyst activity and product selectivities to near their original values.

Comparison of our results with those of previous investigations which monitored the individual reaction pathways with carbon 13 and/or 14 labeling suggest that the product distribution from acetylene is relatively constant at 40-50% polymer (gas phase and surface), 5% ethane, and 45-55% ethylene throughout the course of an experiment. The initial decrease in surface polymer selectivity is closely matched by an associated increase in gas phase polymer selectivity, while the increase in ethane selectivity is largely due to an increasing activity for ethylene hydrogenation. In some cases over a 0.5 wt% Pd catalyst, the catalyst activity for ethylene hydrogenation was being irreversibly poisoned prior to the liquid polymer induced deactivation. The catalyst activity for acetylene hydrogenation was not permanently affected by this poisoning, and could be restored by removing the liquid polymer. The ethylene activity could not.

Based upon these and other results and their comparison with the great body of previously published investigations relating to the adsorption and hydrogenation of acetylene on Pd catalysts, we propose the following model of Pd catalyzed selective acetylene hydrogenation.

The reaction takes place over a surface hydrocarbon complex which is formed on the catalyst Pd during the initial stages of operation. Based upon the observation that the reaction behaves very differently when ethylene, rather than acetylene, is exposed to a clean catalyst first (103,107,136), we believe that this is not disordered carbonaceous
deposits, but some type of ordered surface structure. The rate of reaction increases during this period because this structure increases the surface hydrogen concentration and/or acetylene bonds less strongly to it than to clean Pd. Sites capable of adsorbing and hydrogenating ethylene even in the presence of sufficient amounts of acetylene to terminate it on fresh catalysts are created during this surface complex formation. The data suggest that this second site is equally capable of adsorbing acetylene (the relative strengths of adsorption of ethylene and acetylene are comparable), but is monopolized by ethylene due to its large excess in the reactor.

The rate of this complex formation decreases with the catalyst Pd loading, although the maximum activities on a Pd basis of a number of samples of different Pd loadings are comparable. Although we have no information on the dispersion of our catalyst samples, we believe that dispersion probably increases with decreasing metal loading. The lower rate of complex formation with decreasing loading is therefore a form of structure sensitivity. The maximum reaction rate is not very structure sensitive, if at all, but the time necessary to reach this maximum is. If dispersion does not increase with decreasing metal loading, then the rate of this complex formation must be somehow dependent on the metal loading. It is difficult to imagine what this dependency might be.

Continued operation leads to deactivation by two different mechanisms. A nonvolatile hydrocarbon residue, possibly some form of coke, builds up on the surface. This species initially forms on ethylene hydrogenation sites, as these are poisoned earlier than acetylene sites, and the observed ethylene selectivity increases. This
poisoning is only reversible upon oxidation and/or reduction at elevated temperatures. We propose that the dissociative adsorption of ethylene and perhaps acetylene lead to the formation of this poisoning species. Dissociative adsorption should be favored by large Pd particles, and we would therefore expect them to deactivate relatively faster than small particles, on which dissociation should be much lower.

At the same time, liquid hydrocarbons formed from the polymerization/oligomerization of acetylene accumulate in the catalyst pores, eventually causing the reaction rate to become acetylene pore diffusion limited. This reduces the acetylene surface coverage and allows ethylene to adsorb and react on these sites; the observed ethylene selectivity decreases. This deactivation and the associated decrease in ethylene selectivity are reversible upon the removal of the liquid polymer fraction.

Which of these deactivation processes occurs first is dependent on the Pd particle size. Pd-blacks (134,135,141) and 5 wt% Pd on alumina (77,86,110-112) deactivate fairly quickly, but the ethylene selectivity remains high. In some cases, the original ethylene selectivity is low but increases during continued operation. We propose that these effects are due to the first mechanism of deactivation. Strongly adsorbed, probably dehydrogenated surface species form from dissociated adsorbed species and cover ethylene sites first. With further operation, acetylene sites are poisoned as well. There is a limit to the extent of this deactivation, as stable activities and selectivities can be achieved after these changes (134,135,77,86,110-112).
We know of no studies which continued operation of this type of catalyst for very long periods of time, but we predict that if this were done, at some point liquid polymer, sufficient to cause diffusional deactivation and an increase in ethane selectivity, would accumulate in the catalyst pores (supported samples) or on the metal surface (Pd-blacks). It is of course possible that the formation of liquid polymer does not occur or only occurs to a very small extent over these large Pd particles. To our knowledge this has not been investigated before. However, our results, which show a slight increase in surface polymer formation with increasing metal loading, suggest otherwise.

Over supported catalysts with low Pd loadings (< 0.1 wt%), the situation is somewhat different. The rate of liquid polymer formation is much faster than the rate of surface poisoning due to a decrease in the relative amount of dissociative adsorption; pore diffusion limitations cause catalyst deactivation before irreversible poisoning is observed. Over catalysts of intermediate loadings, both modes of deactivation occur in the same time span. The activity for ethylene hydrogenation of a 0.5 wt% catalyst was poisoned prior to diffusional limitations on the rate of acetylene hydrogenation. The latter was reversed upon removing the liquid polymer; the former was not.

This behavior is most likely due to particle size differences with changes in metal loading. Specifically we suspect decreasing particle size with decreasing metal loading. Both changes in the surface geometry of the deposited Pd and electronic modification of these small Pd particles by the support probably occur. We have no direct evidence
for this loading-dispersion relationship, but if it does not occur, there are serious problems confronting us.

The Pd is certainly the active species on these catalysts. Alumina does not catalyze the hydrogen or polymerization of acetylene to any measurable degree at these conditions. In addition, maximum activities over a series of catalysts of different metal loading are comparable on a Pd basis and do not change in any way suggesting any significant alumina activity. However, if structure sensitivity (changing Pd particle size) is not responsible for the observed changes in the duration of activation and the mode of deactivation, then the Pd/alumina ratio must be. It is difficult to imagine how two Pd crystals otherwise alike could "know" what the Pd/alumina ratio of their parent catalyst is and so act accordingly.

Polymer formation occurs largely during one surface residence time and is terminated by hydrogenation. We propose that it takes place in regions of relatively low hydrogen concentrations. In this mechanism, the polymer selectivity should be very sensitive to the hydrogen/acetylene ratio, specifically decreasing as the latter increases. We have found one report (194) claiming to have observed such an effect, but it provides no details of the observation. Other studies have shown a decrease in the selectivity to gas phase polymers with increasing hydrogen/acetylene ratios (37, 70, 109), and it seems reasonable to assume that the surface polymer selectivity should affected the same way.

Polymers probably form because of the geometry of the catalytic surface. We conceive of bonds forming between closely adsorbed
acetylene molecules in the absence of hydrogen. The product
distribution, specifically the absence of large amounts of aromatic
material, argue against polymerization by a free radical mechanism (67).
Polymerization does not require dissociatively adsorbed species (which
requires multiple surface sites), as the polymer selectivity is not very
sensitive to the Pd particle size; dissociation should be. Dispersion
only affects polymerization by decreasing the number of acetylene
molecules adsorbed closely together.

The initial polymer product is 1,3-butadiene. This may desorb,
undergo hydrogenation to a butene, or add another acetylene to form
adsorbed 1,3,5-hexatriene, which then faces the same possibilities.
Once butadiene desorption or butene formation and desorption occurs,
there is little chance of their being readsoberd and reacting further to
form either butane or a higher polymeric species, at least before
acetylene diffusion control begins. We believe a similar situation
holds for higher molecular weight species.

Once a polyacetylene molecule desorbs from the surface, it too
apparently leaves the reaction cycle. The presence or absence of these
does not appear to affect subsequent behavior to any measurable extent.
They appear to reside on the outside of the catalyst particles, but do
not contribute to diffusional limitations. We believe this occurs
because they are relatively porous, at least compared to the alumina
pores filling with liquid polymer.

There are a number of alternative mechanisms would might also
explain our results. Al-Ammar and Webb (110-112) have proposed a model
whereby an adsorbed hydrocarbon species acts as the primary hydrogen
transfer species for hydrogenation. In addition, their adsorption studies show that independent sites are responsible for ethylene versus acetylene hydrogenation; there is no competitive adsorption. The nearly complete monopolization of reaction by acetylene is therefore due to almost complete hydrogen occlusion away from ethylene sites.

This hypothesis could explain the increasing ethylene selectivities we have observed if we can find some way to provide for the initial hydrogen occlusion away from the ethylene sites and then provide a mechanism for their gradual activation during operation. The existence of separate sites on a fresh Pd catalyst might be due to the exposure of different crystal faces on which one compound or the other cannot adsorb. Once given the existence of these different types of sites it is difficult to reconcile the almost complete occlusion of hydrogen away from those which adsorb only ethylene.

Sites capable of adsorbing and hydrogenating only ethylene certainly exist initially on Pd-black (141), but there is no evidence that the selectivity of these catalysts is not due to competitive adsorption; the majority of sites can adsorb and hydrogenate either ethylene or acetylene. Whether these "ethylene only" sites exist at all times or are formed during the initial hydrocarbon adsorption is not known. We honestly cannot relate all of the experimental data of Al-Ammar and Webb (110-112) with any mechanism which includes the behavior that we and others in similar studies have observed without concluding that there really is no basis for comparison between the two. As no one else has ever conducted many of the adsorption studies they have, it
would seem a prudent choice to see if this behavior is indeed reproducible.

Guczi, Weiss, and various co-workers (138-142) have proposed a mechanism similar to the one we have chosen, except that acetylene reaction takes place directly on the Pd and ethylene hydrogenation sites are the alumina support, activated by hydrogen spillover. We have no real problem with the former. Our surface complex could exist around the active sites and increase activity by increasing the surface hydrogen concentration and/or reducing the strength of the Pd-acetylene bond. The latter is more difficult to reconcile with our results.

We observed a lower relative rate of ethylene hydrogenation with decreasing Pd loading, which presumably represents metal particle size. Hydrogen spillover should occur faster on smaller Pd particles (larger Pd-support interface), which would lead to the opposite behavior. If this ethylene hydrogenation takes place on a large fraction of the support, it should also be very sensitive to the support type and to the metal loading. The former was not observed here, while the latter trend was in the wrong direction (ethane selectivity decreased with decreasing Pd metal loading).

Alumina catalyzed ethylene hydrogenation could still be consistent with our results if only a small number of sites at or near the Pd-alumina interface were involved, but it would seem that the rate of reaction over these sites must be extremely high in order for the rate of ethylene hydrogenation to be a significant fraction of the acetylene rate, catalyzed by Pd. While we cannot disprove ethylene hydrogenation on the alumina support, we feel that these problems with this mechanism,
in conjunction with the observation that ethylene only sites exist on clean Pd-black (141) make this spillover induced alumina activity unnecessary. In their latest investigation (143), these authors observed a decrease in ethane selectivity with increasing dispersion, and concluded that the relative rates of acetylene and ethylene hydrogenation are controlled by the catalyst particle size, not spillover to alumina.

Although many of the basic parts of this mechanism are speculation, we believe that this mechanism is most capable of explaining the great body of work that has previously appeared. It also makes some very definite predictions about behavior which has not yet been investigated, but could be without too much difficulty. These include the relationship between dispersion and polymer formation (the mechanism of deactivation) and the continuity of behavior as the Pd particle size changes. We shall detail methods of confirming or disproving it in the following section.

This mechanism also provides a basis for improving selective acetylene hydrogenation catalysts. Except at very high hydrogen/acetylene ratios, where apparently very little polymer is formed (659), it is the formation of polymer which poses the largest single problem in this reaction. The polymer represents acetylene that could have been ethylene and is responsible for deactivation. The use of low metal loadings is desirable because they are capable of storing relatively more polymer, on a Pd basis, before deactivation begins. In addition, the rate of acetylene diffusion into any catalyst pellet decreases with the same. If it were not for capital equipment
expenditures, an infinitely low metal loading would be most desirable. In practice, there will be a trade off between the advantages of low dispersion and the increased cost of building larger reactor. Current commercial catalysts suggest this limit is 0.02–0.04 wt% Pd.

Eggshell, or peripheral, metal deposition is also beneficial, as this decreases the length of pores through which acetylene must diffuse in order to reach an active site.

Further improvements must come at the expense of lowered polymer selectivities. If polymer formation arises from the dimerization of two neighboring adsorbed acetylene molecules, anything which isolates active Pd sites will decrease it. Increasing dispersion and alloying the Pd with an inactive metal will both produce this results. This would appear to be the most fruitful path to follow.

A more complicated problem is optimization of the hydrogen/acetylene ratio. It is likely that polymer selectivities are rather strongly affected by the value of this ratio, specifically decreasing as it is increased. However, it is not clear whether this decrease in polymer selectivity will be effectively nullified by the simultaneous increase in the surface reaction rate. If the polymer selectivity is only decreased slightly by an increase in hydrogen/acetylene ratio, the reaction might become pore diffusion limited earlier due to the higher rate of surface reaction. Such an effect occurred with increasing temperature in this study; the polymer selectivity decreased with increasing temperature, but not enough to offset the increase in surface rate. The addition of lead, sulphur, boron, or phosphorus, which poison ethylene only sites and/or reduce the
rate of the surface reaction (31,33,36,180,572), in combination with increasing hydrogen/acetylene ratios, which decrease polymer formation, should also be advantageous.

The optimal catalyst would appear to be one of high dispersion, relatively high(er) surface hydrogen concentration, and low surface reaction rate. High dispersion will minimize dissociative adsorption and the irreversible deactivation associated with it. It also should decrease the activity for ethylene hydrogenation, by lowering the number of ethylene only sites, and decrease polymer formation by isolating adsorbed species from one another. The higher surface hydrogen concentration should terminate the polymerization reaction relatively early, before high(er) molecular weight species are formed. The reduced surface rate will minimize the acetylene pressure at which pore diffusion control begins.

In light of the improvements which we believe could be made in the selectivity and lifetime of selective hydrogenation catalysts, we do not believe that the addition of CO is particularly desirable. This causes continuous deactivation from the start of reaction, and in addition may increase the surface polymer selectivity by decreasing the surface hydrogen concentration.
VI. RECOMMENDATIONS

A. Selective Acetylene Hydrogenation

We have observed surface polymer selectivities much higher than anyone previously thought possible. We believe that it is a real phenomenon and not an artifact of any kind. However, such a belief can never be proven and we therefore feel that it is very important that this behavior be reinvestigated and either confirmed or refuted.

Probably the most important question relating to the mechanism of polymer formation is the composition of the insoluble, solid surface polymer fraction. The limited evidence we have is consistent with the existence of polyacetylene. However, polyacetylene has never been reported during acetylene hydrogenation, or indeed on any Pd(0) catalyst. There are a number of techniques (p. 62) that have been successfully used to identify polyacetylene. Unfortunately, we did not have access to any of them. It is unclear to us whether these techniques could be used on the entire catalyst sample without interference from other species or the catalyst itself. If they can, the question of whether polyacetylene is formed can be answered fairly easily. If not, the catalyst pellet may be digested in hydrofluoric acid, as we have done. Care should be taken not to place too many catalyst pellets in the acid at one time, as the process liberates a great deal of heat. We have found that adding one to two 1/8" pellets at a time to about 20 ml of acid will avoid overheating the solution. The polymer may be separated from the acid solution and collected by pouring the solution through filter paper and washing with water.
This procedure leaves the insoluble species apparently intact, but we do not know if it causes any chemical changes. If it does and the identification of the digestion product is inconclusive, further studies of the temperature dependence and products of the thermal degradation in vacuo, hydrogen, or oxygen may shed more light on it.

Regardless of whether the existence of polyacetylene is confirmed, we believe that there are a number of variables which may affect the polymer selectivity that should be investigated in more detail than we have done.

We believe that the hydrogen/acetylene ratio may be the most important parameter affecting both the selectivity to and composition of the polymer formed. The magnitude of this effect, however, is presently unknown. We used only one hydrogen/acetylene ratio throughout this work, and can make no predictions about its extent. Experiments designed to measure this dependency can be rather easily carried out in a reactor system similar to the one we have used. There are specific ways we believe the operation of such a system could be improved, and we will address them in the following section.

Another important question is how the polymer composition changes both during operation and with changes in other reaction parameters such as the hydrogen/acetylene ratio and/or the Pd dispersion. This too can be achieved fairly easily provided that an integrated GC/MS system is available on a continuous basis. A more detailed analysis of both the gas phase polymers of carbon 6 and higher and the soluble liquid polymer should provide a great deal of information about the nature of the surface reaction.
The catalyst Pd dispersion apparently has a large effect on both the duration of activation and the mode of deactivation. Smaller effects on the polymer selectivity and the rate of ethylene hydrogenation are also consistent with our results. We recommend a similar study on a series of well characterized catalysts to investigate these structure sensitivities in more detail. We have no information on the dispersion of our catalysts, and so even though our results are consistent with an increase in dispersion with decreasing metal loading, this remains an unsupported hypothesis which should be tested. It is not very easy to measure the dispersion of very low loaded Pd catalysts, but it has been done (127-131,143,192). We recommend that the range of dispersion used be very large.

We also have very little data about possible support effects, as most of our best data was gathered on one type of support only. This was complicated by the complete lack of catalyst characterization. A thorough study using well characterized catalysts on a range of support surface areas and acidities should be conducted.

We believe that these recommended experiments could answer the significant questions about the mechanism of Pd catalyzed acetylene hydrogenation that still remain.
B. The Combined TGA Reactor System

The TGA reactor system which we have employed has only been reported on one other occasion, rather recently in the literature (254). We believe that the results obtained with it are largely accurate, but there are several areas in which it could be improved.

The largest single problem is the possibility of diffusion up into the large TGA dead volume (see part III C, p. 195). This could theoretically be minimized by increasing the flow rate of helium into the reactor. This, however, will decrease the residence time and require higher catalyst loadings. These in turn may be limited by the capacity of the TGA balance. A more effective method may be using the TGA as the only reactor inlet and putting a small orifice over the top of the catalyst hang-down tube (figure 25, p. 179). This orifice will prevent diffusion into the TGA.

There are problems with this method. The volume of the TGA dead space is huge (2100 cc) and would require a very long initial unsteady state if operated as we have. We would recommend the use of a single tank of gas mixture which can be used to rapidly fill up the entire system (bypassing the flow controllers) after evacuation and immediately prior to operation. Alternatively, flow controllers with very large ranges of flow could be employed with separate feed gas supplies, but this would reduce their accuracy at the normal low flows of operation. Low flow rate controllers (like ours) would require a very long time to fill the system from either vacuum or only He if the TGA volume is included.
A more complicated, though perhaps better, alteration in our system would be to actually reduce the volume of the TGA. The dead space really is just that; dead space. The use of hang-down tubes of smaller diameter and the total redesign of the TGA cover could probably reduce the dead volume to something on the order of several hundred cc's. Both hang-down tubes could be used for gas flow, circulating the reaction mixture through the entire TGA. Diffusional problems would then be eliminated. A system of this design could also be used for batch reactions.

Another possible source of error was the noise caused by the very long hang-down wire on the catalyst side of the TGA. We used a long reactor U-tube in order to ensure that the gas mixture had reached reaction temperature by the time it reached the catalyst. A better solution would be to use a relatively long circular spiral around the actual hang-down tube, leading into it at the bottom. The length of hang-down wire and the size of the reactor oven could therefore be reduced.

The wide (1") opening at the top of the TGA hang-down tube allowed the wire a wide range of motion. At the same time, the much narrower (12 mm) U-tube restricted the motion of the catalyst pan. This made it very difficult to position the U-tube so that the pan was not resting against its side. Just before this report was written, we modified this set-up for use in conjunction with experiments on 1,3-butadiene hydrogenation going on in our lab (658). Specifically, we anchored about 3 inches of 6 mm glass through a 1-1/2 inch stainless steel washer, sealing the connection with high vacuum epoxy. Next, we placed
this glass tube down into the hangdown tube, with the washer resting on the inside body of the TGA. The washer-TGA connection was sealed with vacuum grease. The hang-down wire was threaded through this tube and connected to the pan in the usual way. This eliminated much of the TGA noise by restricting the range of motion of the top of the wire, and apparently prevented diffusion into the TGA by increasing the linear flow rate through this tube (6 mm vs. 1").

With any of these modifications, we feel that this TGA reactor system could be effectively used for further studies of both acetylene hydrogenation and other reactions involving the possible formation of significant amounts of nonvolatile surface species.
VII. REFERENCES

3. Chem. Week, 142(1,2), 1988, p. 45.
12. Oil & Gas J., 86(37), 1988, p. 34.
20. Leaversuch, R., Mod. Plastics, 65(8), 1988, p. 44.


42. U.S. Pat., 2,250,925 (29.7.41); Chem. Abstr., 35, 1941, p. 6983.


44. Spector, M., Heinemann, H., Chem. Ing. Tech., 34, 1962, p. 120.


51. Huang, W., Hydrocarbon Proc., 58(10), 1979, p. 131.


343. Flanagan, T., Oates, W., in "Transition Metal Hydrides", (R.


294.


348. Stoneham, A., in "Vacancies and Interstitials in Metals", (A.
Seeger, D. Schumacher, W. Schilling, J. Diehl, eds.), North-

349. Tanaka, T., Azofeifa, D., in "Vacancies and Interstitials in
Metals", (A. Seeger, D. Schumacher, W. Schilling, J. Diehl,

350. Wicke, E., Brodowsky, H., Zuchner, H., in "Hydrogen in Metals II:
Application-Oriented Properties", (G. Alefield, J. Volkl, eds.),


357. Nandi, P., Pitchai, R., Wong, S., Cohen, J., Burwell, R., Butt,

358. Nandi, P., Georgopoulos, J., Cohen, J., Butt, J., Burwell, R.,


109.

1965, p. 176.


531. Weiss, A., Bell, W., unpublished results.


635. Lin, J., Knifton, J., ACS Symp. Ser., 32(1), 1987, p. 235


VIII. APPENDICES

A. Reaction Acceleration Point Behavior.

Bond and Wells (86) report curious behavior during batch reactions between acetylene and hydrogen over 5 mol% Pd/α-Al₂O₃ catalysts (p. 11). This behavior suggests that the rate of pressure fall accelerated when the surface reaction became acetylene diffusion limited, thus allowing ethylene to adsorb and react on sites that were previously monopolized by acetylene (or if you like, acetylene diffusion limitations allowed hydrogen to reach ethylene-only adsorption sites, with the same result). We can test this possibility using data supplied by Bond and Wells (86).

The rate of the surface reaction may be expressed by:

\[ r = k(P_{H_2})^n(P_{C_2H_2})^n \]

where \( k \) is the reaction rate constant, \( m \) is the reaction order in hydrogen and \( n \) the order in acetylene. The general form of a diffusion equation is \( r = D(\Delta C/\Delta x) \) where \( r \) is the rate of diffusion, \( D \) is the diffusivity or some combination of terms representing the equivalent, \( \Delta C \) is the concentration gradient, and \( \Delta x \) is the length of diffusion. We can equate these two expressions at the point that diffusion control begins, yielding:

\[ k(P_{H_2})^n(P_{C_2H_2})^n = D(\Delta C/\Delta x). \]

We have no data from Bond and Wells (86) to calculate \( k \) (time spans of reactions are not given), \( D \) (no physical characteristics of the catalyst are given), or \( \Delta x \) (the depth of Pd impregnation is unknown). In fact, we cannot even decide what type of diffusion regime we might be in - Knudsen or bulk. However, if we assume that one type of diffusion only was present in all cases, and that the catalyst samples were all
identical, then at any given temperature, \( k \), \( D \), and \( \Delta x \) will be constant with changing acetylene and hydrogen pressures, and acceleration point pressure drops. In this case we can rearrange the equation above to 
\[ k\Delta x/D = \Delta C/(P_{H_2}^m(P_{C_2H_4}^n)), \]
or 
\[ k\Delta x/D = (P_{C_2H_4}^n-P_0)/((P_{H_2}^m(P_{C_2H_4}^n)), \]
where \( P_0 \) represents the acetylene pressure at which ethylene can begin to react on the Pd surface. As \( k\Delta x/D \) should be constant at any given temperature, we can equate the right hand side of the equation for any two given experimental data points and calculate \( P_0 \). Agreement on a value of \( P_0 \) between a number of experiments would support this model, particularly if this value is consistent with other mechanistic studies and a general understanding of both kinetics and diffusion.

In order to carry out these calculations we need to know the values of \( m \) and \( n \) in the kinetic expression, and both hydrogen and acetylene pressures at which the acceleration point occurred. Bond and Wells (29) report that they observed first order in hydrogen \((m=1)\) and \(-0.55\) in acetylene \((n=-0.55)\). They also give the initial acetylene and hydrogen pressures, the total pressure drop at which the acceleration point occurred, and the selectivity to ethylene, expressed as ethylene formed over the sum of ethylene and ethane formed, prior to the acceleration point. Unfortunately, they do not report the range of values of \( C_4 \) selectivities, which are necessary in order to calculate overall ethylene and ethane selectivities. The only \( C_4 \) selectivity value they give is 37% of the acetylene consumed at 16°C using 165 torr acetylene and 160 torr hydrogen. The true values of the product
selectivities are necessary to calculate the acetylene and hydrogen pressure at which the reaction accelerated.

In the absence of these values, we have assumed that the C₄ selectivity was always 37%. It is most likely that the actual values were somewhat lower, as the hydrogen/acetylene ratios were always greater than one. They define ethylene selectivities as

\[ S = \frac{C_2H_4}{(C_2H_4+C_2H_6)}; \text{ we are interested in } \frac{C_2H_4}{X_{C_2H_2}}, \text{ or } \frac{C_2H_4}{(C_2H_4+C_2H_6+C_4)}. \]

Assuming that ethylene, ethane and C₄ species are the only products, the selectivities should sum to 100%. Therefore we assume that

\[ (SC_2H_4)+(SC_2H_6)=100-37=63\%. \text{ Then } S=\frac{(SC_2H_4)}{63\%}, \text{ and as } S \text{ is given, } \]

\[ (SC_2H_4)=S(63\%). \text{ We now have the information needed to calculate the acetylene and hydrogen pressures where acceleration occurred.} \]

At any given pressure drop, \( \Delta p \), assume \( X \) torr acetylene has reacted. Ethylene requires one hydrogen per molecule, so hydrogen and acetylene consumed to form ethylene is \( SC_2H_4(X) \). C₄ species (which are predominately butenes) require one hydrogen per acetylene molecule in them (two), and also contribute to the pressure drop, as four molecules become two. Therefore C₄ species contribute \( 1.5(\text{X})SC_4 \) to the pressure drop. Ethane requires two hydrogens and one acetylene per molecule, and will account for \( 2(\text{X})SC_2H_6 \).

Therefore if \( X \) acetylene is consumed for a pressure drop of \( \Delta p \),

\[ \Delta p = (SC_2H_4)(X)+2(SC_2H_6)(X)+1.5(SC_4)(X). \]

If we know the selectivity values and the pressure drop, we can calculate the acetylene consumed. The reaction stoichiometry and the selectivity values will determine the hydrogen consumed, and we then have the acetylene and hydrogen pressures at which the acceleration occurred.
The values of $\Delta p$, and corresponding acetylene and hydrogen pressures appear below.

**Table A1. Data Set from Figure 1, Reference (86), $T=19^\circ C$.**

<table>
<thead>
<tr>
<th>$PC_2H_2i$ (torr)</th>
<th>$PH_2i$ (torr)</th>
<th>$\Delta p$ (torr)</th>
<th>$PC_2H_2a$ (torr)</th>
<th>$PH_2a$ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>100</td>
<td>46.25</td>
<td>11.68</td>
<td>62.3</td>
</tr>
<tr>
<td>50</td>
<td>130</td>
<td>42.5</td>
<td>14.77</td>
<td>95.5</td>
</tr>
<tr>
<td>50</td>
<td>175</td>
<td>37.5</td>
<td>18.9</td>
<td>144.7</td>
</tr>
</tbody>
</table>

**Table A2. Data Set From Tables 2 and 4, Reference (86), $T=0^\circ C$.**

<table>
<thead>
<tr>
<th>$PC_2H_2i$ (torr)</th>
<th>$PH_2i$ (torr)</th>
<th>$\Delta p$ (torr)</th>
<th>$PC_2H_2a$ (torr)</th>
<th>$PH_2a$ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>100</td>
<td>46.8</td>
<td>11.04</td>
<td>61.56</td>
</tr>
<tr>
<td>50</td>
<td>210</td>
<td>39.0</td>
<td>17.6</td>
<td>178.2</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>32.5</td>
<td>23.1</td>
<td>273.6</td>
</tr>
<tr>
<td>50</td>
<td>395</td>
<td>23.3</td>
<td>30.9</td>
<td>376.4</td>
</tr>
<tr>
<td>50</td>
<td>495</td>
<td>13.8</td>
<td>38.9</td>
<td>484.4</td>
</tr>
</tbody>
</table>

**Table A3. Data Set From Tables 2 and 4, Reference (86), $T=20^\circ C$.**

<table>
<thead>
<tr>
<th>$PC_2H_2i$ (torr)</th>
<th>$PH_2i$ (torr)</th>
<th>$\Delta p$ (torr)</th>
<th>$PC_2H_2a$ (torr)</th>
<th>$PH_2a$ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>100</td>
<td>44.2</td>
<td>13.29</td>
<td>63.9</td>
</tr>
<tr>
<td>50</td>
<td>150</td>
<td>40.2</td>
<td>16.74</td>
<td>117.5</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>34.0</td>
<td>21.87</td>
<td>172.5</td>
</tr>
<tr>
<td>50</td>
<td>243</td>
<td>28.7</td>
<td>26.63</td>
<td>220.6</td>
</tr>
</tbody>
</table>

From these data, we can calculate apparent pressures at which diffusion control (more accurately ethylene hydrogenation, which we have assumed is caused by acetylene diffusion control) begins, given an accurate kinetic equation of the reaction. Bond and Wells (86) report orders of 1.0 in hydrogen and -0.55 in acetylene; we have used these.
Comparing the results of any two experiments, we calculate that

\[(\text{PH}_2)_1(\text{PC}_2\text{H}_2^{-0.55})_1 / (\text{PC}_2\text{H}_2^{-0.55})_2 = (\text{PH}_2)_2(\text{PC}_2\text{H}_2^{-0.55})_2 / (\text{PC}_2\text{H}_2^{-0.55})_2\]

Rearrangement yields \(P_o = ((\text{PC}_2\text{H}_2)(\text{PH}_2)_1(\text{PC}_2\text{H}_2^{-0.55})_1 - (\text{PC}_2\text{H}_2)_2(\text{PH}_2)_2(\text{PC}_2\text{H}_2^{-0.55})_2) / ((\text{PH}_2)_1(\text{PC}_2\text{H}_2^{-0.55})_1 - (\text{PC}_2\text{H}_2)_2(\text{PH}_2)_2(\text{PC}_2\text{H}_2^{-0.55})_2)\)

The results of these calculations appear below, compared two at a time.

Table A4. Calculation of Apparent Pellet Center Acetylene Pressure from Data in Table A1.

<table>
<thead>
<tr>
<th>Initial Hydrogen Pressure (torr)</th>
<th>100</th>
<th>130</th>
<th>175</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-</td>
<td>6.30</td>
<td>6.71</td>
</tr>
<tr>
<td>130</td>
<td>6.30</td>
<td>-</td>
<td>7.40</td>
</tr>
</tbody>
</table>

Table A5. Calculation of Apparent Pellet Center Acetylene Pressure from Data in Table A2.

<table>
<thead>
<tr>
<th>Initial Hydrogen Pressure (torr)</th>
<th>100</th>
<th>210</th>
<th>300</th>
<th>395</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-</td>
<td>5.64</td>
<td>4.81</td>
<td>2.91</td>
</tr>
<tr>
<td>210</td>
<td>5.64</td>
<td>-</td>
<td>0.60</td>
<td>-6.58</td>
</tr>
<tr>
<td>300</td>
<td>4.81</td>
<td>0.60</td>
<td>-</td>
<td>-22.5</td>
</tr>
<tr>
<td>395</td>
<td>2.91</td>
<td>-6.58</td>
<td>-22.5</td>
<td>-</td>
</tr>
<tr>
<td>495</td>
<td>1.46</td>
<td>-10.5</td>
<td>-25.0</td>
<td>-28.7</td>
</tr>
</tbody>
</table>

The values calculated for \(P_o\) in the tables above are all in the range 7.7 to -29 torr, with most between 7 and -6. Similar calculations assuming first order hydrogen and zero order acetylene behavior yield values of 5.6-6.6, 2.25-7.5, and 4.8-9.2, for the three data sets above. Orders of 1.42 in hydrogen and zero in acetylene (reported by Bond, et al (77) over identical catalysts) yield 7.75-9.53, 9.1-12.3, and 9.7-10.8. The results of Margitfalvi, et al (135) and LeViness, et al (138)
suggest that ethylene reaction begins at the acetylene pressure where
the reaction rate goes through a maximum (figure 8, p. 38), which they
found was equal to about 1 torr. Clearly, in light of the method we
have used, the values of \( P_0 \) calculated are not unreasonable.

Table A6. Calculation of Apparent Pellet Center Acetylene Pressure
from Data in Table A3.

<table>
<thead>
<tr>
<th>Initial Hydrogen Pressure (torr)</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-</td>
<td>7.71</td>
<td>5.13</td>
<td>3.45</td>
</tr>
<tr>
<td>150</td>
<td>7.71</td>
<td>-</td>
<td>-2.37</td>
<td>-4.97</td>
</tr>
<tr>
<td>200</td>
<td>5.13</td>
<td>-2.37</td>
<td>-</td>
<td>-10.4</td>
</tr>
</tbody>
</table>

We have assumed \( C_4 \) selectivity values of 37%. It is probable that
the actual values are somewhat lower. How would this effect these
calculations? The production of \( C_4 \) species, which are mostly butenes,
requires two hydrogen molecules per molecule of \( C_4 \) produced, or one
hydrogen per acetylene consumed; the same as ethylene. If \( C_4 \)
selectivities were lower, both ethylene and ethane selectivities would
be correspondingly higher, but as ethane selectivities were always much
lower than ethylene, the increase in ethane would not be significant and
the hydrogen consumption would be substantially the same. The
production of \( C_4 \) species also increases the observed pressure drop, as
two acetylene molecules dimerize. A lower value of \( C_4 \) selectivity would
increase the calculated amount of acetylene consumed at any given
pressure drop, although this too would not be substantial if \( C_4 \)
selectivities did not approach zero. We would not expect them to;
values of 20% appear to be reasonable.
We must also consider why negative values of \( P_0 \) appear in the tables above. The first possibility is that the kinetic expression used to calculate them is incorrect, as negative values do not appear when different expressions are employed, as shown above. Assuming that the expression used is correct, what do negative values represent? They imply that if diffusion control has begun during experiments at lower initial hydrogen pressures, then at higher ones it should have begun at higher acetylene pressures (greater acetylene pressure drops - concentration gradients - through the catalyst pellet) than it did. This occurs because the surface reaction rate and the rate of diffusion have been equated.

Anything that lowers the calculated surface rate, or increases the calculated diffusion rate will tend to increase \( P_0 \). Margitfalvi, et al (135) observed that although the reaction was first order in hydrogen pressure at low hydrogen pressures, at higher pressures it shifts to a somewhat lower value, approaching zero at very high pressures. Such an effect here would decrease the calculated surface rate at higher hydrogen pressures, and decrease the acetylene concentration gradient (increase \( P_0 \)) at which the two expressions are equal. This would increase the calculated values of \( P_0 \), particularly in those cases where it is negative (at high hydrogen pressures).

Given these considerations, we feel that if the reaction acceleration point represented the onset of acetylene diffusion limitations in any one experiment, it did so in all other cases. How likely is it that it occurred once? Bond and Wells (86) report that the catalyst support used was 8-16 mesh (1.6-3.2 mm), apparently
spherical, α-alumina pellets. The metal loading was 5 mol%, and at such a high loading it is reasonable to assume that the metal was impregnated throughout the catalyst pellet, not in a thin, eggshell-type layer. Diffusion effects will occur first in the larger particles, so consider a particle 3.2 mm in diameter.

For this calculation, we will assume the reaction is first order in hydrogen and zero order in acetylene. This simplifies the resulting problem, as the rate of reaction is independent of the concentration of the diffusing species. Instead it is a constant at a given hydrogen pressure. The differential equation is $d^2C/dr^2 + (2/r) dC/dr = k_w C/C_2 / D$. The general form of the solution is given by $C = (k_w C_2 / D / r^2 / 6 - c_1 / r + c_2$.

Boundary conditions are $C = C_0$ at $r = R$ and $dC/dr = 0$ at $r = 0$. From the latter B.C. $c_1 = 0$. $D$ is the diffusion coefficient and is calculated assuming both Knudsen and bulk diffusion in the catalyst pores are possible. Then $D = (2/3) rv$, where $r = 2V_g / S_g$. $D = v / A / 3$. $D = 1 / (1 / D_x + 1 / D_b)$. Three different results from from Table A2, initial hydrogen pressure of 100, 300, and 495 torr, have been employed in these calculations. Catalyst pellet density is assumed to be 0.8 g/cc. One pellet of 3.2 mm has a volume of 0.0171 cc, or a weight of 0.0137 g (13.7 mg). The catalyst is 5 mol % Pd. Pd molecular weight is 106.4 g/mole; Alumina is 102 g/mole. Assume mol% = wt%. Then one pellet has $0.05(0.0137) = 0.685$ mg Pd.

We have calculated acetylene concentration gradients through the catalyst pellet assuming different values for $K$, the support surface area, and the pellet porosity for the three experiments described above. The results of these calculations appear in table A7.
From these results, we cannot conclude that the reaction acceleration point was caused by acetylene diffusion effects. The results are very dependent on the values of $K$, $SA$, and $\varepsilon$, none of which are known. All of the values employed in the calculations for table A7 are possible, and some of them place the reaction in the regime where

Table A7. Calculated Acetylene Concentration Gradients from Data in Table A2.

<table>
<thead>
<tr>
<th>$K$ (/min*torr)</th>
<th>$SA$ m²/g</th>
<th>$\varepsilon$ cc/g</th>
<th>Calculated Acetylene Pressure (torr) at Pellet Radius (mm) of 1.6</th>
<th>1.28</th>
<th>0.96</th>
<th>0.64</th>
<th>0.32</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>50 torr acetylene 100 torr hydrogen</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>4</td>
<td>0.25</td>
<td>11.04</td>
<td>10.3</td>
<td>9.71</td>
<td>9.30</td>
<td>9.05</td>
<td>8.97</td>
</tr>
<tr>
<td>0.04</td>
<td>4</td>
<td>0.25</td>
<td>11.04</td>
<td>9.55</td>
<td>8.39</td>
<td>7.57</td>
<td>7.07</td>
<td>6.90</td>
</tr>
<tr>
<td>0.10</td>
<td>4</td>
<td>0.25</td>
<td>11.04</td>
<td>7.32</td>
<td>4.42</td>
<td>2.35</td>
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</tr>
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<td>1</td>
<td>0.25</td>
<td>11.04</td>
<td>9.96</td>
<td>9.11</td>
<td>8.51</td>
<td>8.15</td>
<td>8.03</td>
</tr>
<tr>
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<td>10</td>
<td>0.25</td>
<td>11.04</td>
<td>8.74</td>
<td>6.95</td>
<td>5.67</td>
<td>4.90</td>
<td>4.65</td>
</tr>
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<td>0.35</td>
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<td>8.67</td>
<td>7.93</td>
<td>7.48</td>
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</tr>
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<td>11.04</td>
<td>9.19</td>
<td>7.75</td>
<td>6.72</td>
<td>6.11</td>
<td>5.90</td>
</tr>
<tr>
<td><strong>50 torr acetylene 300 torr hydrogen</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>4</td>
<td>0.25</td>
<td>23.1</td>
<td>19.9</td>
<td>17.5</td>
<td>15.7</td>
<td>14.7</td>
<td>14.3</td>
</tr>
<tr>
<td>0.04</td>
<td>4</td>
<td>0.25</td>
<td>23.1</td>
<td>16.8</td>
<td>11.9</td>
<td>8.38</td>
<td>6.28</td>
<td>5.58</td>
</tr>
<tr>
<td>0.2</td>
<td>4</td>
<td>0.25</td>
<td>23.1</td>
<td>&lt;0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>1</td>
<td>0.25</td>
<td>23.1</td>
<td>18.5</td>
<td>14.9</td>
<td>12.4</td>
<td>10.9</td>
<td>10.4</td>
</tr>
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<td>23.1</td>
<td>13.3</td>
<td>5.8</td>
<td>0.35</td>
<td>&lt;0</td>
<td></td>
</tr>
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<td>4</td>
<td>0.35</td>
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<td>9.92</td>
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<td>7.40</td>
</tr>
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<td>4</td>
<td>0.15</td>
<td>23.1</td>
<td>15.3</td>
<td>9.17</td>
<td>4.81</td>
<td>2.20</td>
<td>1.33</td>
</tr>
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<td>29.0</td>
<td>25.9</td>
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<td>38.9</td>
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<td>19.0</td>
<td>12.9</td>
<td>9.13</td>
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<td>38.9</td>
<td>28.9</td>
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<td>15.6</td>
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<td>0.25</td>
<td>38.9</td>
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<td>22.1</td>
<td>19.7</td>
<td>18.9</td>
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<tr>
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<td>0.1</td>
<td>0.25</td>
<td>38.9</td>
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<td>6.89</td>
<td>&lt;0</td>
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</tr>
<tr>
<td>0.1</td>
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<td>0.25</td>
<td>38.9</td>
<td>11.0</td>
<td>&lt;0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
diffusion effects reduce the acetylene pressure to zero; others do not. Gigola, et al (192) report that the three $\alpha$-alumina used in their work had surface areas between 13 and 20 m$^2$/g, while Engelhard markets one alumina (AT-9) of 4 m$^2$/g and 0.26 ml/g. It should be noted that if the surface reaction rate really is -0.55 order in acetylene, as reported by Bond and Wells (29), the rate would increase as the acetylene pressure decreases through the catalyst pellet. This would increase the number of conditions in table A7 at which the acetylene pressure is sufficiently low to allow for ethylene reaction and pressure drop acceleration.

In light of these considerations, and the fact that no other plausible explanation for this behavior has been proposed, we conclude that the pressure drop acceleration was most likely due to strong acetylene pore diffusion effects, but we cannot state this with certainty at this time.
B. Ethylene Selectivities and Rate Constants (110-112,132)

In part 1 of a series of studies on the adsorption and hydrogenation of acetylene on metal catalysts, Al-Ammar and Webb (110) present the details of their measurements of the adsorption of $^{14}$C labeled acetylene on Ir, Rh, and Pd catalysts. From figure 2 of this work (see figure 5, p. 26), it appears that monolayer coverage in the primary adsorption layer of alumina Pd is reached at a surface count rate of about 5000/min. The specific radioactivity of the labeled acetylene is given as 0.1 mCi/mmole, or $3.7 \times 10^9$ disintegrations/sec*mole acetylene. There is 0.1 g of 5 wt% Pd catalyst. This corresponds to 0.005 g Pd, or $4.7 \times 10^{-5}$ mole Pd. Assume a $\text{C}_2\text{H}_2$/Pd adsorption stoichiometry of 1. If the counting efficiency of the Geiger-Muller counter used was 100% (all disintegrations counted), then the catalyst dispersion must be

$\frac{(5000/\text{min})(1 \text{ min/60 sec})}{((0.000047 \text{ mole}) \times (3.7 \times 10^9/\text{sec*mole}))} = 0.096\%$.

Alternatively, if we assume a metal dispersion of 10%, we calculate a counting efficiency of 0.96%. A dispersion of 1% yields an efficiency of 9.6%. Similar calculations from data in table 1 of this work, using labelled acetylene of a specific activity of 0.05 mCi/mmole yields identical values as these, indicating that at least during these two sets of experiments, the counting efficiency and the metal dispersions were most likely constant here.

If the counting efficiency was constant, then the corresponding values of dispersion for silica supported Pd are not consistent, as in figure 2, for 0.1 g catalyst and 0.1 mCi/mmole, the turning point
representing the extent of primary adsorption occurs at 2000/min, while from table 1, for 0.1 g catalyst and 0.05 mCi/m mole, it occurs at 2900/min. In this case, we calculate that if the counting efficiency was 100%, the dispersions were 0.0192 and 0.056%, respectively. For d=10%, the counting efficiencies are 0.192 and 0.56%; for d=1%, they are 1.92 and 5.6%. Clearly, there is an inconsistency here which the authors did not notice.

In part 2 of this series (111), they report the details of hydrogenation reactions conducted over these catalysts. The authors report that the reactions were accurately modelled as first order in total pressure, and that rate constants were calculated in this way. Figure 1 of this report, they show the results of a number of reactions carried out over 0.003 g Pd/silica at 298 K. The initial reactant pressures are given as 12.5 torr acetylene, 37.5 torr hydrogen. The reaction rate accelerated, signalling ethylene hydrogenation, at a pressure drop of 13.2 torr (they assumed this occurred after all hydrogen was consumed), which took about 23 minutes to reach during the first reaction. The system employed was a 533 cm³, constant volume batch reactor. The kinetic expression for these conditions is \( K = (1/t) \ln \left( \frac{N_{w} - N_{a}}{N_{a}} \right) \). Assuming that their observation that the reaction was first order in total pressure is correct, then \( K = (1/23) \ln \left( \frac{50}{36.8} \right) = 0.0133/\text{min} \).

In figure 2 of this report, they show the dependence of the first order rate constant (298 K, identical initial reactant pressures as figure 1) on batch reaction number over 0.1 g of Pd on both alumina and silica (see figure 6, p. 29). The initial value of the first order rate
constant for both catalyst types is given as about 0.014. This is most strange, as 33.3 times more catalyst was used in this case, yet the calculated values of the rate constants are almost identical.

It does not matter that we used pressure rather than concentration in calculating \( K \) from figure 1, as in a constant volume system at these pressures and temperature, pressure and concentration are interchangable (we could simply replace \( P \) with \( n/V \), and as \( V, R, \) and \( T \) are constant, \( P_0/P = n_0/N \)). If we had used only the hydrogen pressure (not total pressure), then \( K = (1/23) \ln(37.5/24.3) = 0.019 \). This makes the problem even more acute. If we calculate \( K \) on a catalyst unit weight basis, we find that the values are 4.43–6.33/\( g_{\text{cat}} \) *min from figure 1, and 0.14/\( g_{\text{cat}} \) *min from figure 2. The ratio between these values is 31.6–45.2.

There are, of course, a large number of possible explanations for this discrepancy. A typographical error in the text would certainly explain it satisfactorily. Because a large number of reactions was conducted in each case (\( \geq 5 \) in figure 1, \( \geq 34 \) in figure 2), it would appear unlikely that they simply measured the weight of catalyst incorrectly, unless they only measured it once before the first reaction (which is possible). A large difference in the metal loading or dispersion between the two samples would also account for this difference.

We should note that if the values of \( K \) that we have calculated are correct, then the time span of the first experiment in figure 2 is given by \( t = (1/K) \ln(P_0/P) = (1/0.014) \ln(50/36.8) = 22 \) minutes. The fact that this value is essentially identical to the one reported over 0.003 g in
figure 1 may be due to one of two causes. Either the authors were aware of the large differences in activity between the two samples, and used much more catalyst for the experiments in figure 2, or one of the values of the weight of catalyst is incorrect, as the same amount was actually employed in both cases. We believe that the authors would have mentioned this very large difference in activity if it had in fact been observed, and so conclude that the most likely explanation is a typographical error in the text.

Which of these values is correct? In almost all of the experimental results presented in the first three parts of this series (110-112), 0.1 g of Pd catalysts were used. Thus, from a purely practical standpoint, it would appear that the value of 0.003 g given in figure 1 is incorrect.

We can also compare these values with other reported in the literature. Table 19 (p. 149) compares the values of first order hydrogen rate constants from a number of literature sources. At 298 K, the range of values is 0.0109-0.364 mole/mole*min*torr. In these units, the two values of $K$ calculated here are 0.0109 and 0.364 (the identical values in table 19 were calculated from this work). The value of 0.364 appears to be too high, particularly as the metal loading of this catalyst is 5 wt%, and we would expect its dispersion to be lower than the other samples from table 19. The value of 0.0109, however, appears very reasonable, and we conclude that 0.1 g of catalyst were in fact employed in figure 1 of this work (111).

We can now use this value of the rate constant (0.0109) to try to determine the most likely value of the metal dispersion and hence the
Geiger-Muller counter efficiency. Sarkany, et al (143) report turnover numbers for a variety of Pd catalysts at 298 K at similar acetylene conversions. These numbers are apparently not corrected for hydrogen pressure, but are calculated from observed reaction rates and catalyst site titrations. They report that all conversions were 60-70%. We have assumed a value of 65% in all cases. Ethane selectivities are given, and from this it is possible to calculate approximate hydrogen pressures. We have done this (see Appendix C, p. 520, for more details), and find values between 0.0084/sec at d=2.2% and 0.0218/sec at 45.3% (both values at 300 K and corrected to 1 torr hydrogen assuming first order hydrogen behavior).

If we assume that the values and trends observed by Sarkany, et al (57) are correct, then as their TON's increase with dispersion, they will intersect the possible TON's calculated from the data of Al-Ammar and Webb, above. These curves intersect at d=3.5%. This would correspond to a counting efficiency of 1.6%. In light of the high metal loading (5 wt%) and relatively low support surface area (unknown α-alumina), we believe that d=3.5% is reasonable. Similarly, from the design of the catalyst chamber and the placement of the Geiger-Muller counters (figure 1 in (43)), a counting efficiency of 1.6% does not appear unreasonable.

We now turn to consider the assumptions made by Al-Ammar and Webb to describe their reaction acceleration point and to calculate product selectivities. All batch reaction were conducted with 12.5 torr acetylene, 37.5 torr hydrogen over a 5 wt% Pd on alpha alumina catalyst at 298 K. As in Bond and Wells (Appendix A, or (86)), they give no
details about the support porosity or surface area. Unlike Bond and Wells, however, we do have a value of the rate constant, 0.0109 mole/mole*min*torr. If we simply assume that all catalyst characteristics from Bond and Wells apply here, and that the reaction is first order in hydrogen and zero in acetylene, any initial conditions of hydrogen/acetylene = 3 from Bond and Wells will be comparable to the data of Al-Ammar and Webb (see Tables A1-A3, p. 503). Bond and Wells began with 50 torr acetylene, and all reactions with hydrogen/acetylene = 3 accelerated at a calculated acetylene pressure of about 16 torr.

Because the reaction is first order in hydrogen, and diffusion is "first order" in acetylene, we can simply compare the ratio of initial acetylene pressure to that where acceleration occurs. From Bond and Wells, this value is 50/16=3.125. If a similar ratio is correct here, then the reactions of Al-Ammar and Webb actually accelerated when the acetylene pressure was 12.5/(3.125)=4 torr, not "essentially zero".

Apparently Al-Ammar and Webb calculated ethane selectivities by assuming that all 12.5 torr of the acetylene was consumed and subtracting that value from the observed pressure fall. The remainder represents extra hydrogen consumed to form ethane, and the ethane selectivity is 0.7/(12.5)=5.6%. As they also assumed that ethane and ethylene were the only products, the ethylene selectivity is given by 100-5.6=94.4%, which is the value they report. However, if our assumptions are correct, the extra pressure drop between the measured 13.2 torr and the acetylene consumption of 8.5 torr (4.7 torr) represents both extra hydrogen consumed to form ethane and acetylene dimerized to form C₄ species. If no C₄'s were formed, the ethane
selectivity is 4.7/8.5=55.3%; if no ethane was formed, then the C₄
selectivity is 1.5(4.7)/8.5=82.9%. Of course, at this point any
combination of values between these extremes are possible. If we assume
a C₄ selectivity of 20%, then this accounted for 0.2(8.5)(1/1.5)=1.13
torr of the 4.7 torr remainder. Ethane then accounted for 3.57 torr,
for an ethane selectivity of 3.57/8.5=42%.

Alternatively, we might suppose that Al-Ammar and Webb actually
measured the ethane concentration at the acceleration point, and that
this value was 0.7 torr. In part 1 of this series (43), they describe
their separation method as a GC with a 1 m column of activated silica
gel, operated isothermally at 333 K. Assuming that 0.7 torr ethane was
produced, than 4 torr pressure drop must have come from C₄ formation.
The butene formation is therefore 1.5(4)/8.5=70.6%.

The values of both ethane and C₄ selectivities calculated above
are considerably higher than those usually observed during acetylene
hydrogenation. This is not really a problem here because of the crude
method we have used to estimate the acetylene pressure at which the
acceleration point occurred. These selectivity values are extremely
dependent on the actual amount of acetylene consumed. If, instead of 4
torr acetylene remaining we assume only 2, then the ethane selectivity
is 0.7/10.5=6.7% and the C₄ selectivity is 2(1.5)/10.5=28.6%. These
values are very reasonable in light of other investigations (see table
22, p. 155).

In any case, even without any pore diffusion effects, Margitfalvi,
et al (134,135) have shown that at acetylene pressure less than 1-2
torr, ethylene can adsorb and react; the rate of reaction will then
accelerate. In addition, it is our experience that any packed GC column capable of separating ethane, ethylene, and acetylene, which we must assume describes their silica gel column, cannot elute any species of carbon number 4 or higher without a large increase in column temperature and/or waiting for a very long time (46-60 minutes, versus 5-10 for acetylene). Given the short duration of their batch experiments (22 minutes), and the fact that their column was operated isothermally, we consider it likely that they did not observe any higher hydrocarbons during these reactions. It also appears that they did not even look for them, as if they had we should expect that they would have reported finding none (especially as Webb (115) had recently reviewed the hydrogenation literature and discussed the formation of higher hydrocarbons during acetylene hydrogenation).

We conclude that higher hydrocarbons were formed, that the reaction rate accelerated before complete acetylene consumption, and that the ethylene selectivities calculated in these works are wrong. The actual values of the last must be lower, as other products are formed and less acetylene is consumed than they thought.

Similar considerations can be made in examining the work of Weiss, et al (132). They operated a plug flow reactor with a gas feed consisting of 0.36% acetylene, 0.76% deuterium, 1.68% nitrogen, 45 ppm oxygen, balance ethylene. In the experimental section of their report, they describe the use of a squalane column for total C2-C7 analysis. However, it appears from the rest of the paper that they never used it. They later describe a 20% SE-30 column used to check for higher hydrocarbons in the heptene that they had used to extract spent
catalysts. They observed no detectable polymer in this solution (<0.47-1.86 mg/g catalyst). The formation of higher gas phase hydrocarbons is never mentioned again in the paper (i.e. after describing the method they used to analyze them in the experimental section, they fail to say if any were observed).

The authors do make the tacit assumption that no higher hydrocarbons were formed in any significant quantities, as is apparent from the treatment of their results. As discussed in section B of the literature review (pp. 66-68), with an inlet ethylene to acetylene ratio as high as it is here (97.12/0.35=277.5) it is not possible to accurately measure the rate of ethylene production. Therefore the rates of production of all other product species and the rate of acetylene consumption are measured. The rate of ethylene production (or consumption) is calculated from an assumed material balance amongst all the other species, leaving only the ethylene rate unknown.

If there are other species, such as gas phase or surface polymers, the rates of production of these species will be included in the calculated rate of ethylene production. As the rate of gas phase polymer production usually corresponds to a selectivity of 20-40%, and the surface polymer selectivity has an average value of at least 2.5-5% and possibly much higher during the initial stages of reaction (see pp. 66-68), ethylene selectivities calculated in this way will always be (significantly) higher than the actual value.

In case there is any question of whether these authors actually did calculate ethylene selectivities in this way, we must describe an additional aspect of their original graph which we have reproduced as
figure 7 (p. 35). They had drawn a line from y=1, x=0 (1 mole ethylene produced per mole acetylene in the feed, zero moles ethane produced per mole acetylene in the feed) to y=0, x=1 (0 moles ethylene produced per mole acetylene in the feed, 1 mole ethane produced per mole acetylene in the feed) and labelled it "100% conversion". As in the case of Al-Ammar and Webb above, we must conclude that ethylene selectivities calculated in this work are wrong. Because ethane selectivities were calculated from the observed rates of acetylene consumption and ethane formation, however, these values are correct. The difference between 100% and the ethane selectivities measured, which the authors assumed represented the ethylene selectivity, is actually the sum of the selectivities to gas phase and surface polymer and ethylene.

Sarkany, et al (143) report the TON's of a series of Pd on alumina catalysts of different metal dispersions all at acetylene conversion of 60-70%. This data shows an increase in the acetylene hydrogenation TON by a factor of about eight upon changing dispersion from 2.2% to 61.5%. These values, however, have not been corrected to a standard hydrogen pressure, so it is unclear if this is a real effect or simply an artifact. This suspicion is supported by the fact that although all TON's were calculated at nearly identical acetylene partial pressures (0.003(0.35)(760)=0.8 torr), the selectivity to ethane decreased with increasing metal dispersion. Thus, the hydrogen pressure at which these TON's were calculated increased with the calculated TON.

Sarkany, et al (143) report the ethane selectivities observed over each catalyst sample. These values were calculated from measured acetylene consumption and ethane production rates, and higher gas phase hydrocarbon products were included, so we may take them at face value. Although we do not know the values of ethylene and higher hydrocarbon selectivities, we know their sum (100%-S_{ethane}) and assuming that most of the polymers are C_4 species and that most of the C_4's are butenes (both of which Sarkany, et al (141,142) previously reported over the same catalysts), the hydrogen consumption is the same in either case; 1 hydrogen molecule per acetylene molecule forming each product. Because this work was conducted in a CSTR with a huge excess of ethylene (ethylene/acetylene = 99.2/0.3 = 331), we can ignore changes in the number of gas phase moles due to acetylene dimerization.
The hydrogen pressure in each case may be calculated in the following way. The hydrogen consumed can be calculated from the acetylene conversion (65%, which represents hydrogen consumed if no ethane was produced) plus the acetylene conversion times the ethane selectivity (which represents the extra molecule of hydrogen per molecule of acetylene necessary to form ethane). Dividing this sum by the initial hydrogen/acetylene ratio (0.5/0.3=1.67) yields the hydrogen conversion. The initial hydrogen pressure is 0.005(760)=3.8 torr. From this value and the hydrogen conversion we can calculate the actual hydrogen pressure. Table C1 shows the values of TON calculated by Sarkany, et al (143) along with our values corrected for hydrogen pressure.

Table C1. TON's Corrected for Hydrogen Pressure from (143).

<table>
<thead>
<tr>
<th>Catalyst Dispersion</th>
<th>S$_{\text{ethane}}$ (%)</th>
<th>TON from (57)</th>
<th>$P_{\text{H}_2}$</th>
<th>TON at 1 torr hydrogen</th>
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<tr>
<td>2.2</td>
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<td>0.00589</td>
<td>1.54</td>
<td>0.00384</td>
</tr>
<tr>
<td>6.3</td>
<td>67.2</td>
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<td>1.33</td>
<td>0.00630</td>
</tr>
<tr>
<td>26.5</td>
<td>34.5</td>
<td>0.0105</td>
<td>1.81</td>
<td>0.00580</td>
</tr>
<tr>
<td>45.3</td>
<td>21.0</td>
<td>0.0098</td>
<td>2.01</td>
<td>0.00487</td>
</tr>
<tr>
<td>50</td>
<td>18.2</td>
<td>0.0448</td>
<td>2.05</td>
<td>0.0218</td>
</tr>
<tr>
<td>61.5</td>
<td>15.3</td>
<td>0.0262</td>
<td>2.09</td>
<td>0.0125</td>
</tr>
</tbody>
</table>

The values reported by Sarkany, et al (143) differ at most by a factor of 0.0448/0.00589=7.6. The values we have calculated differ at most by a factor of 0.0218/0.00384=5.7. At first, correcting for hydrogen pressure does not seem to have had much of an effect. A closer inspection shows that although this is true for the difference between
the highest and lowest values in table C1, other differences have been largely removed. The first four values do not increase regularly with dispersion, but instead might be spread around an average value of 0.00520. The last two values are still substantially higher than the other four, regardless of correcting for hydrogen pressure. However, this removes a great deal of the evidence that led Sarkany, et al (143) to the conclusion that TON's increase regularly with metal dispersion. When compared at equal hydrogen pressures, they do not, although samples with dispersions of 50% or more do have significantly higher TON's than those with dispersion lower than 45.3%.

Actually, it seems like we are splitting hairs in saying the above, as it is hard to envision a mechanism whereby the TON will jump by a factor of more than 4 when dispersion is increased from 45 to 50%. A more likely explanation might be that both metal dispersions and calculated TON's are not as accurate as we might like them to be. The conclusion that TON increases regularly with dispersion appears to be unjustified at this time. Of course more accurate measurements in the future might show that it actually does increase, but this data do not support this interpretation now.

This hesitation to make a firm conclusion of increasing TON's with increasing dispersion based on these results of Sarkany, et al (143) is supported by the results of Gigola, et al (192), who observed the opposite trend. Differential conversion experiments conducted at 1520 kPa with a mixture containing 0.72% acetylene, 60.10% ethylene, 9.16% methane, and 30.02% hydrogen, over a series of Pd/alumina catalysts showed a decrease in TON from 5/sec at d=10% to 0.5 at d=77%. Table C2
shows these values, and ones we calculated correcting for hydrogen pressure to 1 torr for comparison with the values of Sarkany, et al (143).

Table C2. TON's Corrected to 1 torr Hydrogen from (192).

<table>
<thead>
<tr>
<th>Catalyst Dispersion</th>
<th>TON at 3428 torr Hydrogen</th>
<th>TON at 1 torr Hydrogen</th>
</tr>
</thead>
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<tr>
<td>10</td>
<td>5.1</td>
<td>0.00149</td>
</tr>
<tr>
<td>20</td>
<td>1.7</td>
<td>0.000496</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>0.000321</td>
</tr>
<tr>
<td>45</td>
<td>0.8</td>
<td>0.000233</td>
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<tr>
<td>58</td>
<td>0.65</td>
<td>0.000190</td>
</tr>
<tr>
<td>77</td>
<td>0.5</td>
<td>0.000146</td>
</tr>
</tbody>
</table>

It is readily apparent that the values we have calculated from the data of Gigola, et al (192) are 2-10 times lower than the values calculated from the data of Sarkany, et al (143) in Table C1. The most likely explanation for this is the assumption that the reaction is first order in hydrogen over the pressure range 1 to 3400 torr. Margitfalvi, et al (134,135) observed that although the hydrogen order was one at low pressures, with increasing hydrogen pressure the reaction rate increased at a slower rate, corresponding to some fractional hydrogen order, until at very high pressure, it appeared to approach zero order in hydrogen. If this is the case, then the TON's calculated in Table C2 above should be higher, perhaps significantly so. Acetylene pressures are not as different between these two investigations (0.8 in (143) and 82 in (192)), although the difference is still large. Any positive or negative order in acetylene, no matter how small, will also change the
relative values of TON calculated. In addition, the values in table C2 were measured at 288 K; those in table C1 at 300 K.

Gigola, et al (192) investigated the possibility of θ-phase hydride on these catalysts because at the high hydrogen pressures and the temperature (288 K) used the thermodynamics of the Pd-hydrogen system favor the formation of a θ-phase (see figure 16, p. 93). The θ-phase was observed on all catalysts of dispersions less than 50% used in this work. The H/Pd stoichiometry decreased with increasing dispersion. Gigola, et al (192) considered this as a possible explanation for the observed decrease in TON, but discounted it because no ethane formation was observed, particularly over samples of low dispersion where the θ-phase surely existed (Borodzinski, et al (398) observed that the θ-phase was more active and more ethane selective than the α-phase. See table 11, p. 101), and activation energies were constant over all samples.

These results are consistent with the results of a number of investigations of 1,3-butadiene hydrogenation over Pd catalysts (127-131). These authors also observed a decrease in TON with increasing dispersion and attributed it to stronger complexation of butadiene on small metal crystallites.

However the number of independent investigations that have observed either an increase or decrease in TON of either acetylene or butadiene with increasing dispersion of Pd catalysts are small, and it would appear prudent to await further experimental results.

Gigola, et al (192) were surprised to observe that although the hydrogenation of acetylene was very ethylene selective up to very high acetylene conversions over catalysts of dispersions of less than 20%,
over samples of higher dispersions, high ethylene selectivities were observed only up to acetylene conversion of 20–30%. A subsequent increase in temperature led to reaction runaway. They attempted to relate this observation to the theory that small metal crystallites might not maintain isothermal conditions during exothermic reactions (193) which might have altered the relative adsorption strengths of ethylene and acetylene and allowed ethylene to react.

However, it appears more likely that this was caused by acetylene pore diffusion effects allowing a small number of sites to adsorb and hydrogenate ethylene, initiating non-isothermal conditions because of the much higher rate of ethylene hydrogenation.

Three catalysts of dispersions less than 20% remained ethylene selective to high conversions; two were industrial (ICI-38-1) Pd on α-alumina. One was a similar sample prepared by the authors. All of the catalysts of dispersion higher than 20% were prepared by the authors. The surface area of the industrial catalysts was 18 m²/g; all of the others were in the range 13–20. Working in a plug flow system at 293 K, atmospheric pressure, 15% hydrogen, 1.03% acetylene over 3–5 mm diameter 0.04% Pd/γ-alumina pellets, I have observed complete reactor runaway from the onset of reaction (89). Crushing the pellets to approximately 40–60 mesh allowed for reaction up to >80% acetylene conversion before runaway occurred again. In light of the very high hydrogen pressures used by Gigola, et al (192), it does not seem unreasonable that a similar effect occurred here.

The difference between the catalyst samples was probably due to both the larger number of sites on the more disperse samples and a
larger depth of impregnation in the samples prepared in their laboratory. Unfortunately, the impregnation profiles of these catalysts were not investigated. However, the industrial samples used here are definitely peripherally deposited in a very thin layer (229), and as such would not exhibit pore diffusion effects. The relatively low values of support surface area support this assumption that Pd was impregnated throughout the catalyst pellets made in their laboratory.
D. Reactor System Calibrations.

The volume of the reactor system was determined by measuring the pressure versus time during filling from 10 torr to 1 atmosphere with a mass flow controlled hydrogen flow of 20 ml/min (figure D1). The volume measured was the entire system minus the circulation pump (valves 2 and 3 to the pump, figure 21, p. 154) and the outlet sample section (valves 7 to 14, 15, and 16). Because the hydrogen mass flow controller was calibrated for an outlet pressure of 1 atmosphere, we used only the points in the pressure range 700 to 750 torr. This took 8.27 minutes, representing 165.33 std. cc hydrogen. Assuming the ideal gas law is accurate under these conditions, the total volume measured must be 

\[(165.33)(760)/(50)=2513\] cc. Alternatively, the line through the data points in figure D1 is described by 

\[y=10.345+6.1950x\] (\(R^2=1.000\)). Taking
the slope, 6.1950 torr/min=0.30975 torr/std. cc H₂. and again assuming
the ideal gas law holds, this represents 760/0.30975=2454 cc volume.
These values differ by only 2.35%, and show that although the mass flow
controller was calibrated for 1 atm outlet, it is very nearly linear
down to 10 torr. Because it was calibrated for 1 atm outlet, however,
we conclude the former value, 2513 cc, is the more accurate.

The volumes of all sections of the apparatus were calculated by
expanding hydrogen from this section into others, or vice versa, and
measuring initial and final pressures. The TGA was filled to 755 torr,
then shut off. The rest of the system was evacuated and the vacuum
system closed. After expansion into the rest of volume measured above
the pressure was 631 torr. The TGA volume is 2513(631)/755=2100 cc.

Similarly the TGA was shut off at 631 torr and expanded into the
evacuated Heise gauge and connecting lines. After the expansion the
pressure was 587 torr. The volume of the Heise gauge and lines is
2100(631)/(587)=2100=157.4 cc. The Heise was closed off at 587 torr,
then expanded into the connecting lines to 406 torr. The Heise gauge
volume is 157.4(406)/587=109cc. The connecting line volume is 157.4-
109=48.5 cc.

The Heise gauge at 406 torr was expanded into the outlet sampling
section to 283 torr. The outlet volume is 109(406)/283-109=47.4 cc. A
similar expansion from the Heise gauge at 283 torr into the outlet
sample section plus the small batch reaction sample section (valve 7 to
8) yielded a final pressure of 190 torr. This volume is 109(283)/190-
109=47.4=6.0 cc.
The TGA, Heise gauge and connecting line at 565 torr were expanded into the circulation loop (without the pump section). The pressure fell to 525 torr, and the loop volume is $2257(565)/525-2257=172$ cc. Similar expansion into the upper and lower loops alone yielded pressure falls of 508 to 488 torr and 525 to 508 torr, representing 95.6 cc and 75.5 cc, respectively. These values also add up to 171.2 cc which is only 0.5% different than the volume measured for both together. Expansion from the TGA, Heise and connecting line into the loop and the pump section resulted in a pressure fall from 488 to 447 torr. The volume of the pump section is $2257(488)/447-2257-172=35$ cc. The volume of the HC mixture inlet line, from valve 1 to valves 17,18, and 19, was calculated by subtracting all other measured volumes from the initial 2513 cc measured. This is $2513-2100-157.4-172=83.6$ cc.

The volume of the TGA-circulation loop connector tube (valves 4 and 6 to the top of the upper flow through tube of the left TGA hangdown tube) was measured by filling with water from a known volume and is about 110 cc. Assuming the HC reaction gas does not flow into the TGA due to the diluent He stream, the reactor volume is the sum of this section (110 cc), the circulation loop (95.6 cc + 75.5 cc), and the pump section (35.5 cc), or 316.6 cc.

Mass flow controllers were calibrated at the factory (Brooks Instrument Division, Emerson Electric Company). The calibration reports appear in tables D1-D4.
### Table D1. Mass Flow Controller Calibration Report

<table>
<thead>
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<td>MODEL NO.</td>
<td>5850C</td>
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<tr>
<td>GAS</td>
<td>Hydrogen</td>
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<tr>
<td>RANGE</td>
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#### 1. CALIBRATION:

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FLOW @ 100%

| EMITTER VOLTAGE    | 10.746        |
| SENSOR VOLTAGE     | 38 MV         |
| VALVE VOLTAGE      | 7.947         |
| ORIFICE SIZE       | 0.002         |
| RESTRICTOR SIZE    | 1 µ full      |


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#### 1. CALIBRATION:

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FLOW @ 100%

| EMITTER VOLTAGE    | 10.090        |
| SENSOR VOLTAGE     | 39 MV         |
| VALVE VOLTAGE      | 6.332         |
| ORIFICE SIZE       | 0.002         |
| RESTRICTOR SIZE    | 0.5 µ full    |

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FLOW @ 100%

EMITTER VOLTAGE 10.863 VDC
SENSOR VOLTAGE 55 MV
VALVE VOLTAGE 5.598 VDC
ORIFICE SIZE 0.002
RESTRICTOR SIZE 0.25 μ full


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<td>MODEL NO. 5850C</td>
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<tr>
<td>GAS Helium</td>
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<td>RANGE 0-100 sccm</td>
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<td>PRESSURE 50 psi in 0 psi out</td>
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FLOW @ 100%

EMITTER VOLTAGE 10.564 VDC
SENSOR VOLTAGE 32 MV
VALVE VOLTAGE 6.824 VDC
ORIFICE SIZE 0.002
RESTRICTOR SIZE 2 μ full
E. Sample Computer Program and Raw Data.

A sample of the computer program used to calculate acetylene conversions, all product selectivities, catalyst polymer loadings, and reaction rate constants appears below. The program was written in Microsoft Basic 2.0 and run on a Macintosh Plus computer with an external 20 MB hard disk drive. A similar program was used to calculate C₄ fraction compositions and the gas phase polymer percentage of carbon number 6 or greater.

Sample Computer Program

REM Define GC response factors (area units/torr).
FC2H6=269
FC2H4=240
FC2H2=202
FC4=8600
FC6=11000
REM Input catalyst weight (grams), metal loading (weight fraction Pd), He and HC flow rates (std.cc/min), and number of lines of data (starting with 2).
INPUT "How much catalyst (grams)"; GPd,WtPd
INPUT "What is the Helium flowrate"; FHE
INPUT "What is the HC mix flowrate"; FH
INPUT "What are first and last sample numbers"; L,M
REM Define dimension of array variables.
DIM T(M),AC2H6(M),AC2H4(M),AC2H2(M),AC4(M),AC6(M),RSUR(M),CC2H2(M),
CH2(M),SC2H6(M),SC2H4(M),SC4(M),SC6(M),SSURF(M),K(M),FC2H2(M),
PC2H4(M),PC2H6(M),PC4(M),PC6(M),FT(M),A(M),POLY(M),PH2(M),FHC(M)
REM Choose DATA line number to begin reading.
RESTORE 1
REM Define Clipboard as destination of output.
OPEN "CLIP:" FOR OUTPUT AS #1
REM Begin calculation.
FOR N=L TO M
REM Enter time (hours), GC areas, rate of catalyst weight increase (mg/min), and weight of polymer on catalyst (mg).
READ T(N),AC2H6(N),AC2H4(N),AC2H2(N),AC4(N),AC6(N),RSUR(N),POLY(N)
REM Calculate gas phase mole fractions of all hydrocarbons.
PC2H6(N)=AC2H6(N)/(FC2H6*760)
PC2H4(N)=AC2H4(N)/(FC2H4*760)
PC2H2(N)=AC2H2(N)/(FC2H2*760)
PC4(N)=AC4(N)/(FC4*760)
PC6(N)=AC6(N)/(FC6*760)
REM Calculate sum of acetylene equivalent gas phase mole fractions.
PT(N)=PC2H6(N)+PC2H4(N)+PC2H2(N)+PC4(N)*2+PC6(N)*3
REM Enter next line of data if this is the first.
IF N=2 THEN 1000
REM Calculate He, HC, and total molar flow rates.
MHE=FHE/24135
MH=FH/24135
MFR=MH*MHE
REM Calculate apparent inlet HC flow rate (moles/min) from carbon
balance assuming CSTR behavior and V=316.6 cc.
MHC=(PT(N-1)*MHE+316.6*PT(N-1)-PT(N-2))/(24135*60*(T(N)-T(N-2))
+RSUR(N-1)/(28*1000))/(.8682-PT(N-1))
REM Calculate apparent inlet HC flow rate (std.cc/min).
FHC(N-1)=MHC*24135
REM Calculate reaction rates (moles/min) of all species except
ethylene.
RC2H2=PC2H2(N-1)*MFR-.07739*MH+(PC2H2(N)-PC2H2(N-2))*316.6/
((T(N)-T(N-2))^24040/60)
RC2H6=PC2H6(N-1)*MFR-.000255*MH+(PC2H6(N)-PC2H6(N-2))*316.6/
((T(N)-T(N-2))^24040/60)
RC4=PC4(N-1)*MFR+(PC4(N)-PC4(N-2))*316.6/((T(N)-T(N-2))^24040/60)
RC6=PC6(N-1)*MFR+(PC6(N)-PC6(N-2))*316.6/((T(N)-T(N-2))^24040/60)
RSUR=RSUR(N-1)/(28*1000)
RH2=RC2H2+RC2H6
REM Calculate hydrogen pressure (torr) in outlet.
PH2(N-1)=((1.318*MH-RH2)*(T(N-1)-T(N-2))*60*PH2(N-2)/
(T(N-1)-T(N-2)))*60*24040/316.6
REM Calculate acetylene conversion and product selectivities (%).
CC2H2(N-1)=(-RC2H2/(MB*.07739))*100
SC2H6(N-1)=100*RC2H6/(-RC2H2)
SC4(N-1)=(200*RC4+300*RC6)/(-RC2H2)
SSURF(N-1)=100*RSUR/(-RC2H2)
SC2B4(N-1)=100-S2H6(N-1)-SC4(N-1)-SSURF(N-1)
REM Calculate amount (mg) of surface polymer per ml pore volume.
Pn=POLY(N-1)/(GPn^3.5)
REM Calculate first order hydrogen rate constant (moles acetylene per
mole Pd per minute per torr hydrogen).
K(N-1)=-RC2H2*106.4/(GPn*Wd*PH2(N-1))
REM Format output and send to clipboard file for transfer to tables
or graphics program.
PRINT #1, USING "###.### #.### #.### #.### #.### #.### #.### #.### #.###
###.### #.### #.### #.### #.### "T(N-1);CC2H2(N-1);SSURF(N-1);
SC2H6(N-1);SC2B4(N-1);SC4(N-1);POLY(n-1);K(N-1);FHC(N-1)
REM Continue to next line of data.
1000 NEXT N
REM Close clipboard file with output.
CLOSE #1
STOP
REM 52.72 mg 0.1 % Pd on alumina. Flows 10.5 and 1.5. 3/6/88
1 DATA 0.544, 26.72, 13251, 747.90, 1003.8, 701.85, 0.01400, 0.4
2 DATA 1.492, 32.06, 15814, 748.89, 2000.0, 1659.5, 0.01350, 1.22
3 DATA 2.512, 141.57, 17132, 672.08, 2676.7, 2235.6, 0.01190, 1.85
4 DATA 3.488, 362.51, 17799, 693.17, 2848.0, 2224.6, 0.00930, 2.70
5 DATA 4.518, 447.82, 18352, 741.94, 2843.7, 2264.5, 0.00650, 3.40
6 DATA 5.503, 506.13, 18617, 759.72, 2772.2, 2146.3, 0.00560, 4.02
7 DATA 6.823, 559.40, 18966, 790.52, 2764.5, 2077.0, 0.00510, 4.52
In practice, this program was run once using the nominal, mass flow controller setting for the HC mix flow rate. The program calculated the apparent inlet HC flow rate from a carbon balance around the reactor assuming CSTR behavior and a reactor volume of 316.6 cc. The program was then run again using a HC flow rate value typical of those after the calculated flow rate had ceased to increase and reached a fairly steady state. The calculated flow rate is constant regardless of the actual flow rate entered.

The HC flow rate value used to calculate catalyst activities and product selectivities is given at the start of each experimental description, while the calculated apparent flow rates appear under the column heading "F (ml/min)" in data tables. The standard catalyst pretreatment is that described in Section IIIA (Apparatus and Procedure, p. 165), 2 hours in flowing oxygen at 200°C, followed by evacuation and 2 hours of flowing hydrogen at 300°C. Samples were cooled overnight in flowing He and evacuated at reaction temperature prior to introduction of the reactant gas mixture.
Experiment #1. Starting Date: 8/3/87. Wt% Pd: 0.5  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 43.97 mg. Final: 42.69 mg. % Loss: 2.9

On TGA pan: 43.97 mg. In Reactor U-tube: 0.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 14. Nominal HC: 2.0  Measured HC: 2.15 (Std.cc/min)

Inlet Acetylene: 1.03%

Table E1. Catalyst Activity and Product Selectivities in Experiment 1.

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<th>Time (hr)</th>
<th>C₃H₂</th>
<th>S₉surf (%)</th>
<th>S₃C₅H₆ (%)</th>
<th>S₃C₂H₄ (%)</th>
<th>S₃C₄ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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<tr>
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</table>

This experiment was one of the first we ran using the TGA to monitor the catalyst weight gain during reaction. Because we were unsure of the effects of stopping the recirculation pump in order to measure catalyst weights, only a small number of C₄ analyses were conducted during the initial stages of operation. The experiment was run until almost complete deactivation, and at the very low conversions
observed in the final analyses, the accuracy of product selectivity measurements was very poor (125.73 and 144.80 hours, in table E1). Similarly, the amount of n-butane produced was very small and the integrator could not pick it up (table E2, below).

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C6+/C4+C6 (%)</th>
</tr>
</thead>
<tbody>
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<td>8.18</td>
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</tr>
<tr>
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<td>8.90</td>
<td>50.76</td>
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</tr>
<tr>
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<td>13.74</td>
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<td>36.03</td>
</tr>
</tbody>
</table>
Experiment #2. Starting Date: 8/16/87. Wt% Pd: 0.5  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 46.50 mg. Final: 44.68 mg. % Loss: 3.9

On TGA pan: 44.68 mg. In Reactor U-tube: 0.

Pretreatment: Standard.

Reaction Temperature: 40°C.


(Std. cc/min)

Inlet Acetylene: 1.03%

Table E3. Catalyst Activity and Product Selectivities in Experiment 2.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>S₄H₆ (%)</th>
<th>S₃H₄ (%)</th>
<th>C₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
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<td>11.01</td>
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</table>

During this experiment the recirculation pump was not shut off for catalyst weight measurements. The rate of weight gain was assumed proportionally equal to that observed during experiment #1. This was conducted to investigate the effects of shutting off the pump on conversion and product selectivity measurements. A much larger number of C₄ analyses were conducted during the initial stages of operation.
Table E4. C₄ Composition and %C₆⁺ in Experiment 2.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene C₆⁺ / (C₄+C₆⁺) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
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<td>28.92</td>
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</tr>
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<td>1.94</td>
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<td>12.24</td>
<td>8.96</td>
<td>42.79</td>
</tr>
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<td>37.54</td>
<td>14.82</td>
<td>10.19</td>
<td>35.72</td>
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<tr>
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<td>56.75</td>
<td>21.35</td>
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<td>5.62</td>
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</table>
Experiment #3. Starting Date: 8/30/87. Wt% Pd: 0.5 Al₂O₃: 33 m²/g.
Catalyst Weight: Initial: 56.20 mg. Final: 54.70 mg. % Loss: 2.7
On TGA pan: 54.70 mg. In Reactor U-tube: 0.
Pretreatment: Standard.
Reaction Temperature: 40°C.
(Std.cc/min)
Inlet Acetylene: 1.05%

Table E5. Catalyst Activity and Product Selectivities in Experiment 3.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>Ssurf (%)</th>
<th>C₂H₆ (%)</th>
<th>C₂H₄ (%)</th>
<th>C₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
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<td>15.97</td>
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</table>

This experiment was conducted to almost complete deactivation over a 33 m²/g alumina supported 0.5 wt% Pd catalyst for comparison with experiment #1. Like that one, product selectivities measured at very low (<5%) conversion were not included due to gross inaccuracies. N-
butane was measured accurately until deactivation began. After that point the total amount was too small even though the relative amount in the C₄ fraction appeared to be increasing.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene C₆/ (C₄+C₆) (%)</th>
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<td>21.27</td>
<td>12.71</td>
<td>15.85</td>
</tr>
<tr>
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<td>1.96</td>
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<td>22.49</td>
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</tr>
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Experiment #4. Starting Date: 9/14/87. Wt% Pd: 0.5 Al₂O₃: 33 m²/g.

Catalyst Weight: Initial: 59.34 mg. Final: 56.20 mg. % Loss: 2.7

On TGA pan: 59.34 mg. In Reactor U-tube: 0.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 36. Nominal HC: 1.50 Measured HC: 1.68
(Std.cc/min)

Inlet Acetylene: 0.35%

Table E7. Catalyst Activity and Product Selectivities in Experiment 4.

<table>
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<tr>
<th>Time (hr)</th>
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<th>S_{Surf} (%)</th>
<th>S₂H₂ (%)</th>
<th>S₂H₄ (%)</th>
<th>S₄ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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This experiment was carried out over the same catalyst type as that in experiment #3 with an inlet acetylene concentration of 1/3 that used in the latter. This was conducted in order to investigate the
effects of acetylene concentration on activity (the reaction order in acetylene), polymer selectivity and deactivation.

Table E8. C₄ Composition and %C₆+ in Experiment 4.

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<th>time (hr)</th>
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<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene C₆+/(C₄+C₆+) (%)</th>
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Experiment #5. Starting Date: 9/27/87. Wt% Pd: 0.5  \( \text{Al}_2\text{O}_3 \): 4 m\(^2\)/g.

Catalyst Weight: Initial: 61.50 mg. Final: 61.50 mg. % Loss: 0

On TGA pan: 61.50 mg. In Reactor U-tube: 0.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 17.5. Nominal HC: 2.50  Measured HC: 2.86
(Std.cc/min)

Inlet Acetylene: 1.09%

Table E9. Catalyst Activity and Product Selectivities in Experiment 5.

<table>
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<tr>
<th>Time (hr)</th>
<th>( \text{C}_2\text{H}_2 ) (%)</th>
<th>( S_{\text{Surf}} ) (%)</th>
<th>( \text{SC}_2\text{H}_6 ) (%)</th>
<th>( \text{SC}_2\text{H}_4 ) (%)</th>
<th>( \text{SC}_4+ ) (%)</th>
<th>Polymer (mg/ml)</th>
<th>( K )</th>
<th>Flow (ml/min)</th>
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This experiment was conducted over a 4 m\(^2\)/g alumina supported 0.5 wt% Pd catalyst to continue the comparison of the effects of catalyst surface area on activity and product selectivities. The catalyst activity (and conversion) was surprisingly low.
Table E10. C₄ Composition and %C₆₊ in Experiment 5.

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<th>butadiene (%)</th>
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Experiment #6. Starting Date: 10/5/87. Wt% Pd: 0.5 $\text{Al}_2\text{O}_3$: 4 m²/g.
Catalyst Weight: Initial: 58.70 mg. Final: 58.40 mg. % Loss: 0.5
On TGA pan: 58.40 mg. In Reactor U-tube: 0.
Pretreatment: Standard.
Reaction Temperature: 40°C.
Flow Rates: Helium: 10.5. Nominal HC: 1.50 Measured HC: 1.77
(Std.cc/min)
Inlet Acetylene: 1.12%

| Table E11. Catalyst Activity and Product Selectivities in Experiment 6. |
|------------------|---------------|-------------|-------------|-------------|---------------|-----------------|---------------|
| Time (hr) | $\text{C}_2\text{H}_2$ (%) | $S_{\text{Surf}}$ (%) | $\text{SC}_2\text{H}_4$ (%) | $\text{SC}_2\text{H}_4$ (%) | $\text{SC}_4^+$ (%) | Polymer (mg/ml) | K | Flow (ml/min) |
| 0.52 | 54.04 | 7.98 | 36.27 | 38.13 | 17.63 | 13.2 | 0.2501 | 1.274 |
| 1.43 | 59.67 | 6.91 | 40.56 | 32.69 | 19.84 | 39.5 | 0.1923 | 1.232 |
| 2.42 | 57.36 | 6.69 | 55.33 | 14.93 | 23.05 | 65.9 | 0.1759 | 1.348 |
| 3.48 | 55.40 | 6.36 | 68.49 | -0.41 | 25.56 | 88.9 | 0.1738 | 1.452 |
| 4.50 | 52.49 | 6.23 | 78.46 | -12.25 | 27.55 | 112.0 | 0.1663 | 1.525 |
| 5.72 | 49.78 | 5.81 | 88.02 | -22.58 | 28.74 | 131.7 | 0.1580 | 1.590 |
| 7.13 | 45.67 | 5.51 | 99.03 | -34.21 | 29.66 | 156.1 | 0.1413 | 1.654 |
| 10.40 | 37.48 | 4.53 | 123.72 | -60.15 | 31.90 | 197.6 | 0.1068 | 1.750 |
| 12.90 | 33.73 | 3.92 | 132.73 | -69.27 | 32.61 | 220.6 | 0.0904 | 1.768 |
| 17.40 | 29.82 | 3.06 | 138.94 | -74.64 | 32.63 | 253.6 | 0.0739 | 1.757 |
| 21.87 | 26.78 | 2.70 | 143.58 | -78.82 | 32.54 | 273.3 | 0.0625 | 1.776 |
| 28.50 | 23.37 | 2.69 | 141.83 | -76.18 | 31.66 | 303.6 | 0.0503 | 1.722 |
| 32.63 | 21.04 | 2.54 | 152.53 | -87.30 | 32.23 | 318.8 | 0.0439 | 1.765 |
| 41.25 | 17.89 | 2.25 | 162.33 | -96.06 | 31.47 | 343.1 | 0.0354 | 1.761 |
| 55.30 | 15.68 | 1.83 | 164.26 | -99.37 | 33.29 | 372.1 | 0.0297 | 1.762 |
| 74.60 | 12.25 | 1.67 | 166.31 | -123.85 | 35.87 | 400.4 | 0.0221 | 1.789 |
| 131.63 | 7.62 | 1.20 | 237.99 | -178.03 | 38.84 | 447.8 | 0.0129 | 1.794 |
| 195.87 | 7.47 | 0.80 | 194.92 | -128.89 | 33.16 | 467.6 | 0.0123 | 1.748 |
| 219.70 | 6.30 | 0.80 | 219.13 | -155.98 | 36.06 | 485.4 | 0.0102 | 1.774 |
| 241.87 | 4.60 | 0.89 | | | 493.3 | 0.0074 | 1.789 |
| 295.80 | 4.27 | 0.74 | | | 507.1 | 0.0068 | 1.779 |

This was essentially a repeat of experiment #5 to check that the significantly lower activity of this catalyst was real and not an artifact of some kind.
Table E12. C₄ Composition and %C₆⁺ in Experiment 6.

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<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆⁺/(C₄+C₆⁺) (%)</th>
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Experiment #7. Starting Date: 10/18/87. Wt% Pd: 0.5 Al₂O₃: 220 m²/g.

Catalyst Weight: Initial: 47.00 mg. Final: 44.90 mg. % Loss: 4.5

On TGA pan: 58.40 mg. In Reactor U-tube: 0.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 10.5. Nominal HC: 1.50 Measured HC: 1.77 (Std.cc/min)

Inlet Acetylene: 1.12%

Table E13. Catalyst Activity and Product Selectivities in Experiment 7.

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<th>C₂H₆ (%)</th>
<th>C₃H₄ (%)</th>
<th>C₄⁺ (%)</th>
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<th>K</th>
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This experiment continued our investigation of the effects of catalyst surface area.
Table E14. C₄ Composition and %C₆⁺ in Experiment 7.

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Experiment #8. Starting Date: 2/1/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 53.78 mg. Final: 52.03 mg. % Loss: 3.3

On TGA pan: 52.03 mg. In Reactor U-tube: 249.3 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 10.5. Nominal HC: 1.50  Measured HC: 1.85
(Std.cc/min)
Inlet Acetylene: 1.16%

The months of 11 and 12/87 and 1/88 were primarily spent connecting the Balzer's quadropole MS to the GC set-up through a glass jet separator and tuning the MS for optimal response. A number of long term experiments over 0.02 wt% Pd catalysts were also attempted during this time span, but the electrical power supply was not kind to us and terminated all but one of these before useful data could be collected. The only one which was not terminated was conducted under conditions where acetylene conversions were too low to accurately measure product selectivities.

The acetylene conversion over this catalyst sample was surprisingly high, and perhaps reflected some paranoia on our part that the experiences of the recent past did not occur again. This experiment was not repeated, however, because of the long time neccessary for deactivation.
Table E15. Catalyst Activity and Product Selectivities in Experiment 8.

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<th>Time (hr)</th>
<th>( \text{C}_2\text{H}_2 ) (%)</th>
<th>( S_{\text{surf}} ) (%)</th>
<th>( \text{SC}_2\text{H}_6 ) (%)</th>
<th>( \text{SC}_3\text{H}_4 ) (%)</th>
<th>( \text{SC}_4^+ ) (%)</th>
<th>Polymer (mg/ml)</th>
<th>( K )</th>
<th>Flow (ml/min)</th>
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<th>butadiene (%)</th>
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Experiment #9. Starting Date: 2/21/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 245.7 mg. Final: (237.7) mg. % Loss: (3.3)


Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 10.5. Nominal HC: 1.50  Measured HC: 1.80
(Std.cc/min)

Inlet Acetylene: 1.13%

Table E17. Catalyst Activity and Product Selectivities in Experiment 9.

<table>
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<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>S_Surf (%)</th>
<th>C₂H₆ (%)</th>
<th>S_C₂H₄ (%)</th>
<th>S_C₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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This catalyst sample was crushed to approximately 60-80 mesh in order to investigate possible acetylene pore diffusion effects causing the ethane selectivity increase observed during experiment #8. The
catalyst powder was placed in the U-tube between plugs of glass wool. For this reason the catalyst weight after pretreatment was unknown. We have assumed that the weight loss during pretreatment was the same as that observed over the whole pellets in #8 (3.25%). Surface polymer selectivities and the total polymer loadings are unknown; ethylene selectivities were calculated assuming polymer selectivities were zero (analogous to past investigations of this type). The values of ethylene selectivity in table E19 above actually represent the sum of ethylene and surface polymer selectivities.

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Experiment #10. Starting Date: 3/6/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 55.57 mg. Final: 52.72 mg. % Loss: 3.9

On TGA pan: 52.72 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 60°C.

Flow Rates: Helium: 10.5. Nominal HC: 1.50  Measured HC: 1.70
             (Std.cc/min)
             Inlet Acetylene: 1.08%

Table E19. Catalyst Activity and Product Selectivities in Experiment 10.

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<th>Sₐ₇H₆ (%)</th>
<th>Sₐ₇H₄ (%)</th>
<th>Sₐ₇CH₄ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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This experiment was conducted in order to investigate the effects of operation temperature on activity (activation energy), product selectivities, and deactivation.
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<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
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Experiment #11. Starting Date: 3/20/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 44.92 mg. Final: 43.32 mg. % Loss: 3.6
On TGA pan: 43.32 mg. In Reactor U-tube: 0 mg.
Pretreatment: Standard.
Reaction Temperature: 70°C.

Flow Rates: Helium: 14. Nominal HC: 2.00  Measured HC: 2.60
(Std.cc/min)
Inlet Acetylene: 1.21%

Table E21. Catalyst Activity and Product Selectivities in Experiment 11.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>Ssurf (%)</th>
<th>SC₂H₆ (%)</th>
<th>SC₂H₄ (%)</th>
<th>SC₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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</table>

This was a continuation of the effects of temperature on catalyst activity and product selectivities.
Table E22. $C_4$ Composition and $\% C_6+$ in Experiment 11.

<table>
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<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>$C_6+/(C_4+C_6+)$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
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<td>32.84</td>
<td>11.73</td>
<td>8.69</td>
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<td>49.93</td>
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<td>1.97</td>
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<td>14.06</td>
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<td>4.15</td>
<td>41.70</td>
</tr>
</tbody>
</table>
Experiment #12. Starting Date: 3/27/88. Wt% Pd: 0.1 \( \text{Al}_2\text{O}_3: 90 \text{ m}^2/\text{g} \).

Catalyst Weight: Initial: 34.00 mg. Final: 32.35 mg. % Loss: 4.8

On TGA pan: 32.35 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 70°C.

Flow Rates: Helium: 14. Nominal HC: 2.00 Measured HC: 2.64 (Std.cc/min)

Inlet Acetylene: 1.23%

Table E23. Catalyst Activity and Product Selectivities in Experiment 12.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>( \text{C}_2\text{H}_2 ) (%)</th>
<th>( S_{\text{Surf}} ) (%)</th>
<th>( \text{SC}_2\text{H}_4 ) (%)</th>
<th>( \text{SC}_2\text{H}_4 ) (%)</th>
<th>( \text{SC}_4\text{H}_4 ) (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.053</td>
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Another investigation of the effects of reaction temperature. Deactivation began immediately at this temperature, and had occurred earlier with increasing temperature below it. For this reason, higher temperatures were not used with this catalyst sample.
Table E24. C4 Composition and % C6+ in Experiment 12.

<table>
<thead>
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<th>time (hr)</th>
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<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C6+/C4+C6+ (%)</th>
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<td>39.62</td>
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</table>
Experiment #13. Starting Date: 3/16/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 35.92 mg. Final: 34.92 mg. % Loss: 2.8
On TGA pan: 35.92 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C

Flow Rates: Helium: 36.5. Nominal HC: 7.5  Measured HC: (9.0)
(Std.cc/min)  Inlet Acetylene: (1.53%/11.6 torr)

Table E25. Rates of Product Formation and Acetylene Pressures in Experiment 13.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>R₂C₂H₆</th>
<th>R₄C</th>
<th>R₆C⁺</th>
<th>P₃C₂H₂ (torr)</th>
</tr>
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<tr>
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<td>0.0414</td>
<td>0.0527</td>
<td>12.64</td>
</tr>
<tr>
<td>1.20</td>
<td>0.0136</td>
<td>0.0461</td>
<td>0.0616</td>
<td>11.80</td>
</tr>
<tr>
<td>1.57</td>
<td>0.0144</td>
<td>0.0490</td>
<td>0.0620</td>
<td>11.09</td>
</tr>
<tr>
<td>1.90</td>
<td>0.0153</td>
<td>0.0507</td>
<td>0.0651</td>
<td>11.17</td>
</tr>
</tbody>
</table>

rₜₜᵤₖₜₑₜₑ═0.80 mole/mole Pd*min

This was the first experiment conducted to measure the pressure dependence of both surface and gas phase polymer formation. For these experiments, the reactor system was filled with helium and the recirculation pump turned on only through the circulation loop (valve 5 open, 4 closed, and helium flowing through valve 6, figure 21, p. 162). The HC gas flow was turned on and monitored through the outlet sample valve. When the total HC pressure equalled the calculated, CSTR steady state value, valve 4 was opened and valve 5 closed, beginning reaction.
These experiments were performed in this way in order to minimize the change in reactant pressures during initial operation.

The production rates of ethane, \( C_2 \), and \( C_6 \) species in the following tables are calculated as moles of acetylene reacting to form each species per mole Pd per min. The values are calculated assuming a HC inlet flow rate of 1.2 times the nominal setting (experiments were terminated before steady state conditions were reached). The observed rate of surface polymer formation during the same reaction time scale is given after each table. The acetylene pressure used to compare rates from different experiments is the actual value observed, shown in the tables.
Experiment #14. Starting Date: 4/4/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 46.20 mg. Final: 45.70 mg. % Loss: 1.1

On TGA pan: 45.70 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 37.8. Nominal HC: 6.0  Measured HC: (7.2) (Std.cc/min)

Inlet Acetylene: (1.24%/9.41 torr)

Table E26. Rates of Product Formation and Acetylene Pressures in Experiment 14.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆⁺</th>
<th>P₃C₂H₂ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>0.0185</td>
<td>0.0431</td>
<td>0.0640</td>
<td>8.71</td>
</tr>
<tr>
<td>1.01</td>
<td>0.0140</td>
<td>0.0480</td>
<td>0.0651</td>
<td>8.93</td>
</tr>
<tr>
<td>1.54</td>
<td>0.0193</td>
<td>0.0494</td>
<td>0.0627</td>
<td>9.06</td>
</tr>
<tr>
<td>2.09</td>
<td>0.0183</td>
<td>0.0516</td>
<td>0.0635</td>
<td>9.11</td>
</tr>
<tr>
<td>2.54</td>
<td>0.0156</td>
<td>0.0546</td>
<td>0.0687</td>
<td>9.07</td>
</tr>
<tr>
<td>3.10</td>
<td>0.0190</td>
<td>0.0525</td>
<td>0.0650</td>
<td>9.02</td>
</tr>
</tbody>
</table>

rₚₑₓₚₑₓ = 0.72 moles/mole Pd⁺min
Experiment #15. Starting Date: 4/5/88. Wt% Pd: 0.1 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 50.40 mg. Final: 48.20 mg. % Loss: 4.4

On TGA pan: 50.40 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 41.0. Nominal HC: 4.50 Measured HC: (5.4)
(Std.cc/min)

Inlet Acetylene: (0.90%/6.85 torr)

Table E27. Rates of Product Formation and Acetylene Pressures in Experiment 15.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>P_C2H6</th>
<th>R_C4</th>
<th>R_C6+</th>
<th>P_{C2H2} (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.0300</td>
<td>0.0471</td>
<td>0.0614</td>
<td>6.39</td>
</tr>
<tr>
<td>1.02</td>
<td>0.0151</td>
<td>0.0485</td>
<td>0.0589</td>
<td>6.55</td>
</tr>
<tr>
<td>1.52</td>
<td>0.0159</td>
<td>0.0512</td>
<td>0.0647</td>
<td>6.68</td>
</tr>
<tr>
<td>2.02</td>
<td>0.0154</td>
<td>0.0527</td>
<td>0.0680</td>
<td>6.62</td>
</tr>
<tr>
<td>2.52</td>
<td>0.0166</td>
<td>0.0563</td>
<td>0.0717</td>
<td>6.66</td>
</tr>
</tbody>
</table>

r_{surf}=0.72 mole/mole Pd*min
Experiment #16. Starting Date: 4/6/88. Wt% Pd: 0.1 Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 46.70 mg. Final: 45.30 mg. % Loss: 3.0
On TGA pan: 45.30 mg. In Reactor U-tube: 0 mg.
Pretreatment: Standard.
Reaction Temperature: 40°C.
Flow Rates: Helium: 42.0. Nominal HC: 3.0 Measured HC: (3.6)
(Std.cc/min)
Inlet Acetylene: (0.61%/4.64 torr)

Table E28. Rates of Product Formation and Acetylene Pressures
in Experiment 16.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆⁺</th>
<th>P₉6H₂ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.0173</td>
<td>0.0301</td>
<td>0.0434</td>
<td>4.38</td>
</tr>
<tr>
<td>1.03</td>
<td>0.0125</td>
<td>0.0430</td>
<td>0.0506</td>
<td>4.37</td>
</tr>
<tr>
<td>1.51</td>
<td>0.0129</td>
<td>0.0443</td>
<td>0.0519</td>
<td>4.44</td>
</tr>
<tr>
<td>2.01</td>
<td>0.0227</td>
<td>0.0367</td>
<td>0.0422</td>
<td>4.47</td>
</tr>
<tr>
<td>2.54</td>
<td>0.0140</td>
<td>0.0484</td>
<td>0.0571</td>
<td>4.38</td>
</tr>
</tbody>
</table>

rₜₜₜ=0.70 moles/mole Pd*min
Experiment #17. Starting Date: 4/11/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 49.44 mg. Final: 47.44 mg. % Loss: 4.0

On TGA pan: 47.44 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 46.5. Nominal HC: 3.0  Measured HC: (3.6)
(Std.cc/min)

Inlet Acetylene: (0.56%/4.23 torr)

Table E29. Rates of Product Formation and Acetylene Pressures in Experiment 17.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆⁺</th>
<th>PC₂H₂ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.0413</td>
<td>0.0874</td>
<td>0.0995</td>
<td>3.70</td>
</tr>
<tr>
<td>1.04</td>
<td>0.0202</td>
<td>0.0788</td>
<td>0.0957</td>
<td>3.15</td>
</tr>
<tr>
<td>1.51</td>
<td>0.0333</td>
<td>0.0951</td>
<td>0.1141</td>
<td>3.14</td>
</tr>
<tr>
<td>2.01</td>
<td>0.0301</td>
<td>0.1012</td>
<td>0.1093</td>
<td>3.07</td>
</tr>
<tr>
<td>2.51</td>
<td>0.0269</td>
<td>0.1036</td>
<td>0.1213</td>
<td>3.03</td>
</tr>
</tbody>
</table>

r₅₅₉=0.62 moles/mole Pd*min
Experiment #18. Starting Date: 4/14/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 45.54 mg. Final: 43.94 mg. % Loss: 3.5
On TGA pan: 43.94 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 48.7. Nominal HC: 1.3  Measured HC: (1.56) (Std.cc/min)
Inlet Acetylene: (0.24%/1.83 torr)

Table E30. Rates of Product Formation and Acetylene Pressures in Experiment 18.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆+</th>
<th>PC₂H₂ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.0523</td>
<td>0.0572</td>
<td>0.0658</td>
<td>1.50</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0554</td>
<td>0.0551</td>
<td>0.0558</td>
<td>1.50</td>
</tr>
<tr>
<td>1.51</td>
<td>0.0285</td>
<td>0.0526</td>
<td>0.0639</td>
<td>1.55</td>
</tr>
<tr>
<td>2.01</td>
<td>0.0442</td>
<td>0.0629</td>
<td>0.0770</td>
<td>1.53</td>
</tr>
<tr>
<td>2.51</td>
<td>0.0434</td>
<td>0.0544</td>
<td>0.0672</td>
<td>1.58</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0369</td>
<td>0.0636</td>
<td>0.0763</td>
<td>1.52</td>
</tr>
</tbody>
</table>

rsurf=0.24 moles/mole Pd*min
Experiment #19. Starting Date: 4/15/88. Wt% Pd: 0.1  Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 50.54 mg. Final: 48.54 mg. % Loss: 4.0
   On TGA pan: 48.54 mg. In Reactor U-tube: 0 mg.
Pretreatment:  Standard.
Reaction Temperature: 40°C.
Flow Rates:  Helium: 48.3. Nominal HC: 1.7  Measured HC: (2.04)
   (Std.cc/min)
   Inlet Acetylene: (0.31%/2.38 torr)

Table E31. Rates of Product Formation and Acetylene Pressures in Experiment 19.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆⁺</th>
<th>PC₂H₂ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.0416</td>
<td>0.0436</td>
<td>0.0461</td>
<td>1.98</td>
</tr>
<tr>
<td>1.02</td>
<td>0.0726</td>
<td>0.0573</td>
<td>0.0580</td>
<td>2.03</td>
</tr>
<tr>
<td>1.50</td>
<td>0.1256</td>
<td>0.0606</td>
<td>0.0582</td>
<td>2.00</td>
</tr>
<tr>
<td>2.08</td>
<td>0.0463</td>
<td>0.0580</td>
<td>0.0594</td>
<td>1.98</td>
</tr>
<tr>
<td>2.53</td>
<td>0.0252</td>
<td>0.0666</td>
<td>0.0670</td>
<td>1.96</td>
</tr>
</tbody>
</table>

rₘₑₓ=0.36 moles/mole Pd•min
Experiment #20. Starting Date: 4/18/88. Wt% Pd: 0.1 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 58.54 mg. Final: 56.09 mg. % Loss: 4.2

On TGA pan: 56.09 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 25.0. Nominal HC: 10.0 Measured HC: (12.0) (Std.cc/min)

Inlet Acetylene: (2.51%/19.1 torr)

Table E32. Rates of Product Formation and Acetylene Pressures in Experiment 20.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>RC₂H₆</th>
<th>RC₄</th>
<th>RC₆⁺</th>
<th>P_{C₂H₂} (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.0152</td>
<td>0.0394</td>
<td>0.0450</td>
<td>20.15</td>
</tr>
<tr>
<td>1.02</td>
<td>0.0096</td>
<td>0.0407</td>
<td>0.0463</td>
<td>21.25</td>
</tr>
<tr>
<td>1.51</td>
<td>0.0093</td>
<td>0.0423</td>
<td>0.0478</td>
<td>21.87</td>
</tr>
<tr>
<td>2.02</td>
<td>0.0092</td>
<td>0.0444</td>
<td>0.0524</td>
<td>22.38</td>
</tr>
<tr>
<td>2.51</td>
<td>0.0093</td>
<td>0.0447</td>
<td>0.0523</td>
<td>22.67</td>
</tr>
<tr>
<td>3.02</td>
<td>0.0094</td>
<td>0.0474</td>
<td>0.0578</td>
<td>22.93</td>
</tr>
</tbody>
</table>

r_{surf}=0.85 moles/mole Pd*min
Experiment #21. Starting Date: 6/6/88. Wt% Pd: 0.02 Al_{2}O_{3}: 90 m^{2}/g.

Catalyst Weight: Initial: 66.00 mg. Final: 59.60 mg. % Loss: 9.7

On TGA pan: 59.60 mg. In Reactor U-tube: 1.473 g.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.65 (Std.cc/min)

Inlet Acetylene: 0.91%

Table E33. Catalyst Activity and Product Selectivities in Experiment 21.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C_{2}H_{2} (%)</th>
<th>S_{surf} (%)</th>
<th>S_{C}H_{4} (%)</th>
<th>S_{C_{4}} (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>43.62</td>
<td>31.96</td>
<td>5.20</td>
<td>56.52</td>
<td>6.33</td>
<td>2.9</td>
<td>0.2178</td>
</tr>
<tr>
<td>1.51</td>
<td>41.91</td>
<td>32.49</td>
<td>5.52</td>
<td>48.57</td>
<td>13.42</td>
<td>7.2</td>
<td>0.1517</td>
</tr>
<tr>
<td>2.52</td>
<td>42.96</td>
<td>31.19</td>
<td>4.35</td>
<td>45.21</td>
<td>19.26</td>
<td>10.1</td>
<td>0.1483</td>
</tr>
<tr>
<td>3.52</td>
<td>45.89</td>
<td>28.49</td>
<td>4.26</td>
<td>45.01</td>
<td>22.24</td>
<td>11.5</td>
<td>0.1601</td>
</tr>
<tr>
<td>4.50</td>
<td>46.17</td>
<td>27.85</td>
<td>4.15</td>
<td>41.77</td>
<td>26.24</td>
<td>13.9</td>
<td>0.1617</td>
</tr>
<tr>
<td>5.64</td>
<td>43.98</td>
<td>28.25</td>
<td>4.43</td>
<td>35.70</td>
<td>31.61</td>
<td>18.7</td>
<td>0.1520</td>
</tr>
<tr>
<td>7.62</td>
<td>46.53</td>
<td>25.31</td>
<td>4.83</td>
<td>36.87</td>
<td>33.00</td>
<td>24.0</td>
<td>0.1637</td>
</tr>
<tr>
<td>11.08</td>
<td>48.80</td>
<td>22.36</td>
<td>5.24</td>
<td>37.88</td>
<td>34.52</td>
<td>31.1</td>
<td>0.1755</td>
</tr>
<tr>
<td>17.21</td>
<td>49.56</td>
<td>17.99</td>
<td>5.74</td>
<td>40.61</td>
<td>35.67</td>
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<tr>
<td>25.53</td>
<td>48.93</td>
<td>14.68</td>
<td>7.32</td>
<td>41.42</td>
<td>36.58</td>
<td>62.3</td>
<td>0.1780</td>
</tr>
<tr>
<td>35.19</td>
<td>50.30</td>
<td>10.53</td>
<td>7.80</td>
<td>44.01</td>
<td>37.66</td>
<td>74.3</td>
<td>0.1856</td>
</tr>
<tr>
<td>48.39</td>
<td>52.44</td>
<td>6.80</td>
<td>8.94</td>
<td>49.03</td>
<td>35.23</td>
<td>91.0</td>
<td>0.1985</td>
</tr>
<tr>
<td>59.32</td>
<td>52.73</td>
<td>5.33</td>
<td>10.35</td>
<td>48.40</td>
<td>35.93</td>
<td>103.5</td>
<td>0.2015</td>
</tr>
<tr>
<td>69.35</td>
<td>52.89</td>
<td>4.49</td>
<td>12.15</td>
<td>46.12</td>
<td>37.24</td>
<td>112.6</td>
<td>0.2042</td>
</tr>
<tr>
<td>95.15</td>
<td>55.85</td>
<td>3.77</td>
<td>14.77</td>
<td>46.33</td>
<td>35.13</td>
<td>134.2</td>
<td>0.2253</td>
</tr>
<tr>
<td>120.84</td>
<td>55.31</td>
<td>3.79</td>
<td>18.81</td>
<td>41.63</td>
<td>35.78</td>
<td>150.9</td>
<td>0.2266</td>
</tr>
<tr>
<td>143.57</td>
<td>57.81</td>
<td>3.61</td>
<td>20.18</td>
<td>43.21</td>
<td>33.01</td>
<td>162.9</td>
<td>0.2456</td>
</tr>
<tr>
<td>170.12</td>
<td>58.75</td>
<td>3.55</td>
<td>22.98</td>
<td>40.21</td>
<td>33.26</td>
<td>174.9</td>
<td>0.2567</td>
</tr>
<tr>
<td>190.30</td>
<td>57.83</td>
<td>3.59</td>
<td>25.52</td>
<td>37.97</td>
<td>32.92</td>
<td>182.5</td>
<td>0.2536</td>
</tr>
<tr>
<td>217.91</td>
<td>57.71</td>
<td>3.56</td>
<td>27.76</td>
<td>36.96</td>
<td>31.72</td>
<td>191.6</td>
<td>0.2560</td>
</tr>
</tbody>
</table>

After a one month hiatus during which we were attempting to develop a GC routine to separate and identify both extracted surface polymers and the species remaining after extraction, we began to investigate 0.02 wt% Pd catalysts for comparison with the 0.1 and 0.5 wt% samples employed earlier. The first attempts were aborted after we
developed major system leaks in both the hangdown tube thermocouple wire tube and the outlet metal-glass connector. These air leaks are very easy to discover during operation, as air elutes at the same time as hydrogen and has a much greater TCD response factor (200 vs. 5).

This was the first successful run on the 0.02% sample. This experiment was not conducted until catalyst death because our understanding of the mechanism of deactivation at that time suggested that this would require operation for at least 1500 hours.

Table E34. C4 Composition and %C6, in Experiment 21.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C6/(C4+C6) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>0.42</td>
<td>33.88</td>
<td>9.60</td>
<td>8.34</td>
<td>47.76</td>
<td>9.37</td>
</tr>
<tr>
<td>1.91</td>
<td>2.21</td>
<td>31.97</td>
<td>9.97</td>
<td>8.11</td>
<td>47.74</td>
<td>24.41</td>
</tr>
<tr>
<td>2.88</td>
<td>1.55</td>
<td>32.59</td>
<td>10.49</td>
<td>8.23</td>
<td>47.15</td>
<td>29.81</td>
</tr>
<tr>
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Experiment #22. Starting Date: 6/16/88. Wt% Pd: 0.02 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 66.00 mg. Final: 59.60 mg. % Loss: 9.7

On TGA pan: 59.60 mg. In Reactor U-tube: 1.473 g.

Pretreatment: The catalyst sample from experiment 21 was evacuated at 40°C until no weight loss was observed in a 24 hour period. This took 90 hours and removed 1.10 out of 4.10 mg (26.8%) of surface polymer. Following evacuation, helium and HC gas flows were restarted at the same values as in experiment 21.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.65 (Std. cc/min)
Inlet Acetylene: 0.91%

Table E35. Catalyst Activity and Product Selectivities in Experiment 22.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>Ssurf (%)</th>
<th>SC₃H₆ (%)</th>
<th>SC₄H₁₀ (%)</th>
<th>SC₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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<td>10.45</td>
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This and the following two experiments were conducted to investigate the role of the surface polymer species in catalyst activation/deactivation and selectivity changes, and to compare the effects of different treatments on both the amount of polymer removed and subsequent reaction behavior.
Table E36. \( \text{C}_4 \) Composition and \%\( \text{C}_6 \), in Experiment 22.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>( \text{C}_6 )/( \text{C}_4 + \text{C}_6 ) (%)</th>
</tr>
</thead>
<tbody>
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Experiment #23. Starting Date: 6/20/88. Wt% Pd: 0.02 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 66.00 mg. Final: 59.60 mg. % Loss: 9.7

On TGA pan: 59.60 mg. In Reactor U-tube: 1.473 g.

Pretreatment: The catalyst sample from experiment 22 was treated in flowing hydrogen at 300°C for 2 hours. During this treatment the sample lost 3.15 out of 3.75 mg (84%) of the surface polymers present.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.65 (Std.cc/min)

Inlet Acetylene: 0.91%

Table E37. Catalyst Activity and Product Selectivities in Experiment 23.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>S_Surf (%)</th>
<th>Sc₃H₆ (%)</th>
<th>Sc₄H₄ (%)</th>
<th>Sc₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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Table E38. C₄ Composition and %C₆ in Experiment 23.

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<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆/(C₄+C₆) (%)</th>
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Experiment #24. Starting Date: 7/5/88. Wt% Pd: 0.02  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 66.00 mg. Final: 59.60 mg. % Loss: 9.7

On TGA pan: 59.60 mg. In Reactor U-tube: 1.473 g.

Pretreatment: The catalyst sample from experiment 23 was treated in flowing oxygen at 200°C for 1/2 hour, followed by hydrogen at 300°C for 2 hours. During this treatment the sample lost 2.25 out of 4.20 mg (53.6%) of the surface polymers present.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.60 (Std.cc/min)

Inlet Acetylene: 0.89%

Table E39. Catalyst Activity and Product Selectivities in Experiment 24.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>Ssurf (%)</th>
<th>SC₃H₄ (%)</th>
<th>SC₂H₄ (%)</th>
<th>SC₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.54</td>
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<td>16.05</td>
<td>101.6</td>
<td>0.1391</td>
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Table E40. C₄ Composition and %C₆ in Experiment 24.

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<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆/(C₄+C₆) (%)</th>
</tr>
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<td>17.05</td>
<td>13.82</td>
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<td>44.98</td>
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</table>
Experiment #25. Starting Date: 7/10/88. Wt% Pd: 0.02 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 57.00 mg. Final: 51.50 mg. % Loss: 9.6

On TGA pan: 51.50 mg. In Reactor U-tube: 0.1655 g.

Pretreatment: Standard.

Reaction Temperature: 80°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.18 (Std.cc/min)

Inlet Acetylene: 0.98%

Table E41. Catalyst Activity and Product Selectivities in Experiment 25.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>S₅surf (%)</th>
<th>S₁₇H₁₆ (%)</th>
<th>S₂₃H₄ (%)</th>
<th>S₄₄ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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</thead>
<tbody>
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<td>37.53</td>
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</table>

This reaction was conducted for comparison with experiment #12, using 0.1 wt% Pd sample on an identical support operated at 80°C, and to calculate the apparent activation energy over this catalyst sample.
Table E42. \( \text{C}_4 \) Composition and %\( \text{C}_6^+ \) in Experiment 25.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>( \text{C}_6^+/(\text{C}_4+\text{C}_6^+) ) (%)</th>
</tr>
</thead>
<tbody>
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<td>0.85</td>
<td>0.88</td>
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<td>8.31</td>
<td>47.90</td>
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</tr>
<tr>
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<td>35.76</td>
<td>12.23</td>
<td>9.21</td>
<td>42.08</td>
<td>43.07</td>
</tr>
<tr>
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<td>13.35</td>
<td>9.86</td>
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</tr>
<tr>
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</table>
Experiment #26. Starting Date: 8/16/88. Wt% Pd: 0.02  Al₂O₃: 90 m²/g.
Catalyst Weight: Initial: 50.00 mg. Final: 46.50 mg. % Loss: 7.0
On TGA pan: 46.50 mg. In Reactor U-tube: 0 mg.
Pretreatment: Standard.
Reaction Temperature: 120°C.
Flow Rates: Helium: 20. Nominal HC: 2.00  Measured HC: 2.15
(Std.cc/min)
Inlet Acetylene: 0.97%

Table E43. Catalyst Activity and Product Selectivities in Experiment 26.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₅ (%)</th>
<th>S₆H (%)</th>
<th>C₂H₆ (%)</th>
<th>C₂H₄ (%)</th>
<th>C₂⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
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</table>
This experiment was conducted to extend the temperature range over which the activation energy of the 0.02 wt% Pd catalyst could be calculated, and to observe the dependence of surface polymer selectivity on temperature over a wider range of temperatures than previously employed.

Table E44. C₄ Composition and %C₆⁺ in Experiment 26.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆⁺/(C₄+C₆⁺) (%)</th>
</tr>
</thead>
<tbody>
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<td>0.85</td>
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</table>
Experiment #27. Starting Date: 7/24/88. Wt% Pd: 0.5 \( \text{Al}_2\text{O}_3: 90 \text{ m}^2/\text{g.} \)

Catalyst Weight: Initial: 55.00 mg. Final: 48.20 mg. % Loss: 12.4

On TGA pan: 48.20 mg. In Reactor U-tube: 0 mg.

Pretreatment: Standard.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.35 (Std.cc/min)
Inlet Acetylene: 0.81%

Table E45. Catalyst Activity and Product Selectivities in Experiment 27.

<table>
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<tr>
<th>Time (hr)</th>
<th>( \text{C}_2\text{H}_2 ) (%)</th>
<th>( \text{S}_{\text{surf}} ) (%)</th>
<th>( \text{SC}_2\text{H}_6 ) (%)</th>
<th>( \text{SC}_2\text{H}_4 ) (%)</th>
<th>( \text{SC}_4+ ) (%)</th>
<th>Polymer (mg/ml)</th>
<th>( K )</th>
<th>Flow (ml/min)</th>
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This experiment was conducted as a test for reproducibility (the same sample and temperature had been used in experiment #1, 8/4/87) and to prepare a deactivated sample for experiment 28.
Table E46. C₄ Composition and %C₆₊ in Experiment 27.

<table>
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<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆₊/(C₄+C₆₊) (%)</th>
</tr>
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</table>
Experiment #28. Starting Date: 7/27/88. Wt% Pd: 0.5  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 55.00 mg. Final: 48.20 mg. % Loss: 12.4

On TGA pan: 48.20 mg. In Reactor U-tube: 0 mg.

Pretreatment: The sample from experiment #28 was evacuated at 40°C for 72 hours, until no further weight loss was observed. During this evacuation, 3.35 out of 11.85 mg (28.3%) of surface polymer was removed. Operation was restarted at identical conditions.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.50 (Std.cc/min)
Inlet Acetylene: 0.86%

Table E47. Catalyst Activity and Product Selectivities in Experiment 28.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>S_Surf (%)</th>
<th>S_C₂H₆ (%)</th>
<th>S_C₃H₄ (%)</th>
<th>S_C₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
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<td>13.60</td>
<td>0.71</td>
<td>70.53</td>
<td>-8.57</td>
<td>37.33</td>
<td>690.6</td>
<td>0.0502</td>
<td>2.513</td>
</tr>
</tbody>
</table>

Table E48. C₄ Composition and %C₆, in Experiment 28.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆⁺/(C₄+C₆⁺) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>0.93</td>
<td>52.13</td>
<td>19.14</td>
<td>13.12</td>
<td>14.68</td>
<td>46.14</td>
</tr>
<tr>
<td>1.89</td>
<td>2.19</td>
<td>54.92</td>
<td>20.96</td>
<td>13.27</td>
<td>8.67</td>
<td>47.91</td>
</tr>
<tr>
<td>2.90</td>
<td>1.39</td>
<td>56.75</td>
<td>21.96</td>
<td>13.45</td>
<td>6.46</td>
<td>46.20</td>
</tr>
<tr>
<td>3.91</td>
<td>2.16</td>
<td>56.73</td>
<td>22.01</td>
<td>13.29</td>
<td>5.81</td>
<td>45.44</td>
</tr>
<tr>
<td>6.16</td>
<td>2.21</td>
<td>57.15</td>
<td>22.00</td>
<td>13.24</td>
<td>5.40</td>
<td>43.47</td>
</tr>
<tr>
<td>9.39</td>
<td>2.39</td>
<td>57.94</td>
<td>21.82</td>
<td>13.12</td>
<td>4.73</td>
<td>43.62</td>
</tr>
<tr>
<td>25.36</td>
<td>4.25</td>
<td>58.55</td>
<td>20.49</td>
<td>12.98</td>
<td>3.72</td>
<td>39.75</td>
</tr>
</tbody>
</table>
Experiment #29. Starting Date: 7/31/88. Wt% Pd: 0.5  Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 55.00 mg. Final: 48.20 mg. % Loss: 12.4

On TGA pan: 48.20 mg. In Reactor U-tube: 0 mg.

Pretreatment: The sample from experiment #29 was evacuated at 200°C for 2 hours, then at 300°C for 3 hours. During this treatment the sample lost 9.15 out of 11.65 mg (78.5%). Helium and HC gas flows were restarted at 40°C.

Reaction Temperature: 40°C.

Flow Rates: Helium: 20. Nominal HC: 2.00 Measured HC: 2.50
(Std.cc/min)

Inlet Acetylene: 0.86%

This sample had no measurable activity during 5 hours operation.
Experiment #30. Starting Date: 9/13/88. Wt% Pd: 0.02 Al₂O₃: 90 m²/g.

Catalyst Weight: Initial: 272.2 mg. Final: (245.2) mg. % Loss: (10)

On TGA pan: 0 mg. In Reactor U-tube: (245.2) mg.

9.09 g alumina added to catalyst in U-tube.

Pretreatment: Standard.

Reaction Temperature: 80°C.

Flow Rates: Helium: 14. Nominal HC: 2.00 Measured HC: 2.50
(Std.cc/min)

Inlet Acetylene: 1.17%

Table E49. Catalyst Activity and Product Selectivities in Experiment 30.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>C₂H₂ (%)</th>
<th>Ssurf (%)</th>
<th>S₂H₆ (%)</th>
<th>S₂H₄ (%)</th>
<th>S₂C₄⁺ (%)</th>
<th>Polymer (mg/ml)</th>
<th>K</th>
<th>Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>44.48</td>
<td>0.00</td>
<td>4.67</td>
<td>78.60</td>
<td>16.74</td>
<td>0.0</td>
<td>1.3678</td>
<td>2.042</td>
</tr>
<tr>
<td>1.28</td>
<td>53.17</td>
<td>0.00</td>
<td>5.46</td>
<td>76.02</td>
<td>18.53</td>
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<td>1.2371</td>
<td>1.889</td>
</tr>
<tr>
<td>2.38</td>
<td>52.84</td>
<td>0.00</td>
<td>6.14</td>
<td>70.44</td>
<td>23.42</td>
<td>0.0</td>
<td>1.1377</td>
<td>2.045</td>
</tr>
<tr>
<td>3.62</td>
<td>52.92</td>
<td>0.00</td>
<td>7.03</td>
<td>65.87</td>
<td>27.10</td>
<td>0.0</td>
<td>1.1254</td>
<td>2.188</td>
</tr>
<tr>
<td>5.22</td>
<td>52.06</td>
<td>0.00</td>
<td>7.86</td>
<td>61.99</td>
<td>30.15</td>
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<td>1.0994</td>
<td>2.297</td>
</tr>
<tr>
<td>7.24</td>
<td>51.37</td>
<td>0.00</td>
<td>8.81</td>
<td>58.78</td>
<td>32.42</td>
<td>0.0</td>
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</tr>
<tr>
<td>9.52</td>
<td>53.45</td>
<td>0.00</td>
<td>9.03</td>
<td>56.97</td>
<td>34.00</td>
<td>0.0</td>
<td>1.1499</td>
<td>2.363</td>
</tr>
<tr>
<td>10.19</td>
<td>54.14</td>
<td>0.00</td>
<td>11.10</td>
<td>56.10</td>
<td>32.80</td>
<td>0.0</td>
<td>1.1838</td>
<td>2.394</td>
</tr>
<tr>
<td>14.43</td>
<td>60.85</td>
<td>0.00</td>
<td>28.29</td>
<td>39.54</td>
<td>32.17</td>
<td>0.0</td>
<td>1.6501</td>
<td>2.418</td>
</tr>
<tr>
<td>24.27</td>
<td>60.69</td>
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<td>34.28</td>
<td>33.36</td>
<td>32.36</td>
<td>0.0</td>
<td>1.7578</td>
<td>2.450</td>
</tr>
<tr>
<td>28.50</td>
<td>56.84</td>
<td>0.00</td>
<td>34.72</td>
<td>33.53</td>
<td>31.75</td>
<td>0.0</td>
<td>1.5451</td>
<td>2.497</td>
</tr>
<tr>
<td>35.67</td>
<td>56.33</td>
<td>0.00</td>
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<td>31.76</td>
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<td>2.525</td>
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<tr>
<td>49.78</td>
<td>56.90</td>
<td>0.00</td>
<td>40.30</td>
<td>27.76</td>
<td>31.94</td>
<td>0.0</td>
<td>1.6105</td>
<td>2.498</td>
</tr>
</tbody>
</table>

This experiment was conducted to investigate the effects of added alumina support on catalyst activity and selectivities. In particularly, we wanted to see if this addition would increase the selectivity to ethane, as ethylene might hydrogenate on the alumina due to hydrogen spillover induced activity.
Table E50. C4 Composition and %C₆⁺ in Experiment 30.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>n-butane (%)</th>
<th>1-butene (%)</th>
<th>trans-2-butene (%)</th>
<th>cis-2-butene (%)</th>
<th>butadiene (%)</th>
<th>C₆⁺/(C₄+C₆⁺) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>1.49</td>
<td>31.15</td>
<td>11.90</td>
<td>8.94</td>
<td>46.52</td>
<td>43.40</td>
</tr>
<tr>
<td>1.65</td>
<td>1.62</td>
<td>31.88</td>
<td>12.65</td>
<td>9.51</td>
<td>44.34</td>
<td>49.00</td>
</tr>
<tr>
<td>2.83</td>
<td>1.25</td>
<td>32.63</td>
<td>13.36</td>
<td>9.80</td>
<td>42.95</td>
<td>51.56</td>
</tr>
<tr>
<td>4.14</td>
<td>1.24</td>
<td>33.35</td>
<td>13.71</td>
<td>10.01</td>
<td>41.69</td>
<td>53.74</td>
</tr>
<tr>
<td>5.71</td>
<td>1.20</td>
<td>33.73</td>
<td>14.00</td>
<td>10.11</td>
<td>40.97</td>
<td>54.14</td>
</tr>
<tr>
<td>7.74</td>
<td>1.14</td>
<td>35.04</td>
<td>14.71</td>
<td>10.43</td>
<td>38.69</td>
<td>54.73</td>
</tr>
<tr>
<td>9.87</td>
<td>1.08</td>
<td>37.28</td>
<td>15.72</td>
<td>10.83</td>
<td>35.09</td>
<td>54.78</td>
</tr>
<tr>
<td>15.34</td>
<td>1.19</td>
<td>46.06</td>
<td>20.59</td>
<td>12.80</td>
<td>19.36</td>
<td>50.87</td>
</tr>
<tr>
<td>24.67</td>
<td>1.14</td>
<td>48.21</td>
<td>21.22</td>
<td>13.11</td>
<td>16.32</td>
<td>49.49</td>
</tr>
<tr>
<td>28.92</td>
<td>1.19</td>
<td>48.71</td>
<td>20.77</td>
<td>12.89</td>
<td>16.45</td>
<td>46.65</td>
</tr>
<tr>
<td>36.02</td>
<td>0.99</td>
<td>49.43</td>
<td>21.05</td>
<td>13.02</td>
<td>15.50</td>
<td>47.39</td>
</tr>
<tr>
<td>49.64</td>
<td>1.28</td>
<td>50.44</td>
<td>21.38</td>
<td>13.25</td>
<td>13.65</td>
<td>47.65</td>
</tr>
</tbody>
</table>
F. Reactor Modeling

Hydrocarbon species in the reactor definitely diffuse up the hangdown tube and into the TGA. We do not know the relative rates of diffusion of each species, but experiments using only the ethylene/hydrogen/acetylene feed, without catalyst samples present, suggest that each species diffuses in proportion to its reactor concentration, so that the relative concentrations of each in the TGA is approximately equal to that in the reactor. In this case, we can model the reactor as a system with two inlets - the HC mixture and helium inlets - and two outlets - the designated reactor outlet and the TGA.

Of the two outlets, the flow rate of any component in the reactor outlet is the concentration of that species times the total outlet flow rate, which is the sum of the observed HC inlet flow and the helium inlet flow. The rate of any component out of the latter is the relative concentration of that species times the "missing" HC flow rate.

In different terminology, we define the rate of reaction of any species as \( r = \text{out} + \text{acc(reactor)} + \text{acc(TGA)} - \text{in} \). The "out" term is the observed exit concentration times the total observed outlet flow (helium in + calculated HC in). The "acc(reactor)" term is the difference in concentration between subsequent analyses times the reactor volume (316.6 cc). The "in" term is the steady state calculated (real) inlet HC flow rate times the inlet concentration of that species. The "acc(TGA)" term is the product of the difference between the steady state (real) and calculated HC inlet flows and the relative concentration of the species in the reactor. The net result is
\( r = \text{out+acc-in,} \) where the flow rates in and out are the observed steady state values. Of course, as the calculated inlet flow rate approaches the observed steady state value, the accumulation term in the TGA approaches zero (diffusion reaches a pseudo-equilibrium, and will only change as the composition of the reactor gas phase changes).

In the second case we assume only ethylene – the major component of the hydrocarbon stream – diffuses into the TGA. In this case, there is no "acc(TGA)" term in the rate expression for any component except ethylene. The flow rate in is the steady state HC flow observed, while the flow rate of any species besides ethylene is the observed flow rate out. Because ethylene reaction rates are not calculated, and ethylene selectivities defined as the difference between 100% and the sum of all other product selectivities, the rate expression for ethylene reaction can also be ignored.

In the extreme case, we ignore the diffusion into the TGA and calculate the rates of reaction based only upon a CSTR model and the calculated inlet HC flow, essentially assuming that the mass flow controller really does take ten hours to warm up and reach the setpoint value.

The raw data from one experiment (see Appendix E, experiment #27) has been analyzed using all three of the models described above. The results of these calculations appear in the following figures.

Figures F1 and F2 show the calculated values of ethane and \( \text{C}_4 \) selectivities, respectively, for each case. Because ethane and \( \text{C}_4 \) selectivities are defined as the rate of production of each over the rate of acetylene consumption, and all three species (acetylene, ethane
and C₄⁺ are treated in the same way regardless of which assumption is used, the calculated values are very similar in all three cases.

Figure F1. Effects of different diffusion assumptions on calculated ethane selectivities. 1) all species diffuse into the TGA. 2) only ethylene diffuses. 3) there is no diffusion of any type.

Figure F2. Effects of different diffusion assumptions on C₄⁺ selectivities. See figure F1 for symbol definitions.
Values calculated assuming no diffusion occurs are slightly higher than the other two in both cases because the reduced inlet flow rate (assuming the calculated inlet flow rate is correct) increases the rate of consumption of acetylene relative to ethane and C₄⁺, as the concentrations of latter two are negligible in the inlet stream.

The calculated acetylene conversion is slightly more sensitive to the diffusion assumption we make (figure F3). Conversions calculated assuming no diffusion are substantially lower than those calculated assuming either type of diffusion because in this case the difference in the molar flow rates of acetylene in and out are reduced due to the assumption of a lower HC flow rate in.

![Conversion vs Time](image)

**Figure F3.** Effects of different diffusion assumptions on calculated acetylene conversions. See figure F1 for symbol definitions.

Because the rate of surface polymer formation is independent of the type of reactor model we employ (weights were directly measured),
the selectivity to surface polymers is more dependent on the diffusion assumption we use than ethane or C₄⁺ selectivities (figure F4).

![Graph showing surface polymer selectivity over time](image)

**Figure F4.** Effects of different diffusion assumptions on the surface polymer selectivity. See figure F1 for symbol definitions.

Surface polymer selectivities calculated assuming no diffusion are significantly higher than those calculated assuming either type of diffusion because the no diffusion assumption reduces the rate of acetylene hydrogenation (the rate of acetylene in is reduced relative to acetylene out) while the rate of polymer formation remains constant.

Similarly, the first order rate constant calculated assuming no diffusion is significantly decreased relative to the other two values because of the decreased rate of acetylene consumption at a constant catalyst loading (Figure F5). As with the rate of surface polymer formation, the amount of catalyst is independent of any assumptions we make about the reactor system behavior.
Figure F5. The effects of different diffusion assumptions on the first order rate constant. See figure F1 for symbol definitions.

The calculated ethylene selectivity is the most sensitive to changes in the diffusion model we employ. Ethylene selectivities are calculated as the difference between the 100% and the sum of all other product selectivities. As ethane, C₄ᵦ, and surface polymer selectivities are all increased by assuming no diffusion, the calculated ethylene selectivity in this case is reduced by the sum of all of these other increases (figure F6).

We should point out that both diffusion models used above are not strictly correct. In the overall carbon balance used to calculate apparent inlet HC flows, the outlet helium flow rate was assumed equal to the inlet helium flow rate. The correct assumption is that the total outlet flow must be equal to the total inlet flow.
Figure F6. The effects of different diffusion assumptions on calculated ethylene selectivities. See Figure F1 for symbol definitions.

The effect of the assumption we have made can be shown by an example from experimental data. Using the data in figure 27 (p. ), we calculated an apparent inlet HC flow of about 2.1 std.cc/min in the very initial stages of reaction. We arrived at this figure by observing that the total HC flow in corresponded to 13.0% of the total flow out. Helium was taken as 14 std.cc/min (the inlet He flow rate). The total flow is therefore 14/(1-0.13)=16.1, and the HC flow is 16.1-14=2.1 std.cc/min. The correct expression is that the HC flow is 13.0% of the outlet flow, which must be 16.35 std.cc/min (14+2.35). The apparent HC flow is then 2.13 and the outlet helium is 14.22 std.cc/min. The net result is that we have overestimated the rate of HC diffusion into the TGA by (0.25-0.22)/0.22=0.136 (13.6%).
This was not an accident, as we wanted to be sure of not
underestimating the extent of diffusion when investigating its effects
on activity and product selectivities. As there is no significant
difference between the limiting cases of diffusion (only ethylene vs.
each species diffusing) using this overestimation of its extent, we can
be sure that there will be no major effects of the actual extent of
diffusion in this portion of operation.
G. Reproducibility of Results

The question of reproducibility is of course very important in studies of this kind. We have conducted a number of experiments at practically identical conditions in order to investigate whether the results we have observed are reproducible. The next 21 figures compare the results of two experiments carried out at 40°C over identical 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst samples almost 1 year apart. The conversion over the second sample is slightly higher at all times (figure G1), but the inlet acetylene concentration in this case was slightly lower (0.81 vs 1.05%), while the total flow rates were very different (22.35 and 16.15 std.cc/min). For these reasons, comparisons of acetylene conversions are not very useful.

Figure G1. Acetylene conversion observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
A more useful comparison of catalyst activities is the first order rate constant (figure G2). The differences between conversion behavior are largely removed in this case. Surface polymer selectivities are essentially identical throughout the duration of each experiment (figure G3).

![Graph](image)

Figure G2. The first order rate constant calculated during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Ethane selectivities are somewhat higher in the second experiment during the first 10-15 hours (figure G4) and identical after that time. C₄⁺ selectivity behavior is largely the same; the values during the second experiment are slightly higher for the first 10 hours (figure G5). Ethylene selectivities, which are calculated as the difference of 100% and the sum of surface polymer, ethane, and C₄⁺ selectivities, are lower during the initial stages of the second experiment (figure G6), as we would expect from the previous figures.
Figure G3. Surface polymer selectivities observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G4. Ethane selectivities observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G5. C\textsubscript{4+} selectivities observed during operation at 40\textdegree C over 0.5 wt\% Pd on 90 m\textsuperscript{2}/g Al\textsubscript{2}O\textsubscript{3} catalysts. 1. Experiment 1. 8/4/87. 1.03\% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81\% inlet acetylene.

Figure G6. Ethylene selectivities calculated during operation at 40\textdegree C over 0.5 wt\% Pd on 90 m\textsuperscript{2}/g Al\textsubscript{2}O\textsubscript{3} catalysts. 1. Experiment 1. 8/4/87. 1.03\% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81\% inlet acetylene.

The percentage of C\textsubscript{6} species in the gas phase polymer is lower in case 2 after about 25 hours operation time (figure G7), while there is essentially no difference between the C\textsubscript{4} fraction percentages of 1,3-
butadiene and 1-butene over each sample (figure G8). Both the 1/2-butene and the trans/cis-2-butene ratios are higher in the second case after about 25 hours operation time, but are essentially identical during the earlier stages (figures G9 and G10).

The rate of polymer formation was higher in the first case after 10 hours of operation (figure G11). Alternatively, we could say that the amount of surface polymer was higher on the first sample at all times greater than 10 hours. Because we might suspect these reasonably high polymer loadings to affect the catalyst activity and selectivity values, we have gone back and compared all of the data from the previous figures at equal polymer loadings.

![Graph showing gas phase polymer % and time (hours)](image)

Figure G7. The percentage of C₆⁺ species in the gas phase polymer observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G8. The percentages of 1,3-butadiene and 1-butene in the C₄ fraction observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G9. The 1/2-butene ratios observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G10. The trans/cis-2-butene ratios observed during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G11. Surface polymer formation during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Although the conversion was higher on the second sample at all times, it was lower at all polymer loadings (figure G12). The behavior is, however, remarkably similar over both samples. The first order rate
constants also behave in very similar fashions (figure G13), although the value in the second case is higher at low polymer loadings, and lower at high loadings.

Surface polymer selectivities are essentially identical at all polymer loadings (figure G14), while ethane selectivities are somewhat higher over the second sample at low polymer loadings, and essentially equal as the amount of surface polymer increases (figure G15). Again, the trends in the values over each sample are remarkably similar. C₄+ selectivities are also higher over the second sample at low polymer loadings, and essentially equal at higher loadings (figure G16). Ethylene selectivities again differ as we expect from the behavior of the other product selectivities (figure G17).

Figure G12. Acetylene conversion compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G13. First order rate constants compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G14. Surface polymer selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G15. Ethane selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G16. C₄⁺ selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G17. Ethylene selectivities compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

The percentages of C₆, species in the gas phase polymers appear to be slightly higher over the first sample (figure G18), but we have no data points at low polymer loadings in this case (C₄ analyses were not conducted in the early stages of this reaction). The percentages of 1,3-butadiene and 1-butene in the C₄ fraction are again essentially identical at all polymer loadings (figure G19). The 1/2-butene ratio is lower over the first sample (figure G20), but we are again missing data points at low polymer loadings. The trans/cis-2-butene ratios are essentially identical (figure G21).
Figure G18. The percentage of C₆₆ species in the gas phase polymers compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G19. The percentage of 1,3-butadiene and 1-butene in the C₄ fraction compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
Figure G20. The 1/2-butene ratios compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.

Figure G21. The trans/cis-2-butene ratios compared at equal polymer loadings during operation at 40°C over 0.5 wt% Pd on 90 m²/g Al₂O₃ catalysts. 1. Experiment 1. 8/4/87. 1.03% inlet acetylene. 2. Experiment 27. 7/24/88. 0.81% inlet acetylene.
In order to accurately measure the catalyst weight during an experiment, it was necessary to shut off the circulation pump for up to 10 seconds. During this time period, it is possible that Pd surface sites may become available for ethylene adsorption and hydrogenation due to acetylene depletion in the static gas surrounding the catalyst pellet(s). If this occurs, the ethane selectivity calculated from the subsequent GC analysis may be artificially high. We have investigated this possibility during experiments at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst sample.

The first experiment was conducted in the usual manner, shutting off the circulation pump for weight measurements. During the second experiment the pump was left running continuously. Because the catalyst weight was not measured in the second case, surface polymer and ethylene selectivities are unknown, and comparisons at equal polymer loadings between the two experiments cannot be made. However, the conditions at which these two experiments were carried out were for all purposes identical, so we may use these comparisons as another measure of the reproducibility of our results.

The acetylene conversions observed during each experiment are very similar, if not identical (figure G22), as are the first order rate constants (figure G23). Ethane (figure G24) and C₄⁺ (figure G25) are also nearly identical in both cases. The percentage C₆⁺ in the gas phase polymers (figure G26), and the composition of the C₄ fraction (figures G27-29) are also identical during each experiment.
Figure G22. Acetylene conversion during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1) Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously. (Experiments 1 and 2).

Figure G22. First order rate constant calculated during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1) Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.
Figure G23. Ethane selectivities observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.

Figure G24. C₄⁺ selectivities observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1. Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.
Figure G26. The percentage of C₆₄ species in the gas phase polymers observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1 Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.

Figure G27. The percentage of 1,3-butadiene and 1-butene in the C₄ fraction observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1 Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.
Figure G28. The 1/2-butene ratios observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1 Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.

Figure G29. The trans/cis-2-butene ratios observed during operation at 40°C over a 0.5 wt% Pd on 90 m²/g Al₂O₃ catalyst. 1 Circulation pump shut off for catalyst weight measurements. 2. Circulation pump running continuously.

Based upon the almost exact correspondence of all values between the two experiments conducted at identical conditions (with and without...
shutting off the pump to measure the catalyst weight), we conclude that
the reproducibility of our results is very good. The generally close
correspondence of values observed during the first two experiments,
which were not conducted at identical conditions (both the inlet
acetylene concentration and the total flow rates were different) further
supports this conclusion. It would appear likely that the small
differences observed between these two experiments are due only to the
slightly different conditions used. Shutting off the circulation pump
for short periods of time, in order to record the catalyst weight, also
does not appear to effect the subsequent activity and selectivity
values. We should point out that this conclusion only applies to
experiments conducted in the same way. The pump was shut off for 5-10
seconds, and the next GC analysis was not conducted until 30 minutes
afterwards. Of course, if we were to leave the pump off for an extended
period of time and then take a sample 5 minutes later, it is likely that
serious changes, particularly in ethane selectivity values, would be
observed.
H. Detail of Extracted Surface Polymer Analysis.