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Selective hydrogenation of 1,3-butadiene in 1-butene over alumina supported palladium and palladium/copper catalysts

Furlong, Brian Keith, M.S.

Rice University, 1994
Rice University

Selective Hydrogenation of 1,3-Butadiene in 1-Butene Over Alumina Supported Palladium and Palladium/Copper Catalysts

by

Brian K. Furlong

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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Houston, Texas

September, 1993
Abstract

Selective Hydrogenation of 1,3-Butadiene in 1-Butene Over Alumina Supported Palladium and Palladium/Copper Catalysts

by

Brian K. Furlong

Copper addition to palladium increases both activity and selectivity in the selective hydrogenation of 1,3-butadiene to n-butenes. The bimetal catalyst (Cu/Pd:2/1(atomic)) hydrogenates the diene to virtually 100% conversion without significant n-butene isomerization or butane formation. While at moderate conversions monometallic palladium is quite selective for n-butene production, 1-butene is quickly isomerized and saturated at higher conversions resulting from butadiene's inability to monopolize the active surface at lower partial pressures. Copper also promotes higher trans-2-butene selectivity and modifies the rate dependence on 1,3-butadiene from zero to negative order. These results suggest a donor "ligand" effect in which copper changes the palladium's electronic character. The apparent activation energy for 1,3-butadiene hydrogenation over palladium is 14.9 ± 0.2 kcal/mol.
Acknowledgments

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Brian Furlong
Houston, TX
September, 1993
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<td>Al(61)</td>
<td>alumina (61 m²/g)</td>
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<tr>
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<td>butane</td>
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<td>Mass Flow Controller</td>
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I. Introduction

C₄ hydrocarbons have numerous uses in the petrochemical industry. 1,3-Butadiene (BD) is employed to make polybutadiene and styrene-butadiene synthetic rubbers. n-Butenes are utilized for both petrochemistry and gasoline production. In the production of linear low-density polyethylene (LLDPE), 1-butene is used as a co-monomer with ethylene. 2-Butenes are used to synthesize methyl-ethyl ketone (MEK) and alkylate. Methyl tertiary butyl ether (MTBE) and butyl rubber are produced from isobutene feedstocks (2).

In the United States, catalytic cracking and industrial thermal operations are the greatest sources of butylenes (27.9 billion pounds produced in 1989, 3). Since these processes are not highly discriminating, selective hydrogenation is widely used to remove trace quantities of butadiene and butyne impurities from the n-butene cut prior to use in some demanding reactions. In the purification of butene streams prior to alkylation, production of LLDPE, and other petrochemical processes, the concentration of 1,3-butadiene must be decreased to a few parts per million. Pd catalysts are used because of their high activity at low temperature, high selectivity for the hydrogenation of acetylenes and diolefins without significant saturation of the olefins, and relative stability in the presence of most organic impurities. Unfortunately these catalysts also have the following problems (4):

1) Pd catalyzed isomerization of n-butenes occurs rapidly in the absence of butadiene. This hampers the production of high purity 1-butene for use in LLDPE feedstocks due to 1-butene loss by isomerization to 2-butenes.

2) Pd-catalyzed oligomerization of 1,3-butadiene fouls the catalyst and causes a loss in activity with time on stream.
3) COS, H$_2$S, and some mercaptans poison Pd catalysts.

Currently, the catalysts most widely used for industrial selective hydrogenation employ Pd as the active ingredient, often with the addition of a second metal, supported on a porous refractory oxide. In particular, the addition of group Ib metals increases activity, selectivity, and stability for the hydrogenation of certain target hydrocarbons. Recently, the selective hydrogenation of butadiene has been studied over Pd-Ag(5,6,7), Pd-Co(8), Pd-Cr(9), Pd-Au(7), and Pd-Zn (10) unsupported and supported catalysts.

The objective of this work was to prepare a set of bimetallic Cu-Pd catalysts to selectively hydrogenate 1,3-butadiene impurity in 1-butene streams without 1-butene loss. To accomplish this objective computer automated equipment were constructed to speed the acquisition of characterization and hydrogenation data. Temperature programmed reduction was used to analyze catalyst reducibility and composition. The effect of copper addition on the palladium catalyzed hydrogenation of 1,3-butadiene was studied in a plug flow reactor.
II. Literature Survey

The Selective Hydrogenation of 1,3-Butadiene over Transition Metal Catalysts

E.F. Meyer and R.L. Burwell Jr. 1963

Meyer, et al. studied 1,3-butadiene hydrogenation/deuteration over alumina supported Pd as early as 1963 (11). The vapor reactions were performed in a flow reactor at 40°C with varying H2/BD ratios. They found that for H2/BD < 0.9 the formation of butane was only 0.1% of the total product and that the selectivities were invariant for hydrogen or deuterium. The selectivities were: 0.048, 0.420, and 0.532 for c-2-butene, t-2-butene, and 1-butene respectively. At hydrogen/butadiene ratios > 0.9 significant amounts of butane and 1,3-butadiene were detected in the product. They described a typical run:

Once butane appeared, the content in 1-butene fell rapidly, that in cis- and trans-2-butene rose. For example, for a sample with 4.2% butane and no butadiene, we give the observed percent and in parentheses, the per cent if butene isomerization had not occurred: cis-2-butene 17.1 (4.6), trans-2-butene 52.3 (40.2), and 1-butene 26.4 (51.0).

Meyer et al. also suggested a mechanism for 1,3-butadiene hydrogenation that was based on deuteration and n.m.r. experiments. They found that the isotopic distribution patterns of 1-B and t-B (the two major products) were nearly identical and that nearly 70% of the initial products were CH2FCH=CHCH2F and CH2=CHCHFCH2F (F is a deuterium atom). The mechanism involved a π-adsorbed butadiene followed by reaction with H- at carbon 4 to give an adsorbed allylic species that further reacts with H- at carbon atoms 1 or 3. They explained an observed higher than equilibrium trans/cis-2-
butene ratio (8.75, equilibrium is \( \approx 2.9 \) at 40\(^\circ\)C) as the result of steric hindrances between the adsorbed butadiene's terminal methyl groups.

Bond, Wells et al. 1964

Early work on the selective catalytic hydrogenation of BD over 5 mole % metal supported on alumina was reviewed by Bond and Wells in 1964 (12-14). In each case the reaction orders were positive in hydrogen and zero or negative order in BD, indicating a very strong adsorption of HC relative to \( \text{H}_2 \). The strengths of adsorption for the reactants were: 1,3-butadiene > butenes > hydrogen > n-butane. Initial n-butene and trans/cis 2-butene ratios were determined for various metals.

Over all catalysts, except those containing Pd, butane was an initial product of the batch reaction from 0-250\(^\circ\)C and \( \text{H}_2/\text{BD} \) ratios as high as 4 for alumina supported and bulk metals. In addition, the other metals studied (Ru, Rh, Pt, and Ir) exhibited a temperature and pressure dependence on the initial rate of butene vs. butane production.

Trans/cis ratios for the catalysts studied did not correspond to thermodynamic equilibrium. Fe, Ni, Cu, Rh, Os, Ir, and Pt supported on alumina all gave trans/cis ratios below equilibrium values at temperatures of 240, 80, 110, 80, 70, -20, and 15\(^\circ\)C respectively, while the Pd (at 20\(^\circ\)C eq. \( \approx 3.2 \)) and Co (at 125\(^\circ\)C eq. \( \approx 2.2 \)) catalysts both had ratios of near 10. They used this observation as evidence that butene isomerization does not occur before desorption for Pd and Co catalyst and speculated that the high trans/cis ratios for these catalysts may reflect the relative amounts of gas phase BD in the syn or anti (which predominates) conformation during reaction. They also reported Trans/Cis \( \approx 1.6 \) for the Pd/alumina catalyzed hydroisomerization of 1-butene at 0\(^\circ\)C, which is well below the equilibrium value of 3.6.
After a mechanistic isotopic tracer study of BD hydrogenation (13), Bond and co-workers proposed the following steps: adsorption of hydrogen and/or butadiene, formation of a reversible half-hydrogenated C₄H₇(ad) species, and the hydrogenation of this species to butene. Isomerization was explained by the inter-conversion of butenes through an adsorbed C₄H₉ intermediate that is absent for Pd catalysts.

Wells and Bates (14) studied the BD hydrogenation over Pd, Pt, Rh, and Ir wires. For the Pd sample, a rapid decrease in trans/cis 2-butene ratios (14.4 at 10°C and 2.6 at 190°C) with a simultaneous increase in 1-butene vs. 2-butene formation occurred with increased temperature. They attributed this phenomenon to the increasing importance of BD interaction with Pd by one double bond at higher temperatures. They also found that butene product composition (or selectivity) was dependent on temperature but was independent of activity, initial H₂ pressure, and BD conversion between 0 and 50%. After 50%, the yield of 1-B fell while those of butane and 2-butene rose. They concluded that the reaction mechanism was a characteristic of the metal whether supported or not.

Bates et al. 1970

In 1970, Bates and co-workers (15) investigated BD hydrogenation over 5 mole% Rh, Pd, and Pt catalysts supported on α-alumina. In a deuteration study over these catalysts they determined that butene surface species produced by hydrogenation of BD desorb before isomerizing. Their results agree with the previous results of Bond and Wells (13,14) for Pd. While stepwise addition was the dominant mechanism for butene formation, sites at which fast multiple exchange occurs also exist. They speculated that butane formation sites may be distinct from those where butene formation occurs.
Furukawa et al. 1973

In a series of three papers published in 1973 (16-18), Furukawa, et al. reported the effects of various additives on the liquid phase selective hydrogenation of a typical industrial C4 fraction under plug flow (single pass flow reactor) and batch conditions. Their attention was in the following areas: removal of BD over Pd/alumina catalysts (16), removal of BD over various metal catalysts in the presence of CO(17), and 1-B preparation from BD(18).

The effects of presulfiding with H2S and the effects of some inorganic compounds during the hydrogenation of BD were examined over a 0.1 wt%Pd/Al(95m^2/g) catalyst. They found that to obtain high selectivities for low BD concentrations it was necessary to presulfide the catalyst with H2S at low temperatures and to maintain a sulfur presence in the reaction system, although this also caused a loss in activity. 100 ppm of H2S were sufficient for BD removal down to 20 ppm with little butene loss. In addition, they found that isomerization was slow in the presence of BD and that Pd catalysts treated in H2S showed a strong resistance to poisoning; catalyst life was projected at 1-2 years. Moreover, addition of Cl2, COCl2, N2O, N2O3, and SO2 to the gas stream also improved reaction selectivities. CO completely depressed the isomerization of 1-B.

CO virtually eliminated 1-butene isomerization with Pd but had a lesser effect on isomerization for the other metals studied (Pd > Ni > Pt ~ Co). Although CO addition increased selectivity by reducing isomerization it also penalized the activity of the reaction (Fe > Pt > Co > Pd > Ni). For the Pd catalyst, high temperatures raised the activity, but increased the amount of 1-B that isomerized as well. At 100°C, 100% BD removal was achieved with 90% of the 1-B remaining. Moreover the effects of CO on the Pd catalyst
were reversible. Approximately 250 ppm of H$_2$S or a CO/H$_2$ ratio of $\approx$0.4 in the reactant stream was required for best results in the hydrogenation of BD.

Boitiaux et al. 1983-5

In 1983 Boitiaux et al (19,20) studied the effect of palladium dispersion on $\alpha$-alumina(9m$^2$/g) and silica in the hydrogenation of 1,3-Butadiene and 1-butyne. They prepared 15 different catalysts by impregnation with Pd(AcAc)$_2$/benzene(19) with dispersions between 10 and 100%. Both hydrocarbons showed a marked dependence of turn over frequency (TOF) on dispersion (See Figure 1) while the intermediate alkenes showed no such dependence. Additional IR studies with the chemisorption of CO on these catalysts showed large shifts in the CO spectrum with increased dispersion, indicating an increased strength of adsorption for small Pd particles. They concluded that the dependence of TOF on dispersion is due to much stronger adsorption of the highly unsaturated hydrocarbons on the smaller Pd particles than on the larger crystallites and suggested that addition of an electron donating compound (ligand) to the catalyst may be beneficial to activity.
TOF vs. Dispersion for 1,3BD Hydrogenation

Figure 1) TOF dependence on dispersion for 1-By hydrogenation on Pd/Alumina
Boitiaux et al. (21)

Selectivities for parallel reactions tB/cB and 1B/2B's were invariant with dispersion. They proposed that the tB/cB ratio formed by butadiene hydrogenation (12.0 eq ≈ 3.2) at 20°C may be attributable to the predominance of the anti form (95%) in BD, in agreement with Bond (12).

<table>
<thead>
<tr>
<th>Dispersion %</th>
<th>15</th>
<th>37</th>
<th>44</th>
<th>60</th>
<th>81</th>
</tr>
</thead>
<tbody>
<tr>
<td>% nB at 90% 13BD conversion</td>
<td>0.45</td>
<td>0.6</td>
<td>1.5</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>%nB at 99% 13BD conversion</td>
<td>2</td>
<td>3.7</td>
<td>3.9</td>
<td>7.8</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Table 1) Typical Butane Product Composition - Boitiaux et al. (20)

Later (1985), Boitiaux et al. (21) studied the effect of adding an electron donating compound (piperidine) to the reaction mixture in the hydrogenation of 1,3-butadiene and 1-butyne (1By). Upon addition of piperidine, TOFs and selectivities for 1By increased considerably at the higher dispersions (for dispersions > 80% TOFs were 4-5 times higher)
while no effect was seen at dispersions less than 20%. In addition, the rate of hydrogenation of 1-butene decreased considerably decreased (40 times lower). Surprisingly, BD hydrogenation was unchanged with piperidine addition. An IR study of CO adsorption indicated that the electron donating species such as piperidine can transfer charge to the COπ* anti bonding orbital at high dispersions; however, at low dispersion this becomes insignificant when the metal bulk dilutes any additional negative charge. They explained this effect on hydrogenation activities qualitatively by a schematic "volcano" curve (Figure 2) representing the effect of TOF on Dispersion and addition of piperidine.

**Effect of Dispersion and Piperidine on 1By, 1-B, and 13BD TOFs**

![Graph showing the effect of dispersion and piperidine on 1By, 1-B, and 13BD TOFs.](image)

<table>
<thead>
<tr>
<th>Adsorption Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volcano Curve</td>
</tr>
<tr>
<td>High D. With Disp.</td>
</tr>
<tr>
<td>Low Disp.</td>
</tr>
<tr>
<td>High D. w/o Piperid.</td>
</tr>
</tbody>
</table>

**Figure 2**) Effect of dispersion and piperidine on 1By, 1-B, and BD TOFs

Boitiaux et al. (21)
In a review of hydrogenation catalysts in 1985, Boitiaux and coworkers discussed the applicability of recent results to industrial situations. They proposed (21) that the stability of organic species adsorbed on Pd can be controlled by choosing an appropriate ligand (e.g. piperidine). This can be particularly important in the case of alkynes and diolefins that strongly bind to Pd and in some cases lead to dissolution of Pd from the catalyst support (e.g. vinylacetylene). Since nitrogen containing additives generally must be removed from the product stream before the product can be used in further reactions they are not economical in industrial applications. They found that group Ib metals when added to Pd catalysts were donor ligands that acted similarly to piperidine and could solve this problem.

Nagamoto et al. 1986

In 1986 Nagamoto and Inoue (22) studied the hydrogenation of butadiene over a Pd membrane. Hydrogen contacted the hydrocarbon gas after permeation through the Pd membrane, the rate of which was controlled by the hydrogen pressure. They found that under conditions of hydrogen permeation limitation (BD pressure was > 20kPa) the selectivity was invariant with product compositions of approximately (57% 1-B, 31% t-B, 10% c-B, and 2% Butane, estimated from their figure #3) and the activity was almost linear with the rate of hydrogen permeation. For lower BD pressures (< 20 kPa) the rate of reaction depended on BD partial pressure and showed a remarkable change in product composition with a sharp increase in butane formation, loss in 1-Butene, and increase in 2-Butenes. They also found that for similar H$_2$ pressures the rate of hydrogenation for the permeated hydrogen was much faster than that of the catalysts reacted in a H$_2$/HC mixture. For hydrogen mixture systems, they concluded that the surface H$_2$ concentration
is very small because butadiene adsorption and/or reaction strongly affects hydrogen adsorption.

Boitiaux et al. 1987

Boitiaux et al. published further studies on the liquid phase hydrogenation of 1-B, BD, and 1-By over Pd, Pt, and Rh alumina and silica supported catalysts. Their focus was in the following areas: Kinetic study of hydrogenation over Pt, comparison of the kinetics of Pt and Pd with Rh, and the quantitative selectivity ranking of all three metals using a single reaction scheme. The studies were performed in a continuous stirred tank reactor (CSTR) at constant pressure and temperature.

In studies of Pt catalysts (23), the hydrogenation of butadiene was zero order in BD and first order in H₂; their results were invariant with dispersion and effectively modeled by a "simple" Langmuir-Hinshelwood equation. On the other hand, 1-By exhibited a strong dependence of TOF on catalyst dispersion (similar to Fig 2) and an apparent negative order for 1-By hydrogenation. They found that at low 1-By concentrations the rate equation was invariant with hydrocarbon for any metallic dispersion and that at high 1-By concentrations the apparent negative order increased from 0 to near -1 with increasing dispersion. The following empirical equation fit their rate data well, where K' is a constant for a given catalyst and increases with dispersion.

\[ v = \frac{k}{1 + K'C_{ar}} \]  \hspace{1cm} (A)

Boitiaux explained these results by an equilibrium between active Pt sites and inactive Pt sites complexed by two 1-By molecules. The active form would come from the adsorption
of a single 1-By molecule: Pt-By. Assuming an equilibrium in which $K'$ is the "multi-
complexation constant" they obtained:

\[
\text{Pt-By + By } \leftrightarrow \text{By-Pt-By}
\]

active $K'$ inactive

From this theory and the assumption that the reaction rate is equivalent to the surface area
covered by Pt-By, they found the following rate equation:

\[
v = k \frac{KC_{by}}{1 + KC_{by}(1 + K' C_{by}) + K_cC_o}
\]  \hspace{1cm} (B)

The surface being covered with the most unsaturated HC ($K_{by} >> 1 + K_C C_o$) gives the
experimental equation (A).

In a similar study with Rh supported on alumina (24), they found a sensitivity to
dispersion for both BD and 1By hydrogenation and a negative order rate dependence at
high dispersions. Tables 2 and 3 compare the results of these three metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Negative Apparent Order?</th>
<th>1-B</th>
<th>1,3-BD</th>
<th>1-By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Pd</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Rh</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 2) Negative apparent order at high dispersions of Pt, Pd, and Rh supported catalysts
Boitiaux et al. (24)

<table>
<thead>
<tr>
<th>Metal</th>
<th>TOF Sensitivity to Dispersion?</th>
<th>1-B</th>
<th>1,3-BD</th>
<th>1-By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Pd</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Rh</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 3) Sensitivity of TOF on dispersion of Pt, Rh, and Pd supported catalysts
Boitiaux et al. (24)
In each case, except the Pd/BD system, the reaction kinetics was accurately described by either equation (A) or a simple Langmuir-Hinshelwood model. Tables 4 and 5 show the values of $k$ and $K'$ found for the various metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Disp</th>
<th>1-B</th>
<th>1,3-BD</th>
<th>1-By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td></td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Pd</td>
<td>90</td>
<td>20</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Rh</td>
<td>90</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

Table 4) Multi-complexation constants for Pt, Pd, and Rh - Boitiaux et al. (24)

<table>
<thead>
<tr>
<th>Metal</th>
<th>1-B</th>
<th>13BD</th>
<th>1By</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>13</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Pd</td>
<td>19</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Rh</td>
<td>25</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 5) Intrinsic kinetic constant for Pt, Pd, and Rh - Boitiaux et al. (24)

Next, Boitiaux and coworkers developed a system of ranking the selectivities of Pt, Pd, and Rh in terms of a single reaction equation for all three catalysts. They found that Pt and Rh behave similarly and are not very different from Pd except for their initial formation of butane for these catalysts. The derivation of this equation is given in the Dimensionless Selectivities section of this dissertation. These results fit the following scheme:
where $BD =$ butadiene, $B1 = 1$-butene, $B2 = 2$-butenes, $Ba =$ butane, 
$k =$ reaction coefficients, $K =$ adsorption coefficients.
$k1: BD ightarrow 1\text{-}B, k2: 1\text{-}B ightarrow nB, k3: BD ightarrow nB, k4: 1\text{-}B ightarrow 2\text{-}B, \text{and } k': BD ightarrow 2\text{-}B.$

Selectivity for formation of $1\text{-}B$ from Butadiene (1-2 addition) $S^{1-2} = \frac{k1}{k1' + k3}$

Selectivity of 1-4 addition: $S^{1-4} = \frac{k1'}{k1}$

Selectivity of direct formation of butane: $S^{ba} = \frac{k3}{k1}$

Selectivity of consecutive reactions: $Sc = \frac{k1}{k2 + k4} \frac{Kbd}{Kb1}$

<table>
<thead>
<tr>
<th>Metal</th>
<th>13BD Hydrogenation</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>trans/cis</td>
<td>S(BA)</td>
<td>S(1-4)</td>
<td>S(1-2)</td>
<td>Sc</td>
</tr>
<tr>
<td>Pt</td>
<td>3.7-4</td>
<td>.4-.9</td>
<td>.3-.5</td>
<td>.7-1.3</td>
<td>3</td>
</tr>
<tr>
<td>Pd</td>
<td>12</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Rh</td>
<td>3.5</td>
<td>.3-.6</td>
<td>.6-.9</td>
<td>.7-1.2</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6) Dimensionless Selectivities of Pt, Pd, and Rh - Boitiaux et al. (25)

In addition Boitiaux et al. observed that for a great variety of catalysts the
formation of butane coincided with low trans/cis 2-butene ratios during BD hydrogenation
(25). This trend appeared to be general and to have mechanistic significance. They
hypothesized that butane formation occurs from a semi-hydrogenated species originating
from a syn-diadsorbed BD from which c-B also forms. They proposed the reaction scheme given in Figure 3.

They hypothesized the following:

1) 1-B can come from either syn or anti adsorbed BD: the trans and cis forms come from anti and syn species, respectively.

2) The high trans/cis ratio of Pd reflects a very low conformational inter-conversion (c.i.) of adsorbed BD. For Pd catalysts the trans/cis ratio is a direct indication of the anti/syn ratio (about 19 in gas phase) of BD. On the other hand, for metals like Pt and Rh the inter-conversion is significantly higher.

3) For Pd the main products formed from BD are 1-B and t-2B; c-2B formation is negligible and thus the reaction mechanism follows closely that described in the left hand side of the figure. For Pt and Rh the mechanism is probably a combination of both right and left hand sides for which conformational inter-conversion is high.

Figure 3) Proposed Reaction Scheme for BD hydrogenation - Boitiaux et al. (25)
In a series of articles published in 1987-88, Oudar, Pradier, et al (26-28) reported the hydrogenation of BD on single crystals. Their paper in 1987 (26) dealt with BD hydrogenation and H₂-D₂ exchange on Pt(110). They found that the kinetics of hydrogenation depended on hydrogen pressure. At high hydrogen pressures (P₁H₂ > 130 torr) the reaction was first order in hydrogen and zero order in BD. Below 125 torr of hydrogen, the hydrogen reaction order changed from first to second order and the selectivity towards butane decreased as the hydrogen pressure decreased. LEED analysis following the reaction at high hydrogen pressures revealed a monolayer of randomly oriented BD molecules. At lower hydrogen pressures more carbon deposited on the catalyst than was observed at higher hydrogen pressures. They speculated that deactivation occurs by the selective poisoning of hydrogen dissociation sites by some hydrocarbon species.

The reaction mechanism that Oudar and co-workers proposed is based on the formation of half-hydrogenated butadiene as the rate determining step. They concluded that hydrogen dissociation is unlikely to be rate limiting because the H₂-D₂ equilibration reaction was an order of magnitude faster than the hydrogenation reaction. They measured an activation energy for BD hydrogenation of 39.3 KJ/mol.

Later, Pradier et al (27) studied 1,3-butadiene hydrogenation over Pt(100). They proposed a kinetic model in which hydrogen dissociatively adsorbs but does not compete with hydrocarbon adsorption, and where the hydrogenation of the C₄H₇(ad) species is the rate determining step. However, in this model the reaction is 1/2 order with respect to H₂. Furthermore, they indicated that butane mainly forms from the hydrogenation of 1-butene. They also examined the role sulfur plays in altering the kinetics of BD.
hydrogenation, finding that the overall reaction order and activation energy varied with sulfur coverage.

Additional studies by Pradier et al (28) concerned BD hydrogenation over Pt(111). The reaction orders for hydrogen and butadiene were first and zero, respectively. They concluded that butadiene hydrogenation is structure sensitive on a clean surface with the TOF increasing with the roughness of the surface: Pt(111) < Pt(100) < Pt(110).

Ouchaib 1989

In 1989 Ouchaib et al (29) studied the competitive hydrogenation of butadiene and butenes on Pt and Pd catalysts. In order to distinguish between the hydrocarbon formed in the reaction and the molecules already present as reactants, their experiments followed the sequence: competitive hydrogenation of a BD-propene mixture, and competitive hydrogenation of a 1-B-propene mixture. They employed a modified Langmuir-Hinshelwood model with hydrocarbons and hydrogen competing for the same sites on an energetically uniform surface and dissociative adsorption of hydrogen. In addition, they assumed that the reaction and adsorption coefficients of the 3 butene isomers are similar.

\[
R_{\text{cd}}(p) = \frac{k_{\text{cd}} A \text{bd} P_{\text{cd}} f(H_2)}{(1 + A \text{bd} P_{\text{bd}} + A \text{d} P_{\text{d}} + A n \text{h} P_{\text{h}}^2)}
\]

and for propene

\[
R_{p}(b) = \frac{k_{p} A \text{bd} P_{p} f(H_2)}{(1 + A \text{bd} P_{bd} + A \text{p} P_{p} + A n \text{h} P_{h}^2)}
\]
Thus the ratio of the hydrogenation rates is a linear function of the ratio of partial pressures:

\[
\frac{R_{bd}}{R_p} = \frac{(k_{bd}A_{bd})}{(k_pA_p)} \frac{P_{bd}}{P_p}
\]

This equation is similar to that proposed earlier by Boitiaux et al. for 1-butyne and butadiene hydrogenation (30). From the slope of this plot the ratio of adsorption and reaction coefficients can be calculated. In the absence of propene the rate of butadiene hydrogenation can be expressed as \( R_{bd}(0) = k_{bd}f(H_2) \), from which comes a simplified equation that is independent of reaction coefficients:

\[
\frac{R_{bd}(0)}{R_{bd}(p)} = 1 + \left( \frac{A_p}{A_{bd}} \right) \frac{P_p}{P_{be}}
\]

The adsorption and reaction coefficient ratios are given in table 7:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Abd/Abe</th>
<th>kbd/kbe</th>
<th>Rbd/Rbe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/SiO2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>2.9</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Stabilized</td>
<td>12</td>
<td>0.33</td>
<td>3.9</td>
</tr>
<tr>
<td>Pt/SiO2</td>
<td>0.95</td>
<td>0.8</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 7) Reaction and Adsorption Coefficient Ratios - Ouchaib, et al. (29)

bd = BD, be= butenes

They concluded that the high selectivity of Pd for the competitive hydrogenation of BD is due to the higher capacity of the metal for adsorbing the diene relative to the alkene.
Riley 1989

Riley (2) studied the gas-phase hydrogenation of 1,3-butadiene over various supported Pd catalysts. The kinetics of the reaction on a 0.02% Pd/alumina catalysts were studied in the presence and absence of CO for which the activation energies were 15.5 ±0.5 and 13.3±0.8 kcal/mol, respectively. CO addition suppressed BD hydrogenation, the rate being proportional to the negative one-half power of the CO pressure in the range of 25 to 145 ppm CO. This effect was associated with decreased surface hydrogen caused by adsorbed CO. Riley also completed some tracer studies with $^{13}$C labeled 1-butene showing that butane was the hydrogenation product of n-butenes. He did not conclusively state whether or not butane was formed directly from BD.

Boitiaux et al. 1989

In a continuing investigation of the liquid phase hydrogenation of BD, Boitiaux et al. published two papers in 1989 on the influence of nitrogen-, Ph-, O-, S-, and Cl-containing compounds on the catalytic performance of Pt and Rh catalysts. They examined the effect of CO and piperidine co-adsorption on the IR spectra over Pt and Rh and found that the CO absorption band was shifted to lower frequencies (e.g. CO was less strongly adsorbed) by the piperidine. It had been recently established that a similar shift can be observed by changing CO coverage on Pt because of dipole-dipole coupling between the chemisorbed species. However, in a similar study on Pt with the co-adsorption of CO and some electron donating compounds (e.g. benzene), Primet et al. (31) showed that the dipole-dipole coupling effect can be neglected and the large shifts in
CO IR absorption frequencies can be attributed to electron transfer. Therefore, Boitiaux et al. interpreted their results by the following:

the chemisorption of electron-donor compounds induces an electron transfer towards Pt which increases the extent of back-donation from platinum towards carbon monoxide.

The effects of piperidine on the hydrogenation reactions are summarized in table 8.

<table>
<thead>
<tr>
<th>Metal</th>
<th>1-B</th>
<th>1,3-BD</th>
<th>1-By</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TON</td>
<td>TON</td>
<td>TON</td>
</tr>
<tr>
<td>Pt</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Pd</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Rh</td>
<td>S-</td>
<td>+</td>
<td>S+</td>
</tr>
</tbody>
</table>

Table 8) HC apparent reaction order for different hydrogenation systems with piperidine addition - Boitiaux et al. (32)  
S= Slightly

They concluded that piperidine decreases the "self-inhibition" of the highly dispersed catalyst due to strong adsorption and that electron donating compounds act like ligands, which can decrease the electron deficient character of the small metal particles. In terms of selectivities, Boitiaux et al. observed an increase in both the selectivity for direct formation of 1-B from BD (S1-2) and the selectivity of consecutive reactions (Sc). A high value of Sc means that very little 1-B is converted to B.

Next, Boitiaux and coworkers discussed the additive effects of other inorganic molecules to Pt catalysts (33). By investigating a variety of compounds, they were able to divide the additives into two categories: acceptor ligands (containing O-, S-, or Cl-), and donor ligands (containing N- or P-, e.g. piperidine).

The effects of these additives on activities and selectivities are shown in tables 9 and 10:
<table>
<thead>
<tr>
<th>Additive</th>
<th>Cadd/Cbd</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>13BD</td>
<td></td>
<td></td>
<td></td>
<td>1-B</td>
</tr>
<tr>
<td>BD</td>
<td>TOF</td>
<td>TOF/a</td>
<td>0.6</td>
<td>0.12</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(s^-1)</td>
<td>(s^-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>3</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Piperidine</td>
<td>0.036</td>
<td>1.6</td>
<td>0.53</td>
<td>0.6</td>
<td>0.12</td>
<td>0.23</td>
</tr>
<tr>
<td>(CH3)3CCI</td>
<td>0.033</td>
<td>2.3</td>
<td>0.77</td>
<td>3.6</td>
<td>0.72</td>
<td>0.94</td>
</tr>
<tr>
<td>CO</td>
<td>1.00E-04</td>
<td>0.25</td>
<td>0.083</td>
<td>0.6</td>
<td>0.12</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 9) Effect of Various Additives on Activity of BD Hydrogenation

Cadd= additive conc., Cbd = BD conc., TOF/a = TOF with additive

Boitiaux et al. (33)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Cadd/Cbd</th>
<th>Sp(Ba)</th>
<th>Trans/Cls</th>
<th>Sp(1-2)</th>
<th>Sp(1-4)</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>0.87</td>
<td>3.3</td>
<td>0.7</td>
<td>0.54</td>
<td>3</td>
</tr>
<tr>
<td>Piperidine</td>
<td>0.036</td>
<td>0.37</td>
<td>3.8</td>
<td>1.17</td>
<td>0.49</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.38</td>
<td>4.2</td>
<td>1.18</td>
<td>0.47</td>
<td>100</td>
</tr>
<tr>
<td>(C4H9)3P</td>
<td>0.135</td>
<td>0.56</td>
<td>3.8</td>
<td>1</td>
<td>0.43</td>
<td>n.m.</td>
</tr>
<tr>
<td>(C2H5)2O</td>
<td>0.038</td>
<td>0.77</td>
<td>3.4</td>
<td>0.77</td>
<td>0.53</td>
<td>2.5</td>
</tr>
<tr>
<td>CO</td>
<td>1.00E-04</td>
<td>0.84</td>
<td>3.2</td>
<td>0.75</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>C4H9SH</td>
<td>7.10E-05</td>
<td>1.1</td>
<td>3.6</td>
<td>0.64</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>(CH3O)2SO2</td>
<td>0.039</td>
<td>1.5</td>
<td>3</td>
<td>0.48</td>
<td>0.56</td>
<td>2.5</td>
</tr>
<tr>
<td>(CH3)3CCI</td>
<td>0.028</td>
<td>1.6</td>
<td>2.5</td>
<td>0.44</td>
<td>0.63</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>1.7</td>
<td>2.5</td>
<td>0.43</td>
<td>0.61</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 10) Additive effects on selectivity of BD hydrogenation

Boitiaux et al. (33)

See pgs. 12-13 for an explanation of selectivities

They attributed the observed activity and selectivity changes to a shift in the volcano curve (Figure 2). Donor ligands shift to the left on the curve and acceptor ligands shift to the right. However, this method does not give a conclusive understanding of the effects of the additives on reaction rates of 1-B and BD, because the relative positions of the two hydrocarbons with respect to the curve's maximum is unknown.

Another mechanism proposed is based on the work of Hub et al. (34). Using mass and microwave spectroscopy, Hub et al. found that 1-By hydrogenation proceeds either through a mono-adsorbed species giving 1-B or through a multi-adsorbed species
(carbenes and carbynes) giving n-butane. This led Boitiaux et al. to propose the mechanism for BD hydrogenation shown in Figure 4.

They concluded that for a metal which does not promote carbene formation, e.g. Pd, the thermodynamic equilibrium of anti and syn BD would be reflected in the adsorbed BD species and would preferentially follow path I to give high trans/cis 2-butene ratios and little butane. On the other hand, a metal which allows carbene formation would have both direct butane formation from BD and inter-conversion between adsorbed cis and trans butene species prior to desorption (e.g. Pt and Rh).

They further concluded that the additive effect of the electron accepting ligands would reinforce the HC metal bond and thus promote carbene formation, while donor ligands would have the opposite effect.
Figure 4) Proposed Mechanism for BD Hydrogenation over Pd, Pt, and Rh Catalysts
Boitiaux (33)
Meyer et al. 1990

Meyer and coworkers (5) studied the selective gas phase hydrogenation of BD and H₂-D₂ exchange on unsupported polycrystalline palladium-silver alloys. They examined the catalytic behavior of Pd, 10%Ag-Pd, and 30%Ag-Pd in a CSTR. The alloys were prepared in an induction oven by melting the physical mixture, followed by treatment at high temperature in a reducing atmosphere. Before hydrogenation reactions, all samples were oxidized and reduced at 800°C. Meyer et al. found:

1) Apparent activation energy decreased with increasing silver content.
2) The initial rate of BD hydrogenation was a maximum for the 10%Ag/Pd alloy.
3) H₂-D₂ exchange was negligible on Pd and 30%Ag/Pd, although it was significant on the 10%Ag/Pd alloy.
4) Butene selectivity was nearly 100% for the 30%Ag/Pd alloy.

The activation energies found are given in table 11.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Pd 42</th>
<th>10%Ag/Pd 17</th>
<th>30%Ag/Pd 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-70</td>
<td>kcal/mol 10</td>
<td>4.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 11) Eapp as found in Meyer et al. (5)

Primet et al. 1990

Primet et al. studied the influence of support on the gas phase deactivation of Pt catalysts in the hydrogenation of BD (35). They used MgO, alumina, silica/alumina, and HY as supports with Pt loadings from 0.5-1.0 wt %. The kinetic experiments were carried out in a flow reactor at 333K with gas flow ratios of 3:10:97 1,3-butadiene, hydrogen,
and argon, respectively. For Pt supported on HY and alumina the activity decreased drastically and after 10 hours on stream stabilized near 2% and 35% of their original activities, respectively. Pt supported on MgO and SiO₂-Al₂O₃ exhibited a decrease and subsequent increase in TOF for BD hydrogenation. The SiO₂-Al₂O₃ supported catalyst had the greatest increase in TOF and almost regained its initial activity after 10 hours on stream. The authors cite work by Sarkany et al (36) who had observed a similar increase in acetylene hydrogenation activity using Pd/alumina. The migration of carbonaceous deposits, formed during deactivation, enabled activated hydrogen to "spill-over" onto the alumina for ethyne hydrogenation. The total loss in activity, observed by Primet et al. for the HY supported catalyst, was explained by the total polymer build-up inside support cavities, which would prevent reactants from reaching Pt sites.

They concluded that support acidity may induce an electron transfer through the metal-support interface that modifies the bond strength of unsaturated hydrocarbons with the metal sites thereby changing reaction activities and selectivities. In addition, they state that the acidic and porous properties of the support may affect the catalyst deactivation process.

Sarkany et al. 1992

Sarkany et al (6) examined the catalytic effects of Ag addition to Pd supported on α-alumina or Na modified alumina. Kinetics and selectivities were studied under plug flow conditions at ambient temperatures and atmospheric pressure. By increasing the reduction temperature, they were able to increase both the activities and selectivities for the Na containing samples. However, reduction at 423 and 623K made little difference in the results for the α-alumina supported catalysts. Selectivity and activity were higher for
the α-alumina supported catalyst. Reaction orders were near zero for BD and slightly less than unity for hydrogen for all samples. Activation energies ranged from 54 to 67 kJ/mol and selectivities depended strongly on H₂ pressure.

They also studied the hydrogenation of $^{13}$C-BD/1-B (1:20) in a batch reactor for the α-alumina supported catalysts with an H₂/BD ratio of 1.2. In each case 1-B selectivity remained positive above 90%. However, the Pd-only catalyst showed at least a factor of two more butane at high BD conversions. From the tracer studies (Table 12) they observed a decrease in butane formation from BD and an increase in trans/cis 2-butene ratios produced from BD. These results agree with the earlier work of Boitiaux et al. (23-25) and indicate a ligand donor effect of Ag on Pd.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Conv %</th>
<th>nB</th>
<th>1-B</th>
<th>t-B</th>
<th>c-B</th>
<th>Trans/Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Pd</td>
<td>95.3</td>
<td>0.22</td>
<td>0.13</td>
<td>0.47</td>
<td>0.17</td>
<td>2.76</td>
</tr>
<tr>
<td>1Pd1Ag</td>
<td>98.2</td>
<td>0.16</td>
<td>0.34</td>
<td>0.37</td>
<td>0.13</td>
<td>2.85</td>
</tr>
<tr>
<td>1Pd2Ag</td>
<td>96.3</td>
<td>0.07</td>
<td>0.62</td>
<td>0.27</td>
<td>0.04</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Table 12) Results of $^{13}$C Tracer studies and Selectivities(BD) for Pd/Ag Catalysts. H₂/BD=1.2, S=Selectivity. 13C= $^{13}$C Sarkany et al. (209)

Miura et al. 1992

Miura et al (7) studied the selective hydrogenation of BD on egg-shell type alumina supported Pd-Ag and Pd-Au catalysts. The Au and Ag preferentially deposited on the Pd particles through a liquid phase reduction of the catalysts. CO adsorption confirmed this result. The "fresh" catalysts were studied in a pulse reactor between 0 and 120°C to vary the conversion. Addition of Au and Ag to the Pd catalyst suppressed both butane and 2-butene formation even at low concentrations of BD.
Recently, Sarkany et al (10) investigated the support effects of ZnO on the Pd catalyzed gas phase hydrogenation of BD. They prepared several Pd catalysts using various precursors and studied their hydrogenation in a plug flow reactor. Hydrogen treatment at temperatures exceeding 423K caused a marked decrease in activity and a simultaneous increase in selectivity for butene formation. This thermal treatment caused partial reduction of the ZnO support and resulted in the formation of Pd-Zn inter-metallic phases (XRD results). H2 chemisorption, CO chemisorption, and XPS measurements suggested that Zn metal "decorated" Pd crystallites which significantly decreased the availability of Pd adsorption sites. The TOFs, reaction orders and activation energies found for these catalysts were independent of Zn decoration. High temperature reduction also decreased the trans/cis 2-butene ratio, which they hypothesized was due to the slow inter-conversion between the syn and anti conformation of BD adsorbed on the reduced Zn surface.

The hydrogenation of BD over alumina supported Pd-Co catalysts was also analyzed (8). TOFs were higher on the Pd-Co catalyst than on Pd or Co monometallic catalysts. This was attributed either to weakening the BD complexation or increasing the number of BD adsorption sites in the vicinity of Pd or Pd-Co ensembles. 1-Butene isomerization commenced in the presence of higher BD concentrations over Pd-Co than was observed over the Pd sample during the hydrogenation of a BD/1-B mixture. Co by itself did not cause significant 1-B hydrogenation, although it did promote BD hydrogenation at higher temperatures.
III. Equipment Design, Automation, and Procedures

The equipment was designed to obtain high quality information about catalyst characterization and reaction kinetics. A chemisorption apparatus was constructed for temperature programmed reduction (TPR), temperature programmed desorption (TPD), and chemisorption measurements. A batch reactor\(^1\) and plug flow reactor (one pass flow reactor) were constructed for isotopic, deactivation, and "steady state" selectivity studies.

Catalyst preparation prior to use in hydrogenation reactions often includes high temperature treatments in air (to remove surface impurities, e.g., organic species) and hydrogen (reduced metal surface required for hydrogenation reaction). How these steps are carried out can have a great impact on the properties of the catalyst (e.g. dispersion). With the addition of a second metal this temperature sensitivity becomes critical as the movement of one metal relative to the other can have profound effects on both activity and selectivity. A computer controlled linear temperature ramp ensured catalysts exactly the same thermal history regardless of which apparatus was being used.

Experiments were automated to speed data acquisition and provide reliable data. Following is a number of variables encountered during previous work\(^2\) (* = computer controllable):

I. Catalyst Preparation Methods  
   A. pH of solution  
   B. Pretreatment of support  
   * C. Calcination  
   D. Reduction  
II. Batch Reactor  
   A. Pressure of gases  
   * B. Time

---

\(^1\)Basic design taken from Sarkany Antal, Institute of Isotopes, Budapest, Hungary  
\(^2\)Unpublished Work at the Institute of Isotopes, Budapest, Hungary.
An IBM 286 computer equipped with data acquisition (AD510 and DA600 Real Time Devices Inc.) boards provided data acquisition and control. The AD510 was a 12 bit A/D converter with 8 single ended input channels and 9 TTL channels for control of sampling valves. The board read between -5 to +5 volts, allowed programmable gains of 1,10 and 100, and could read information at 7 Hz. The 12-bit DA600 board had a 0-10 volt output.

Temperature was read after the thermocouple voltage was linearized and amplified by an electronic device. The resulting voltages were calibrated between 0 and 80°C using a platinum resistance thermometer to obtain thermocouple temperature readings ±0.3°C in this range. Above 80°C the temperature was assumed linear with the thermocouple device output, which according to specs should be within ±2°C all the way up to 750°C.

GC and TCD signals -10 to 10 Volts (used for the reactors and chemisorption device, respectively) were read after division. The accuracy of the reading depends entirely on the signal size as the software uses the highest gain possible for any input.

---

3Designed and Built by Dick Chronister
4Accuracy ± 0.0001 °C, Courtesy of Dr. Kobayashi
0-5 V D/A outputs controlled gas flowrates to the plug flow reactor and the furnace temperature. A furnace controller\textsuperscript{5} converted the voltage signal to a variable A/C furnace input. An MKS 247C flow meter allowed partial pressures of four different gasses to be set manually while the total flow rate (space velocity) was adjusted by a computer controlled 0-5 V set point signal.

\textsuperscript{5}Designed and Built by Dick Chronister
A. Furnace Control

The objective was to construct a computer controlled furnace to heat a quartz reactor at precisely 20°C/min, and to reach temperatures as high as 750°C. This would ensure that each time the catalyst is heated it will have exactly the same thermal history and will eliminate a large portion of the uncertainty involved in testing catalysts under different reaction or pretreatment conditions. The furnace design characteristics required for controllability are:

1) The reactor must be enclosed in the furnace (physical).
2) The furnace must react quickly to an input voltage step change.
3) The furnace must be able to reach temperatures as high as 750°C
4) The furnace must be removable from the reactor so a liquid bath may be used to control the temperature during hydrogenation reactions.

Traditionally, bulky 6-7 pound ceramic furnaces (see fig 5) were used for both pretreatment (oxidation/reduction) and reaction temperature control. Mainly, the reactors were designed for steady-state reaction studies and were never meant to be operated under transient conditions.

![Figure 5) Design of Old Furnaces Used in Laboratory](image)
The design ultimately used (Figure 6) included high temperature heating tape (Omega) and a ceramic insulator (Kaowool) which together could withstand temperatures up to 750°C for limited periods. This arrangement satisfied all the conditions for controllability discussed earlier.

![Top View](image)

![Side View](image)

Figure 6) New Furnace Design
The heat balance equation for the system was used for implementing computer temperature control. Unfortunately this equation is highly nonlinear and so the furnace required thorough characterization.

\[
\alpha(T) = \text{Specific Heat of Reactor} \\
T = \text{Temperature} \\
t = \text{time} \\
\frac{\alpha dT}{dt} = Qin - Qout \\
Qin = \sum_{i=1}^{n} (\text{Power Input to Furnace}) \cdot h_i \\
h_i = \text{Scaling Vector} \\
Qout(T, t) = \text{Power loss}
\]

**Heat Balance Used for Furnace Temperature Control**

Pin(Input) (Power as a function of D/A input) was measured by taking voltage and current readings at a variety of D/A inputs. A fourth degree polynomial fit the curve well (fig. 7).

Qout (T) was found by setting a constant input power and waiting for SS. A typical plot is shown in fig. 8.

We calculated the specific heat (α) for three different temperature regions. (0-150°C, 150-500°C, and 500-750°C). Within each of these regions a power step change was implemented and the specific heat was calculated with the following equation:

\[
\alpha(T) = \frac{Pin - Qout(T)}{dT/dt}
\]
Furnace Power Input vs. D/A Input

![Graph of Furnace Power Input vs. D/A Input for a Typical Furnace](image)

Figure 7) Furnace Power Input vs. D/A Input for a Typical Furnace

Furnace Power Loss vs. Reactor Temperature

![Graph of Furnace Power Loss vs. Temperature for a Typical Furnace](image)

Figure 8) Power Loss vs. Temperature for a Typical Furnace
In using the previous equation we made the tenuous assumption that the reactor is close to SS and that Qin = Pin and Qout(T,t) = Qout(T). This was by no means an accurate calculation of α and was only used to provide a first approximation.

The time weighted vector $h_i$ was calculated by the following procedure: split up the total temperature range into 3 equal regions; use PI control to achieve a steady state temperature in the middle of each region; send a power impulse to the reactor, and record the resulting temperature output while keeping the power input which was required to keep the furnace at steady state. Figure 9 shows a typical impulse response.

**Reactor Temperature Response to Power Impulse**

![Graph showing reactor temperature response to power impulse](image)

Figure 9) Typical Reactor Response to a Power Impulse

Since an input affects the temperature of a reactor for as long as 20 minutes, it is an important factor to consider when writing the control algorithm.

This temperature response was mathematically treated using Matlab to give the smooth curve shown in fig. 10. These data were further treated to calculate $h_i$ in the following manner (fig. 11):
\[ h_0 = 0 \]
\[ h_i = a_i - a_{i-1} \quad i = 1, 2, \ldots, T \]

\( a_i \) = temperature at the \( i \)th sampling period
\( T \) = model horizon

**Cubic Spline of Reactor Temperature after Power Impulse**

![Cubic Spline of Reactor Temperature after Power Impulse](image)

*Figure 10* Spline of Impulse Response (Matlab Treatment)
A predictive method using feed-forward and PI control (see fig 12) gave the best results for computer control. The feed-forward control accounts for all the past power inputs and how they affect the present; the PI control takes care of any model inconsistencies and outside perturbations.
Figure 12) Flowchart of Predictive Method with PI Control

With some fine tuning of the PI parameters we achieved modest temperature control (± 3°C) below 500°C. Beyond this temperature, though, control became unstable mainly due to on/off power input (the open circles of figure 13) experienced when using the predictive algorithm. The instability probably originates from the strong variation in $h_i$ over each temperature region.
Figure 13) Temperature Control Using Predictive Method
Open Circles = Power Input, Solid Line = Temperature

To combat the effects of On/Off control the power input data was averaged as a function of temperature. Using this function we can calculate the power needed at any particular temperature for the ramp without regard to past inputs or h values. This greatly simplified the programming and smoothed the temperature response of the furnace to enable accurate computer control at temperatures higher than were previously possible. Moreover, this technique enables the program to "learn" from previous runs. The Power input data, modified by PI control, can be used to readily calculate a new Pin(T).

Generally only 1 or 2 runs were required to fine-tune the Pin function to achieve consistent results.

Often during pretreatment a catalyst temperature is ramped to a maximum and held to ensure that the catalyst has equilibrated at that temperature. The SS power
requirement for the desired temperature was used in addition to PI control for maintaining this temperature with very little overshoot. A typical result is shown in fig 14.

Figure 14) Typical Reactor Temperature Response
Ramp at 20°C/min. to 400°C and hold 10 min. - (400°C, 10min.)

This furnace design has proven to be very efficient when coupled with computer process control for the linear temperature ramping of the quartz reactor. For the study of catalytic reactions, errors associated with catalyst pretreatment have been virtually eliminated and thus a better reproducibility for catalytic and characteristic measurements has been realized. The computer automation of the pretreatment process also led to a successful computer automation of the Batch Reactor, PFR, and Chemisorption apparati.
B. Reaction Temperature Control

Originally we used the furnaces described in section III-A for all phases of pretreatment and reaction temperature control in the batch, plug flow, and chemisorption reactors. Unfortunately, since many reactions had to be controlled precisely near room temperature or below, these furnaces simply were not effective. An alternative was to surround the reactor with a stirred water bath to which warm water or ice could be added as needed. Such a method could maintain the temperature only within ±2°C and prompted us to seek a more precise control method that would maintain a pre-determined temperature without attendance by an operator.

An Execal circulating bath (±0.1°C accuracy) was used to control constant reactor temperatures from 15°C-70°C (Fig. 15). For control below ambient temperatures a cooling mixture of ethylene glycol and water, provided by a recirculating cooler (FTS Systems, Inc.), was cycled through a heat transfer coil located in the liquid bath. The liquid from the Execal bath was circulated through a large jacketed beaker.

A beaker, (Figure 2) specially equipped with baffles to improve heat transfer, was filled with water and continuously stirred by a magnetic stirbar. The quartz catalyst holder could be placed inside the beaker and insulated from the environment with Styrofoam. Reaction temperatures during batch and plug flow experiments were taken periodically by the computer from a thermocouple situated in a well submerged in the bath and calibrated to within ±0.3°C of a PRT. Following a step change, this temperature was able to reach "SS" in fewer than 30 minutes and remain constant within ±0.2°C during reactions lasting as long as 30 days.
Figure 15) Reaction Temperature Control

Figure 16) Design of Jacketed Beaker
C. Chemisorption Apparatus

The chemisorption apparatus shown in Figure 17 was built to characterize the Pd,Cu catalysts used in this study. Depending on the condition of the catalyst, carrier gas, and valve positions, this equipment could be used for Temperature Programmed Reduction (TPR), Temperature Programmed Desorption (TPD), or dispersion measurements.

TPR/TPD:

Temperature programmed reaction studies have been reported as early as 1957 (5) and were first introduced into catalysis by Cvetenovic(9) in 1966. Since these times ultrahigh vacuum equipment, down-stream analysis of the effluent (e.g. mass spectrometry), and automation of the equipment have been introduced. In each case a carrier gas flows over a metal catalyst which in the case of TPR is in an oxidized state; for TPD the surface is covered with a sorbed species. The carrier gas used is generally 10%H₂/Ar for TPR, Ar for TPD of H₂, and He for TPD of other materials. The temperature is raised at a constant rate and peaks result at temperatures at which metal reduction and/or desorption of surface species occur.

TPR gives information on the number and relative amounts of reducible species in a sample, the activation energy of reduction (by changing the rate of temperature ramp, see reference 9), and whether or not there is interaction between two metals in a bimetallic catalyst.
Chemisorption Apparatus

Figure 17) Chemisorption Apparatus
TPD can be used to determine the number of different surface sites available for adsorption on a catalyst, the amount of gas adsorbed at various temperatures, the number of acid sites present on a catalyst, and the activation energy of desorption.

Dispersion measurements:

This equipment can also be used to measure metal dispersions by titrating the metal surface with small amounts of adsorbate gas. The total metal surface area is determined from the amount of gas adsorbed and the area of metal surface covered by each adsorbed molecule.

Equipment:

The apparatus (Figure 17) was built entirely from glass and stainless steel. Greased 2-way and 3-way stopcocks were used to detour gas flows appropriately. High precision mechanical flow controllers were used for the 10%H2/Ar and Ar streams to eliminate baseline noise due to flow rate fluctuations. A stainless steel 8-port Valco valve with matching 0.1 ml sample volumes was used to inject small amounts of H2, O2, or N2O into the Ar or 10%H2/Ar carrier gas streams. This valve was equipped with an air actuator which could be directly controlled by the computer. The furnace used was described earlier (Furnace Design and Control). Constant temperature control for titrations could be maintained through use of the constant temperature liquid bath described earlier (Reaction Temperature Control). Continuous analysis of the effluent TPR stream was performed by an Antek Instruments thermal conductivity detector (TCD) equipped with matching GOW-MAC Instruments tungsten-rhenium filaments.
The TCD signal was read and stored directly into an IBM AT computer equipped with Real Time Devices AD500 and DA600 data acquisition cards. The TCD signal was read and displayed continuously on a Hercules mono-chrome monitor. After the reaction was complete, all files were transferred to a Gateway 2000 386 computer for analysis and final storage of chromatograms on a Colorado systems tape backup. An example TPR is given in Figure 18.

![Example TPR](image)

**Figure 18**) Example of TPR spectra

Gases:

The various gases employed in the chemisorption experiments are shown in Table 13 along with further steps in purification. All gases were first passed through separate model XG3162 Union Carbide Gas Purifiers to remove water. The dried gases were passed through Messer Greisham Oxisorb cartridges to decrease O₂, CO, CO₂, and other gases down to 1 ppm in the gas phase.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Manufacture</th>
<th>Grade</th>
<th>Oxisorb</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Linde</td>
<td>Repurified</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>10%H2/Ar</td>
<td>Linde</td>
<td>Repurified</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>H2</td>
<td>Linde</td>
<td>High Purity</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>O2</td>
<td>Linde</td>
<td>Dry Grade</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>N2O</td>
<td>MG Ind.</td>
<td>UHP</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 13) Gases used for Chemisorption Experiments

Calibration of Sample Loops:

The average volume of the Valco sample loops was approximately 0.114 ml, as determined in a series of temperature programmed reduction experiments. Peak areas resulting from the TPR of carefully weighed amounts of CuO were compared directly with those found by hydrogen titration from the sample loops into the carrier gas. The average uncertainty in these measurements was ± 4%.

TPR/TPD Procedure:

1) Pretreat the catalyst under the same conditions as required for the reaction of interest. (For TPR do not include the final reduction)
1a) (For TPD only) Adsorb the desired gas on the catalyst surface at the temperature required.
2) Flow the carrier gas (10%H2/Ar for TPR or Ar for TPD of H2) over the catalyst, through a dry ice/acetone trap, and into a TCD. The trap removes condensable gases, such as water vapor, which are evolved during the reduction and heating.
3) Pass hydrogen through the sample loop.
4) Run the program Ramp.c which will:
   - Store important information (e.g. catalyst, pretreatment, weight, date and
time, etc.).
   - Send two pulses of H2 to the TCD and integrate them for calibration.
   - Ramp the temperature between ambient and 750°C at 20°C/min. (see
section on Furnace Control).
   - Sample the TCD and store data.
   - Turn off the furnace when the maximum temperature is reached.

Titration procedure:

1) Pretreat the catalyst under the required conditions.
2) Allow the sample to reach the required adsorption temperature.
3) Run the program Titrate.c which will:
   - Titrate 0.1 ml of gas every 5 minutes.
   - Sample the TCD and store data.

Analysis of TPR/TPD:

Two programs were written to analyze (Anlrmp.cpp) and subsequently compare
and plot (Plot.cpp) TPR spectra. Anlrmp.cpp allows the individual graphical analysis and
manipulation of TPR spectra in the following ways:

1) Baseline Shift/Unshift - Allows a correction for a drifting baseline.
2) Zero/Unzero Data.
3) **Zoom/Unzoom on a specific area** - Allows analysis of a small region of the spectra.

4) **Find Max/Min** - Gives the time and temperature at which a max or min occurs in the spectra.

5) **Integrate Peak** - Allows one to input the start and finish points within which the integration will be performed under any of three options:
   a) Use the lowest endpoint as the baseline.
   b) Use zero as the baseline.
   c) Draw a straight line between the endpoints and use as the baseline.

6) **Save** - Saves the data such as zero and baseline shift to a file which are subsequently used in the plot program.

Also, a log is kept of all actions and results of the analysis while running this program under *.adj which can be referenced later.

Plot.cpp allows the comparison of up to six TPR spectra at the same time. After each file has been analyzed by Anlrip.cpp and the baseline adjusted, the user can order plot.cpp to perform the following functions with only the click of a mouse:

1) **Normalize the peaks with respect to catalyst weight** (for comparison).

2) **Zoom/Unzoom on a specific area of the TPR's**.

3) **Add moveable titles to the plot**.

4) **Add a main title to the plot**.

5) **Plot the data with lines and/or circles**.

6) **Print the plot on the Hewlett Packard Deskjet printer** (for example see fig 19).
Figure 19) Example of Comparison of TPR's
D. Hydrogenation Reactors

To examine the selective hydrogenation of BD, computer automated batch and plug flow reactors were built. The batch reactor was designed for easy examination of aged catalyst activity and also for future isotopic studies which are not economical in a flow reactor. The PFR reactor was built to examine the transient aging of Pd catalysts in the hydrogenation of butadiene and also to examine activity and selectivity as a function of BD conversion. Both reactors were constructed entirely of glass, stainless steel, and Teflon and included "greaseless" stopcocks to eliminate the sorption of hydrocarbon in the grease. The stopcocks were positioned in each case to minimize reactor dead volume.

Batch Reactor:

The batch reactor design (fig. 20) was obtained (with the exception of features for the automation of sampling) from the Institute of Isotopes in Budapest, Hungary. This design can take up to 3 samples of gas in a matter of seconds, or up to 89 samples for sample intervals greater than six minutes. The minimum sampling time of 6 minutes is a function only of the chromatogram time. The magnetic 4-valve circulation pump was made from glass and had a Teflon piston which contained a 1" stir-bar magnet. This pump could circulate gasses at 4.4 liters/hour (15.7 reactor volumes per hour). Hydrogen was purified by diffusion through a Pd/Ag thimble before use.
Figure 20) Batch Reactor

The individual volumes of the various equipment sections found by expansion of air from a flask of known volume are:

- Pressure Gauge: 101 cc
- Circulation Section: 214 cc
- Manifold: 165 cc
- Sample Holder: 66 cc
Procedure:

I Pretreatment of Catalyst
   a) Evacuate the catalyst for 20 minutes at ambient temperature.
   b) Allow 30 torr H₂ or O₂ into the reactor (reduction or calcination) and start
      the circulation pump. Gas should be circulating over catalyst.
   c) Immerse trap in liquid N₂ to remove water produced during metal
      reduction.
   d) Place furnace over the sample holder and react at desired temperature.
   e) After cooling the sample holder, place the liquid bath around the sample
      holder and set at the desired temperature.
   f) Evacuate the system. If the catalyst is reduced, first close off
      the sample holder before evacuation. This maintains a small amount of H₂
      near the catalyst sample to prevent it from oxidizing.

II Prior to Reaction (The sample holder is closed to the rest of the reactor.)
   a) Allow 30 torr of BD into the reactor and freeze it in the trap with
      liquid N₂.
   b) Allow 30 torr of H₂ into the reactor and close the valve that leads to the
      manometer.
   c) Remove the liquid N₂ and allow the gases to circulate and mix in the
      reactor for a few minutes.

III Reaction - at t=0 min. open the catalyst to the reaction mixture.
   a) For very fast reactions (manual):
      1) At t = 1 min. - Take the first sample.
2) At $t = 2$ min. - Allow the second gas to expand into the sample loop.

3) At $t = 3$ min. - Isolate the catalyst sample from the rest of the reactor.

4) Take the second sample after the first chromatogram has eluted.

5) Take the third sample after the second chromatogram has eluted.

b) For slower reactions - Run program React.c which will do the following:

- Save an information file about the run. (e.g. catalyst, weight, initial gas pressures, temperatures, date and time, etc.)

- Take and initial sample prior to reaction (The catalyst sample must be opened to the reactants manually at the moment of the first sample)

- Allow the sampling of chromatograms for as long as desired and with a sampling time as short as 6 minutes.

- Sample the FID signal 5.33 times per second while saving the data in separate chromatogram data files and plotting each chromatogram on the computer monitor.

Automation:

For batch reactions the only automation required was that for the sampling and data acquisition. Basically, only three valves (Figure 21) are involved in the sampling process: 2 stopcocks and a Valco sampling valve. The following configuration exists at the start of a reaction: valve 1 is open, valve 2 is closed, valve 3 is in the load position. In this configuration the sample loop is being constantly evacuated. In taking a sample, the following procedure is followed:
1) close valve 2
2) open valve 1, wait 2 seconds
3) close valve 1
4) inject sample (valve 3)
5) load sample (valve 3)
6) open valve 2

The actual loading of the gases up until the point where the gases are admitted to the catalyst is done manually. After this point, the computer (React.c) takes over the tedious process of taking samples and acquiring chromatogram and temperature of reaction data. The sampling sequence discussed above was maintained exactly constant by an electronic box\(^1\) which when activated by a 5 volt pulse from the computer proceeded to actuate the different valves in a timed sequence.

![Diagram of Sampling Valves for Batch Reactor]

Figure 21) Sampling Valves for Batch Reactor

Plug Flow Reactor:

Originally this apparatus (Figure 22) was designed to be both a plug flow and continuous stirred tank (CSTR) reactor. However, because of inadequate flow caused by

---

\(^1\)Designed by Dick Chronister
a significant pressure drop in the catalyst bed, the experiments conducted on this apparatus were done in plug flow mode. Four MKS Industries (model 1259B) mass flow controllers were calibrated for the flowrates and type of gas required for a variety of reaction conditions. The calibrations were as follows:

1) \( \text{N}_2 \) \( 0-100 \text{ SCCM} \)
2) \( \text{H}_2 \) \( 0-100 \text{ SCCM} \)
3) Mixture 15\%\( \text{H}_2/\text{N}_2 \) \( 0-20 \text{ SCCM} \)
4) Butenes \( 0-20 \text{ SCCM} \)

The model 247C mass flowmeter could control each gas stream separately or in ratio to the \( \text{N}_2 \) stream. Set points for the various flowrates could be fixed manually or by computer A/D signal, with an accuracy of \( \pm 0.2\% \) of the MFC range.

Reaction samples were taken at the exit of the reactor through an air actuated Valco 6 port sampling valve. The sampling valve could be actuated either manually or by a 5 volt computer pulse.

Procedures:

(For deactivation reactions)

I Pretreatment of Catalyst

a) Evacuate the catalyst for 20 minutes at 3e-2 torr.

b) Flow 30 SCCM of \( \text{H}_2 \) or air over the catalyst.

c) Place furnace over the sample holder and react at desired temperature. (Between reduction and oxidation let \( \text{N}_2 \) flow for 10 minutes)

d) After cooling the sample holder, place the liquid bath around the sample holder and set at the desired temperature.
e) Evacuate the system. If the catalyst is reduced, first close off the sample holder before evacuation. This maintains a small amount of H₂ near the catalyst sample to prevent it from oxidizing.

f) Flow the N₂, 10%H₂/N₂, and HC stream in the correct proportions and flowrates past the reactor (the sample holder is still closed).

II Reaction - Run React.c which will do the following:

- Take an initial sample. (The gas must then be manually diverted over the catalyst)
  - Take samples as often and for as long as required (6 minute minimum sampling time and 89 maximum samples)
  - Sample the FID at 5.33 times per second while writing the information to separate chromatogram data files and plotting the chromatogram on the computer screen.

(for SS reactions - after the catalyst has deactivated)

I Prepare equipment

1) Set the temperature and absolute flowrates required for this experiment.

II Run Experiment React.c which will do the following:

- Sample for as often (more than 15 minutes, depends only on the lowest flowrate and volume between the catalyst sample and the sampling valve.) as is desired
- Take up to 89 samples.
- Change the total flowrate (at the moment of the previous injection) of the gasses without affecting the initial partial pressures of gasses.
Sample the FID while writing the information to separate chromatogram data files and plotting the chromatogram on the computer screen. React.c changes the flowrate linearly with respect to the inverse flowrate to ensure a similar change in conversion for each change in flowrate. Because of the first order dependence of butadiene hydrogenation on hydrogen partial pressure this is only an approximation.

GLC Analysis:

0.1 ml samples of gas from both batch and plug flow reactors were separated in a Varian model 3700 gas chromatograph equipped with FID. Separation occurred at 40°C in a 6' x 0.125" stainless steel column filled with 0.165 wt% picric acid on Graphpac-GC. This system gave baseline separation, with a total retention time of less than 10 minutes. Actually, all interesting peaks (C4) were eluted between 4 and 10 minutes which permitted computer sampling every 6 minutes.

The FID signal was read and stored by an IBM AT computer equipped with Real Time Devices AD500 and DA600 data acquisition cards. The FID signal was read 5.33 times per second and displayed continuously on a Hercules mono-chrome monitor. After the reaction was complete, all files were transferred to a Gateway 2000 386 computer for analysis and final storage on a Colorado systems tape backup system.

Integration of the chromatograms was performed by a program (Int.cpp). This program provides more accurate results than the HP integrator and facilitated computer data entry. The program analyzes batch or plug flow experiments with up to 89 chromatograms. An outline is shown in table 14: The program was designed to not only
do this analysis, but also to save the results directly to a file (*.xls) which can be read by a spreadsheet (EXCEL) and analyzed. Table 15 is a typical example of an *.xls file.

1) Read information from *.inf file.
2) Read data for first chromatogram.
3) Zero Data.
4) Calculate the first derivative at each point.
5) Find the peaks.
6) Integrate each peak and save the information to *.xla.
7) Determine the area of peaks for 1-B, nB, c-B, t-B, and BD and save information to *.xls.
8) Open the next chromatogram.
9) If there is another chromatogram go to 3, otherwise end.

Table 14) Basic Outline of Int.CPP
PFR reaction pz3n
Performed: 3-28-1993 at 17:36:11.0

Comment: lower H2 pp

Catalyst: pz3

Weight (mg): 209.1

Average reaction temperature was 40.2°C. This temperature remained between 40.100000 and 40.300000°C.

Samples were taken every 15.000000 minutes for 1185.000000 minutes.

Hydrocarbon FR (SCCM): 5
Mixture FR (SCCM): 3.045
Nitrogen FR (SCCM): 101.95
Hydrogen FR (SCCM): 0

Flowrates were changed by a 1/X model from 101.950000 to 20.000000 SCCM N2. When finished the flowrate was set to 100.000000 SCCM N2.

<table>
<thead>
<tr>
<th>Areas</th>
<th>Time</th>
<th>1-B</th>
<th>B</th>
<th>c-B</th>
<th>t-B</th>
<th>BD</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1495.027</td>
<td>1.395478</td>
<td>2.083744</td>
<td>8.089115</td>
<td>120.9003</td>
<td>1627.495</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1397.599</td>
<td>1.325188</td>
<td>2.638613</td>
<td>13.01035</td>
<td>105.5</td>
<td>1520.073</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1396.454</td>
<td>1.375834</td>
<td>2.879292</td>
<td>13.68415</td>
<td>101.6378</td>
<td>1516.031</td>
</tr>
</tbody>
</table>

Table 15) Example Output From the Chromatogram Integration Program

Integration techniques:

Two basic methods of integration were employed. For high 1-butene content (>60%), the 1-butene peak exhibits a long "tail" (see fig. 23). So, the 1-butene area is estimated as the entire area from the beginning of the 1-B peak to the start of the t-B peak minus the areas (as calculated by the shaded regions of the figure 23) of nB, c-B, and isobutylene. For smaller values of 1-B all peak areas were measured by simply dropping a line from the minimum at the valley of two peaks (figures 24 and 25).
Fig 23) Chromatogram - High 1-B Content

Figure 24) Chromatogram - High BD Content
Relation Between Signal and Hydrocarbon Content:

The nature of the FID signal depends mainly on the amount of carbon in the hydrocarbon and varies little with saturation.\textsuperscript{2} According to Uden\textsuperscript{3}, the signal donation for olefinic relative to paraffinic carbon is about 0.95. So, the signal/mole ratio of C4 mono-olefins and butadiene should be close to 0.975 and 0.95, respectively, in comparison with a butane ratio of unity. We attempted to calibrate the C4 gases, however signal variations well within the range of experimental error and so hydrocarbon concentrations were directly related to peak areas.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chromatogram.png}
\caption{Chromatogram - Intermediate Concentrations}
\end{figure}

\textsuperscript{2}Josef Novak, "Quantitative Analysis by Gas Chromatography", Marcel Decker, Inc, N.Y. (1975), p. 57
IV. Results and Discussion
A. Catalyst Preparation

All catalysts were prepared using high purity Catapal Alumina (Vista Chemical). The untreated Catapal alumina was highly crystalline (XRD\(^1\) measurement) with a surface area of 270 ± 5 m\(^2\)/g (BET\(^2\) measurement). The pore volume distribution\(^2\) of the untreated Catapal alumina, determined from nitrogen desorption (39), is shown in Figure 26.

![Pore Volume Distribution - Untreated Catapal Alumina](image)

**Figure 26**) Pore Structure - Untreated Catapal Alumina
Average Pore Radius = 21\(\AA\)

The XRD spectrum in Figure 27 (curve d) indicates that the untreated support is crystalline, with some but not all peaks attributed to \(\gamma\)-alumina. A mild decomposition in He (curve c) or treatment in \(\text{H}_2\) (curves a and b) at 500°C was sufficient to cause the support to become more amorphous and for the surface area to decrease to 190 m\(^2\)/g.

---

\(^1\)Measurements were made between 20° and 100° with a goniometer speed of 1/16°/minute. Resolution was 0.05°.

\(^2\)Measurements were taken with a Micromeritics Accusorb 2100E machine.
Curves a and b show the futility of using the XRD technique to determine Pd/Cu alloy formation or metal crystallite size. The predominant alumina peaks far outmatch the signal of the Pd and Cu loadings used for these measurements. The pore volume distribution for an alumina sample treated at 550°C for 26 hours (figure 28) reveals an increased average pore radius of 59Å.

Figure 27) XRD Results
a) 1Pd5.1Cu/Al (Red(500C)), b) 1Pd1Cu/Al (Red(500C,10min.))
e) Catapal Alumina (Ar(500C,10min.), d) Catapal Alumina (Untreated)
Pore Volume Distribution - Catapal Alumina, Calcined (550°C, 26 hrs.)

Figure 28) Pore Distribution - Calcined (26 hrs., 550°C) Catapal Alumina
The data points were fitted with a cubic spline.
Average Pore Radius = 59Å

To stabilize the alumina and reduce the number of acid sites (which can act as sites for polymerization), a portion of Catapal alumina was sintered for 8 days in flowing air at nominal furnace temperature of 1000°C. This process took a total of 10 days, with one day to heat the Lindberg furnace containing the reactor and a final day to cool to room temperature. Originally a stainless steel reactor was used, but it could not withstand the high temperatures involved without separation of its constituent components. A flaky black material had mixed with the alumina taken from the reactor. Before abandoning this sample, we attempted to remove most of the contamination by sieving through a 100 mesh screen. A TPR examination of the resulting support (Figure 29) shows a high temperature peak during the initial reduction of the sample (715°C) and another (600°C) after the same sample was oxidized at 400°C. Quantitatively, the peak areas corresponded to about 0.1 wt% of metal contamination (based on H/Pd). Probably one or more
reducible metals such as Fe, Cr, or Zn were leached from the stainless steel alloy during high temperature calcination. This example illustrates the power of the TPR device for detecting small metal loadings.

![Graph showing TPR of Contaminated Alumina](image)

**Figure 29) TPR of Contaminated Alumina**

A second attempt was made to calcine the Catapal alumina. This time a quartz fluidized bed reactor was designed, complete with a quartz frit, which could easily
withstand reaction temperatures as high as 1000°C without danger of metal contamination or melting. Again, the alumina was treated at high temperature for 8 days, but this time the TPR profiles showed no reduction peaks (figure 30). The negative peaks appearing below 100°C result from flow disruptions during calibration; they occur with or without a sample in the apparatus.

Figure 30) TPR of "Clean" Alumina (61m²/g)
The BET\textsuperscript{3} surface area (61±3 m\textsuperscript{2}/g) and pore distribution\textsuperscript{4} (figure 31) of this newly formed alumina were measured by N2 adsorption/desorption isotherms. The particle size distribution, determined by sieving, is shown in figure 32. All particles were smaller than 0.6 mm in diameter.

**Pore Volume Distribution - Catapal Alumina, Calcined (1000°C, 10 days)**

![Pore Volume Distribution Graph]

Figure 31) Pore Distribution - Catapal Alumina, Calcined (≈1000°C, 8 days)

The data points were fitted with a cubic spline.

Average Pore Radius = 115Å

The "clean" alumina (to be called Al(61)) was impregnated using the incipient wetness method with solutions containing Pd and/or Cu organo-metallic precursors. Pd(II)acetylacetonate was weighed, dissolved in benzene, and contacted with the alumina to produce 0.45 weight % of Pd (P(61)). Bimetal catalysts were prepared by impregnating portions of P(61) with aqueous Cu(II)acetate (Baker Analyzed 99.8%). The quantities of Cu(II)Acetate used were sufficient to prepare catalysts with 0.2, 1.0, and 2.0 Cu/Pd atomic ratios (PC5,CP1, and CP2 respectively). A copper catalyst (0.57wt%Cu/Al

\textsuperscript{3} Measured on a Micromeritics Accusorb Machine.
or C(61)) was prepared by wetting the Al(61) with benzene, drying overnight at 110°C, and impregnating with aqueous Cu(II)acetate. After final impregnation, all catalysts were dried overnight in an oven at 110°C, placed in sample vials, and stored in a dessicator. A summary of the catalysts produced and their loadings is given in table 1.

**Distribution of Particle Diameters Al(61)**

<table>
<thead>
<tr>
<th>Micro-meters</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-600</td>
<td></td>
</tr>
<tr>
<td>300-500</td>
<td></td>
</tr>
<tr>
<td>250-300</td>
<td></td>
</tr>
<tr>
<td>149-250</td>
<td></td>
</tr>
<tr>
<td>105-149</td>
<td></td>
</tr>
<tr>
<td>&lt;105</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 32** Size distribution of Al(61) support

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt%Cu</th>
<th>wt%Pd</th>
<th>Cu/Pd (at)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>-</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>PC5</td>
<td>0.054</td>
<td>0.45</td>
<td>0.20</td>
</tr>
<tr>
<td>CP1</td>
<td>0.286</td>
<td>0.45</td>
<td>1.06</td>
</tr>
<tr>
<td>CP2</td>
<td>0.55</td>
<td>0.45</td>
<td>2.05</td>
</tr>
<tr>
<td>C(61)</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 16) Composition of Prepared Catalysts

---

4Measurements by XPS.
B. TPR Analysis

Temperature programmed reduction (TPR) was employed to determine both catalyst reducibility and composition of the catalysts after different pretreatments. The technique involves passing a dilute (10%) hydrogen/argon mixture over a supported metal oxide or precursor while linearly increasing the temperature (20°C/min.). Peaks are observed at temperatures sufficient for metal reduction or desorption of surface species. Water and most side reaction byproducts are removed by a dry ice/acetone trap.

Robinson and Mol 1988

Robinson et al. (40) studied the temperature programmed reduction of several Cu/alumina (195 m²/g) catalysts with Cu loadings from 2 to 24 wt% and after oxidation from 247°C to 827°C. The catalysts were prepared by impregnating γ-alumina with aqueous solutions of copper nitrate and drying in an oven overnight at 110°C. TPR was carried out in a flow apparatus with a hydrogen-argon mixture (2:1) and a temperature ramp of 10°C/min. They found that samples calcined from 327 to 627°C containing 4 to 24 wt% Cu showed only one clear reduction peak (near 227°C). Catalysts with 8 wt% Cu or less that were oxidized at 247°C exhibited a second, higher temperature peak near 290°C. After calcination at or above 477°C, the 2 wt% copper catalyst yielded primarily a broad reduction peak between 287 and 327°C. In addition, Robinson et al. made some observations about the hydrogen consumption calculated from each TPR spectra (Figure 33). Samples oxidized below 477°C consumed hydrogen in excess of that needed for full reduction of cupric oxide. They concluded that this effect was due to reduction of the nitrate precursor remaining on the catalyst after calcination; this theory was supported by
TPD measurements. The samples calcined at 477 and 627°C showed quantitative reduction of CuO to metallic Cu; oxidation at 827°C was sufficient to cause bulk CuAl₂O₄ formation (proved by XRD) and thus decrease the concentration of easily reducible copper.

Figure 33) Hydrogen Consumption in the TPR of Cu/alumina Catalysts
Calcination Temperatures (○) 247°C; (●) 327°C; (△) 477 and 627°C; (□) 827°C
Robinson and Mol (40)
Dumas and co-workers (41) studied the TPR of a series of Cu/alumina catalysts with high copper loadings (6 to 20 wt%) and calcination temperatures from 500 to 1000°C. The samples were prepared by impregnating an alumina support (either 100 m²/g or 200 m²/g) with aqueous copper nitrate and drying them in an oven for 24 hours at 120°C. TPR was carried out in a flow apparatus with a 1% hydrogen/argon mixture and a temperature ramp of 5°C/min. After calcination at 500°C, catalysts with 6% metal loading showed one thermo-reduction peak near 242°C. They ascribed this peak to the reduction of Cu²⁺ ions with strong support interactions rather than the reduction of Cu oxide. They explain that at low metal loadings Cu is unable to form solid oxides on alumina but instead forms a structure related to the CuAl₂O₄ (spinel). Catalysts with higher copper loadings were accompanied by a second thermo-reduction peak at 312°C which they attributed to the reduction of CuO crystallites that formed only after the alumina adsorption sites were saturated with copper ions. In confirmation, a catalyst supported on the 100 m²/g alumina had a much larger second peak and a smaller low temperature peak than an equally loaded catalyst with twice the support surface area. Copper spinel formed after oxidation at temperatures above 750°C and copper aluminate resulted from the diffusion of Cu ions into the support.

Results:

To identify the source of catalyst reduction peaks, the TPR of unsupported copper and palladium compounds likely to be present on the catalysts were inspected. Small amounts (20 mg.) of these compounds were ground to powder and physically mixed with
about 200 mg. of Al(61). Baker analyzed 99.8% Cu(II)Acetate, Baker analyzed
Cu(II)Oxide 99.9%, Fisher Scientific Cu₂(I)Oxide 99.5%, and Aldrich Chemicals 99%
Pd(II)acetylacetonate were examined (Figure 34).

TPR of Cu and Pd Compounds

![Graph showing TPR of Cu and Pd Compounds](image)

Figure 34) TPR of Unsupported Copper and Palladium Compounds

Reduction/decomposition of the copper compounds occurs near 630K. Full
reduction of cuprous and cupric oxide happens in a single step. Palladium acetylacetonate
and palladium oxide fully reduce at lower temperatures (308K and < room temperature,
respectively) than the copper containing compounds. The nearly symmetric peaks found
during cupric acetate reduction indicate a two stage reduction. The shoulder found on the second copper acetate thermo reduction peak and the H/Cu ratio of 2.12 (greater than the stoichiometric ratio of 2) possibly indicate a side reaction involving the acetyl precursor.

We suggest the following reaction sequence:

\[
\begin{align*}
\text{Cu(OOCCH}_3\text{)}_2 + \frac{1}{2}\text{H}_2 & \rightarrow \text{CuOOCCH}_3 + \text{AcH (ad)} \quad (1) \\
\text{Cu(OOCCH}_3\text{)} + \frac{1}{2}\text{H}_2 & \rightarrow \text{Cu} + \text{AcH (ad)} \quad (2) \\
\text{Cu(OOCCH}_3\text{)} + \frac{1}{2}\text{H}_2 & \rightarrow \text{Cu} + \text{CO}_2(v) + \text{CH}_4(v) \quad (3) \\
\text{AcH (ad)} & \rightarrow \text{AcH (v)} \quad \text{Tbp} = 118^\circ\text{C} \quad (4) \\
\text{AcH (ad)} & \rightarrow \text{CO}_2(v) + \text{CH}_4 (v) \quad \text{Decomposition} \quad (5) \\
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \text{Kp at 450^\circ\text{C} \approx 151}^1 \quad (6) \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{Kp at 450^\circ\text{C} \approx 1105} \quad (7)
\end{align*}
\]

As acetic acid forms, it probably desorbs and becomes trapped in the "dry ice"/acetone trap. Beyond a certain temperature, though, decomposition of the acetic acid may also occur (probably catalyzed by the metallic Cu present at higher temperatures) and if CO and/or CO\textsubscript{2} are products of this reaction then reactions 6 and 7 become favorable and the consumption of additional H\textsubscript{2} can be expected. Theoretically, if all the acetyl precursor reacted in this way we would get H/Cu ratios as high as 10. Also, CO\textsubscript{2}, CO, and CH\textsubscript{4} would escape the dry ice/acetone trap and affect the thermal conductivity of the effluent stream. Thermal conductivities for Ar, H\textsubscript{2}, 10%H\textsubscript{2}/Ar, CO\textsubscript{2}, CO, and CH\textsubscript{4} are 42.5e-6, 434.3e-6, 81.68e-6, 39.6e-6, 55.49e-6 and 81.83e-6 cal/s/cm/C\textsuperscript{2}, respectively.

Having a thermal conductivity similar to that of the H\textsubscript{2}/Ar feed stream, CH\textsubscript{4} released into

\footnote{Physical and Thermodynamic Properties of Elements and Compounds*, p30-31, Girdler Chemical, Inc.}
the gas phase probably would not show up as a significant peak. On the other hand, CO₂ and CO would give the appearance of additional H consumption.

Temperature programmed reduction of the supported copper mono-metallic catalyst (C(61)) resulted in two easily distinguishable peaks resembling those found for the Cu(II)acetate/alumina physical mixture. Since the sample had been impregnated with aqueous Cu(II)acetate and dried under mild conditions (110°C), a large portion of the compound remained on the surface. Hydrogen consumed during this reduction, though, was over three times (H/Cu=6.4) that expected for reduction of the metal alone. This coupled with the asymmetry of the peaks supports the conclusion that acetyl precursor decomposes and reduces in a side reaction to consume excess hydrogen. Probably the large second peak and its apparent shift to higher temperature can be explained by the combination of a metal reduction and secondary reaction peak. A more intimate contact of the copper compound and alumina in the impregnated sample seems to increase acetic acid decomposition and/or hydrogenation over simple desorption.

After initial reduction to 750°C, the sample was repeatedly calcined and reduced using various calcination temperatures. Calcination removes surface organics that might interfere with the TPR signal and places the metal in an oxidized state. Copper reduction occurred (415K) at a much lower temperature than found for reduction of unsupported copper oxides (630K). This difference indicates that copper does not exist on the surface as copper oxide but instead exists as well dispersed Cu²⁺ ions which interact with the alumina as suggested by Dumas(41). Hydrogen consumption depended on the previous calcination temperature. As calcination temperature increased from 300°C to 500°C, H/Cu ratio decreased from near two to about 1.3. High temperature calcination probably causes Cu²⁺ migration into the alumina support and makes it more difficult to reduce. The formation of bulk Cu/alumina spinel is not expected under any of the conditions
studied, as it becomes thermodynamically favorable at calcination temperatures exceeding 617°C; Dumas et al. (41) found significant spinel formation at 750°C, whereas at 600°C none was observed. This does not rule out, however, the presence of a spinel-like surface species.

TPR of Supported Cu Catalyst – C(61)

Figure 35) TPR of 0.59 wt% Cu/Al(61) – C(61)

Initial Reduction of the palladium monometallic catalyst (P(61)) occurred between 350 and 850K with a maximum near 650K and a total hydrogen consumption more than 10 times (H/Pd=23) the value expected for metal reduction alone. Because Pd(II)acetylacetonate (or Pd(AcAc)$_2$) was the metallic precursor used and Pd$^0$ is more active than Cu$^0$ at low temperatures, it is not surprising that acetic acid decomposition/hydrogenation reaction is prevalent for P(61).

TPR of Supported Pd Catalyst – P(61)

Figure 36) TPR of .45wt%Pd/Al(61) - P(61)
Following subsequent oxidation (400°C, 10min.) and reexamination by TPR, only a negative peak with a minimum at 369K (96°C) was observed. This peak corresponds to the liberation of H₂ resulting from decomposition of the Pd hydride phase and represents a H/Pd ratio of about -0.7. Since the actual reduction of PdO occurs below room temperature (44), it does not appear in the figure. This sample was repeatedly calcined and reduced at different calcination temperatures with no apparent effect on the resulting hydrogen desorption.

A comparison between the initial reduction of all Cu and Pd catalysts is shown in figure 37. In each case a large amount of excess hydrogen was consumed, though, the amount of hydrogen consumed decreased with increasing copper loading. This seems contradictory as the concentration of acetyl groups present on the catalyst should increase with increasing copper content and may indicate that copper decreases the activity of palladium for the side reaction. For all catalysts, the bulk of the reduction occurs around 650K and appears to be complete below 900K.

Catalysts reduced (750°C) and calcined (400°C, 10min) had much simpler TPR spectrum (figure 38 and table 18). This pretreatment removes most of the organic impurity from the catalyst surface and allows examination of the actual metal reductions without interference. Convolution of the negative palladium/hydride decomposition peak and the of the positive copper reduction peak creates an apparent shift in copper reduction temperature and a decrease in the observed H/Cu ratio. Full metal reduction of all catalysts occurs below 523K (250°C).
TPR of Al(61) Catalysts – Initial Reduction

Figure 37) TPR of Al(61) Catalysts - Initial Reduction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H/Cu</th>
<th>H/Pd</th>
<th>Extrema K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>-</td>
<td>23</td>
<td>656</td>
</tr>
<tr>
<td>PC5</td>
<td>87</td>
<td>17</td>
<td>677</td>
</tr>
<tr>
<td>CP1</td>
<td>13</td>
<td>13</td>
<td>663</td>
</tr>
<tr>
<td>CP2</td>
<td>4</td>
<td>8</td>
<td>622</td>
</tr>
<tr>
<td>C(61)</td>
<td>6</td>
<td>-</td>
<td>600 716</td>
</tr>
</tbody>
</table>

Table 17) TPR Comparison of H/Metal ratios - Initial Reduction
TPR of Al(61) Cat's - Red/Cal(400C, 10min)

Figure 38) TPR of Al(61) Catalysts - Red(750C)/Cal(400C, 10min.)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H/Cu</th>
<th>H/Pd</th>
<th>Extrema K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>-</td>
<td>-0.7</td>
<td>346</td>
</tr>
<tr>
<td>PC5</td>
<td>-</td>
<td>-0.7</td>
<td>367</td>
</tr>
<tr>
<td>CP1</td>
<td>0.6</td>
<td>-</td>
<td>358</td>
</tr>
<tr>
<td>CP2</td>
<td>1.5</td>
<td>-</td>
<td>389</td>
</tr>
<tr>
<td>C(61)</td>
<td>1.8</td>
<td>-</td>
<td>412</td>
</tr>
</tbody>
</table>

Table 18) TPR of Al(61) Catalysts -- Red(750C)/(400C,10min.)
Temperature programmed reduction of the catalysts was also studied after calcination at 300°C and 400°C for one hour. Calcination at these temperatures was insufficient to remove all organic impurities present as we had H/Metal ratios above that expected for metal reduction (about 8 and 3 for calcination at 300 and 400°C, respectively). These reduction profiles (shown in figure 39 for calcination at 400°C only) were complex and difficult to interpret. Since peaks due to metal reduction could not be separated from those due to organic decomposition/reduction, we are unsure what temperature is sufficient for full metal reduction.

TPR of Al(61) Cat's - Cal(400C, 1 hr)

Figure 39) TPR of Al(61) Catalysts - Cal(400C, 1 hr)
C. Activation/Deactivation

In the gas phase hydrogenation of butadiene, deactivation of the Pd catalyst by butadiene polymerization is unavoidable. Understanding this process and its effect on final catalyst selectivity and activity is crucial for the scale-up of gas phase studies to liquid phase industrial reactors. Hydrogenation of butadiene in the liquid phase tends to minimize the build-up of surface oligomer/polymer due to the solvent action of the liquid hydrocarbon. In this section, we examine the effect of temperature and Cu addition on the activities and selectivities of BD hydrogenation during the deactivation process. In addition we examine the effects of various regeneration treatments on the aged catalyst and their subsequent "re-deactivation".

All experiments were performed near ambient temperatures and atmospheric pressure under constant plug flow conditions. Typical gas flowrates used were 5:5:100 SCCM for 9%BD/1-B: 15%H₂/N₂: and N₂ respectively. This notation (e.g. 5:5:100) will be used throughout this text and will denote the same order and units. Sample names in this and the following section will begin with PP and PZ for the P(61) and CP2 catalysts, respectively. Selectivities used are defined below:

\[ \text{Selectivity}(H_2) = \frac{\text{moles HC produced}}{\text{moles } H_2 \text{ consumed}} \]

Note: Selectivity can be negative if the HC is consumed in the reaction.

\[ \text{Trans} / Cis = \frac{\text{moles trans} - 2 \times \text{Butene produced}}{\text{moles cis} - 2 \times \text{Butene produced}} \]
Analysis of P(61) Catalyst:

The deactivation of four separate P(61) samples was examined under the reactor conditions shown in Table 19:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. °C</th>
<th>Weight (mg)</th>
<th>HC</th>
<th>15%H2/N2</th>
<th>N2</th>
<th>Deact. Time hours</th>
<th>BrkThruPt %BD Conv</th>
<th>Trans/Cis Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP1</td>
<td>10.9</td>
<td>32.6</td>
<td>6</td>
<td>6</td>
<td>90</td>
<td>5.8</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>PP2</td>
<td>25.8</td>
<td>32.6</td>
<td>6</td>
<td>6</td>
<td>90</td>
<td>4.2</td>
<td>8.3</td>
<td>1.1</td>
</tr>
<tr>
<td>PP3</td>
<td>15.9</td>
<td>60.7</td>
<td>6</td>
<td>6</td>
<td>90</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>PP4</td>
<td>15.9</td>
<td>210</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>50</td>
<td>8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 19) Conditions of Deactivation of P(61) Samples
Trans/Cis is averaged between 20 and 99% BD Conversion

Selectivity vs. % BD conversion varied little with deactivation temperature or sample weight (Figure 40 shows curves for PP1). In each case 1-butene was consumed (negative 1-B selectivity) until low BD conversions were reached. The point at which 1-B selectivity becomes positive is called the breakthrough point. Butane was produced throughout the deactivation process.

Typical Deactivation of P(61) - Sample PP1

![Graph showing typical deactivation of P(61) sample PP1](image)

Figure 40) Selec. vs. BD Conv. - Deactivation of PP1
Activity loss exceeded 95% in all cases. The time required to reach this low activity, though, increased dramatically with sample weight. Stabilization of PP1 (figure 41) and PP2 required only 6 hours, whereas sample PP4 that weighed nearly 4 times the other samples required 50 hours to reach steady state.

**Typical Deactivation of P(61) Catalyst - Sample PP1**

![Graph showing deactivation of P(61) Catalyst](image)

**Figure 41** BD Conv. vs. Time - Deactivation of PP1

Catalyst activation/deactivation was also investigated after either evacuating or purging with N₂. Aged sample PP2 (21 hours on stream) regained ≈95% of its original activity and experienced re-deactivation (similar to Figures 40 and 41). Surprisingly, the final "SS" activity of the aged catalyst was nearly twice that found after the initial deactivation of the sample. Another stabilized sample (PP3 after 25 hours TOS) was reactivated under flowing N₂ for 8 hours at 35°C with similar results. Unfortunately, this deactivation (Figure 42) cannot be compared with the initial deactivation of the sample as those data were lost; however, we can compare it with the results of PP2 (Figure 43).
Deactivation of PP3 After Reactivation in Flowing N2 8 hrs.

Figure 42) Deactivation of Aged P(61) Catalyst after Activation by N2

Comparison of Deactivations for PP2 and PP3

Figure 43) Comparison of Selectivities for P(61) Deactivations

Figure 43 shows that the breakthrough point appears to be affected by time on stream for the catalyst. From the fact that PP1-2 and PP4 which had different
temperatures and catalyst weights all had the breakthrough point of their initial
deactivations close to 10% BD conversion, it seems reasonable that this also occurred for
PP3. It appears the catalyst undergoes a slow change during reaction with butadiene that
improves the selectivity for hydrogenation of BD. This change may be due to the
formation of high molecular weight polymeric materials which cannot desorb from the
surface of the metal. The increase in activity observed after evacuation or exposure to N₂
could be attributed to removal of low molecular weight surface adsorbed species that may
cover sites otherwise available for either butadiene or hydrogen adsorption.

Analysis of CP2 Catalyst:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temp°C</th>
<th>mg</th>
<th>HC</th>
<th>15%H₂/Ar</th>
<th>N₂</th>
<th>Deact. Time</th>
<th>BrkThruPt.</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ1</td>
<td>16</td>
<td>68.7</td>
<td>6</td>
<td>6</td>
<td>90</td>
<td>4.2</td>
<td>82.5</td>
<td>2.8</td>
</tr>
<tr>
<td>PZ2</td>
<td>15.9</td>
<td>62.4</td>
<td>6</td>
<td>6</td>
<td>90</td>
<td>5</td>
<td>90.5</td>
<td>2.6</td>
</tr>
<tr>
<td>PZ3</td>
<td>15.9</td>
<td>209.1</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>28</td>
<td>96</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Table 20) Deactivation of CP2 samples
Trans/Cis is averaged between 20 and 99% BD Conversion
Catalysts were Red(750°C)/Ox(400°C, 10min.)/Red(250°C, 10min.)

During deactivation, all CP2 catalyst samples gave selectivity vs. BD conversion
curves similar to those shown in Figure 45. Clearly even in the transient mode this
catalyst is far more selective than the Pd-only catalysts in the last section, i.e., the 1-B
selectivity remains positive until more than 90% of the BD has reacted. BD conversion for
the deactivation of these three samples is shown in Figure 46.
Initial Deactivation of CP2 Sample PZ3
Red(750)/Ox(400,10)/Red(250,10)

Fig 44) Selec. vs. % BD Conv. Initial Deactivation of CP2

Initial Deactivation of CP2 Samples

Figure 45) %BD Conversion vs. Time - Deactivation of CP2

For one aged sample (PZ1 after 3 days TOS), the effects of low temperature reduction and oxidation/reduction were studied. The results of the respective deactivations following these treatments (Figure 46) show a small loss in 1-B selectivity
with Red(250°C,10min.) and a significant loss after the catalyst was Ox(400°C,10min.)/ Red(250°C,10min.).

It is improbable that the oxidation state of Cu or presence of surface organic species caused this variation in selectivity because catalyst reduction and oxidation/reduction made no improvement. Instead, it appears to be due to a change in surface composition (Pd/Cu). In the Pd-Cu system, copper segregates to the surface of Pd when treated at temperatures above 500K in vacuum, oxygen, or nitrogen (42). Surface segregation of the Cu and subsequent migration to the alumina surface under these conditions may account for our results.

**1-B Selectivities of PZ1 - Transient**

![Graph](image)

**BD Conversion**

Fig 46) Comparison of Deactivation of Cu/Pd:2/1 Catalyst After Various Pretreatments
- PZ1X) Red(750C)/Ox(400C)/Red(250C) - Fresh Catalyst
- PZ1Y) PZ1X - Red(250C)
- PZ1Z) PZ1Y - Ox(400C)/Red(250C)
Summary:

1) CP2 was more 1-butene and butene selective during deactivation than P(61) samples (A comparison is shown in Figure 47). The breakthrough point was consistently above 80% for CP2 and below 11% for P(61).

2) Drastic deactivation occurs for both catalysts in which more than 95% of the activity of the sample is lost before stabilization. Probably, the initial buildup of polymer/oligomer is so great that the reactants lose accessibility to some pores.

3) Selectivities were independent of deactivation temperature.

4) Evacuating or N\textsubscript{2} purging the aged Pd-only catalyst causes a dramatic increase in activity and a corresponding loss in 1-B selectivity. After re-stabilization one sample had nearly twice the "SS" activity as the freshly deactivated catalyst.

5) Reduction and oxidation/reduction treatments of the aged copper-containing CP2 catalyst are detrimental to selectivity. After Ox(400°C, 10min)/ Red(250°C, 10min.) the aged CP2 catalyst behaved like P(61) indicating Cu separation from bimetal crystallites.

6) Trans/Cis ratios for the deactivation of all catalyst samples slowly increased as the catalysts aged to their SS values at low BD conversions. For the P(61) catalyst this ratio when averaged from 20 to 99% BD conversion was between 0.9 and 1.6 for the samples studied. The CP2 catalyst samples, on the other hand, exhibited Trans/Cis ratios from 2.6 to 3.3. Riley (200) observed similar trends in Trans/Cis ratio during hydrogenation of butadiene.
Comparison of Initial Deactivations P(61) and CP2 Catalysts

Fig 47) Selec. vs. %BD Conv. - Comparison of Initial Deactivation of P(61) and CP2 Catalysts
D. 1,3-Butadiene Hydrogenation over Stabilized Catalysts

Hydrogenation reactions were performed on the P(61) and CP2 catalysts after Red(750°C)/Ox(400°C, 10min.)/Red(250°C, 10min.) pretreatment and stabilization (See Activation/Deactivation). The minor component, 1,3-butadiene, was selectively removed from a dilute 1-B/hydrogen stream in a plug flow reactor at atmospheric pressure and near ambient temperature. Typical reactant flow ratios were approximately 5:5:100 = 15%H₂/N₂ : 9%BD/1-B : N₂. Results of these studies will be discussed and comparisons made between the mono and bimetallic catalyst.

Selectivities for this section are defined:

\[
Selectivity(H_2) = \frac{\text{moles } HC \text{ produced}}{\text{moles } H_2 \text{ consumed}}
\]

\[
\text{Trans} / \text{Cis} = \frac{\text{moles } t-2-\text{Butene produced}}{\text{moles } c-2-\text{Butene produced}}
\]

\[
2-B / B = \sum \frac{\text{moles } 2-\text{Butenes produced}}{\text{moles Butane produced}}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sample</th>
<th>Temp. °C</th>
<th>Weight (mg)</th>
<th>FlowRates SCCM</th>
<th>Deact. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>PP1</td>
<td>10.9</td>
<td>32.6</td>
<td>6 6 90</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>PP2</td>
<td>25.8</td>
<td>32.6</td>
<td>6 6 90</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>PP3</td>
<td>15.9</td>
<td>60.7</td>
<td>6 6 90</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>PP4</td>
<td>15.9</td>
<td>210</td>
<td>5 5 100</td>
<td>50</td>
</tr>
<tr>
<td>CP2</td>
<td>PZ1</td>
<td>16</td>
<td>68.7</td>
<td>6 6 90</td>
<td>4.2</td>
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<td>PZ2</td>
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<td>62.4</td>
<td>6 6 90</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>PZ3</td>
<td>15.9</td>
<td>209.1</td>
<td>5 5 100</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 21) Summary of Catalyst Samples and Their Deactivation Conditions
Analysis of Selectivities

P(61) Catalyst:

After deactivation of P(61) sample PP2, random measurements were made at total flow rates from 102 to 34 SCCM and temperatures between 25 and 55°C with the ratio of flow rates maintained at a 1:1:15 ratio. Measurements were taken approximately 40 minutes after changing the temperature and/or flowrate to ensure a constant product concentration. The results (Figure 48) appear to show that selectivity is independent of changes in temperature and flow rates and dependent only on overall conversion. However, under identical flow and temperature conditions, conversions were not reproducible and a definite decrease in overall activity occurred with TOS, indicating that the deactivation slowly continued even after several days on stream.

Random Experiments at SS - P(61) Cat - Red(750)/Ox(400)/Red(250)

Fig 48) Selectivity vs. % BD Conversion - Random SS measurements of CP2 Sample PP2
Sample PP3, which was twice PP2's weight and was deactivated at a lower temperature, maintained positive 1-B selectivity at higher conversions than PP2. Following this experiment, the catalyst slowly deactivated under constant plug flow conditions and selectivities (Figure 49) tracked the initial "SS" curve.

Pd Cat. SS and Deactivation from High BD Conv.

Figure 49) Deactivation of PP4 above the Kink point

Selectivities for sample PP4 were examined by varying total flow rate at constant temperature and inlet composition. An initial "blank" run (no catalyst) demonstrated that HC partial pressure was constant (±.5 SCCM) for C4 flow rates above one SCCM. Below this setting the controller became unstable and HC partial pressure increased. Total hydrogen flow rates were checked with a bubble flowmeter.
Twenty-five sequential experiments were made at temperatures from 16 to 45°C and H₂/BD ratios from unity to 3.3. In each case, the selectivities were constant up until the kink point (see Figure 50), where butenes begin to compete for adsorption sites. Selectivities found prior to the kink point were virtually constant, except the Trans/Cis ratio which decreased with temperature and increased with H₂/BD ratio (Figure 51).

Typical Selectivities for the P(61) PP4 Sample

![Graph showing selectivities for various compounds over BD conversion.

Fig 50) SS Meas. 25.5°C Flow Rate Lowered/Raised 10 min. Sample Time
Temperature and H₂/BD ratio also affected hydrogenation results after the kink point. Increasing reaction temperature (Figure 52) or H₂/BD ratio (Figure 53) decreased the BD conversion at which the kink point occurred. On the other hand, butane selectivity (Table 22) appeared to increase with H₂ partial pressure (or H₂/BD ratio).
Effect of Temperature at H2/BD: 1/1

% BD Conversion

Fig 52) Effect of Temperature on P(61)'s 1-B Selectivity

Effect of H2/BD at 20.6°C

% BD Conversion

Fig 53) Effect of H2/BD on P(61)'s 1-B Selectivity
<table>
<thead>
<tr>
<th>Expt PP4</th>
<th>TOS min</th>
<th>Temp °C</th>
<th>H2/BD</th>
<th>% Butadiene Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>W</td>
<td>545</td>
<td>35.2</td>
<td>1</td>
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</tr>
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<td>570</td>
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<td>0.140</td>
</tr>
<tr>
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<td>20.7</td>
<td>1.1</td>
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</tr>
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<td>380</td>
<td>30.5</td>
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<td>0.233</td>
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<td>R</td>
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<td>M</td>
<td>306</td>
<td>20.7</td>
<td>3.3</td>
<td>0.382</td>
</tr>
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</table>

Table 22) Comparison of Butane Selectivities (H2) for P(61) Sample PP4
Uncertainty in butane selectivity ≈ 0.003

Finally, we examined the effect of the kink point on both Trans/Cis (Figure 54) and 2-Butenes/Butane (Figure 55). At the kink point, Trans/Cis selectivity drops suddenly to a value (1.6) similar to that found for deactivation of the fresh catalyst. The 2-B/B ratio also drops suddenly at the kink point and maintains a value of around 5. This ratio is an indication of the amount of butene which is isomerized rather than hydrogenated.
Relationship of Trans/Cis Ratio and Kinkpoint

Figure 54) Relationship between Trans/Cis and kink point for P(61) catalyst
Equilibrium trans/cis 2-butene ratio (25°C) ≈ 3.1

Relationship of 2-Butenes/Butane Ratio and Kinkpoint

Figure 55) Relationship between 2-B/B and kink point for P(61) Catalyst
CP2 Catalysts:

After deactivation at 15.9°C both PZ2 and PZ3 showed similar SS selectivities for BD hydrogenation. Figure 56 shows typical selectivities for CP2 when the total flow rate and sampling were computer controlled to provide 40 samples while monotonically decreasing the flowrate from 110 to 22 SCCM and then 40 samples while returning to the original flowrate. The results indicate a catalyst with positive butene production up to >99.9% BD conversion with only 1% butane formation.

A direct comparison can be made between the P(61) sample PP4 and this experiment because both samples were the same weight and were deactivated in the same manner. The only difference between the samples, besides the presence of Cu in PZ3, was in the deactivation times; the P(61) and CP2 catalysts required 50 and 28 minutes, respectively (See Activation/Deactivation Section). After deactivation, both samples showed similar selectivities when reacted under plug flow conditions at 15.9°C. Information for this run was limited to BD conversions below 40% because this catalyst had only about 1/2 the activity of the CP2 catalyst. A comparison between typical 1-B selectivities for the PP4 sample at a higher temperature and those of this run is shown in figure 57. Clearly under these conditions the PC2 catalyst is better in terms of selectivity and activity for butadiene removal from butene streams.
Computer Controlled "SS" Measurements of CP2 Catalyst

% BD Conversion

Fig 56) SS Measurements of Cu/Pd:2/1 at Constant Temperature
T=15.9°C, FR Varied 1:1:15

Comparison of "SS" behavior of P(61) and CP2 Catalysts

% BD Conversion

Figure 57) Comparison of P(61) and CP2 Catalyst "SS" Selectivities
The P(61) Sample PP4 was reacted at 25.6°C
The CP2 Sample PZ3 was reacted at 15.9°C
Ratio of Flowrate remained 5:5:100
while the total was changed between 110 and 22 and then back to 110 SCCM
Experiments were conducted with this sample at temperatures varying from 16 to 44.8°C and with H₂/BD ratios of 1 and 1.64. The results showed that the selectivity is almost invariant with either temperature or H₂/BD ratio up until the conversion is reached at which the trans/cis ratio begins to change. Typical Trans/Cis and 2-Butene/Butane ratios for the PC2 catalyst are shown in Figure 58. In this case the kink point occurs around 65% BD conversion where both selectivities begin to decrease rapidly with increasing conversion until reaching final values of 1.6 and 1.9 Trans/Cis and 2-Butene/Butane ratios in the absence of butadiene.

\[
\text{Comparison of Selectivities for CP2 Catalyst at "SS"}
\]

\[
\begin{align*}
\text{2-B/BD} & \quad \text{Trans/Cis} \\
\% \text{ BD Conversion} & \\
\end{align*}
\]

Figure 58: Typical 2-Butene/Butane and Trans/Cis Selectivities for the CP2 catalyst

Trans/Cis ratios appear to be temperature and H₂/BD dependent in the region prior to the kink point (Figure 59). Unfortunately, since these experiments were not random, an analysis of variance could not be performed. What appears to be a temperature dependence may actually be a catalyst aging effect. The dependence on H₂/BD ratio is more reliable because these experiments were done in different order
depending on the temperature and in all cases showed a decrease in trans/cis ratio for the lower partial pressure of hydrogen.

**Dependence of Trans/Cis on Temp. and H/BD Ratio CP2 Catalyst**

![Graph showing the dependence of Trans/Cis ratio on temperature and H/BD ratio.]

Figure 59) Apparent Dependence of Trans/Cis ratio on Temp and H2/BD Ratio

Table 23 compares average selectivities prior to the kink point for P(61) and CP2 catalysts. In both cases very little butane is produced. However, these catalyst varied significantly with lower 1-B/2-B and higher trans/cis selectivities for the CP2 catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1-B</th>
<th>B</th>
<th>c-B</th>
<th>t-B</th>
<th>BD</th>
<th>1-B/2-Bs</th>
<th>Trans/Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>0.716</td>
<td>0.001</td>
<td>0.065</td>
<td>0.218</td>
<td>-0.999</td>
<td>2.53</td>
<td>3.33</td>
</tr>
<tr>
<td>SDEV</td>
<td>0.010</td>
<td>0.001</td>
<td>0.007</td>
<td>0.008</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP2</td>
<td>0.619</td>
<td>0.002</td>
<td>0.061</td>
<td>0.317</td>
<td>-0.998</td>
<td>1.64</td>
<td>5.19</td>
</tr>
<tr>
<td>SDEV</td>
<td>0.012</td>
<td>0.001</td>
<td>0.009</td>
<td>0.010</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 23) Comparison of Average "SS" Selectivities for P(61) and CP2 Catalysts

After the kink point, as in the case of P(61), the rates of both butene isomerization and hydrogenation increased markedly. Table 24 lists the butane selectivities(H2) found
for all 14 experiments. Unfortunately, the activity of the catalyst was not sufficient in the case of catalysts reacted under a H₂/BD ratio of 1 to give much useful information. For those experiments with H₂/BD equal to 1.64, there is a definite decrease in butane production with temperature increase. Whether this effect is truly due to the temperature or TOS we do not know.

<table>
<thead>
<tr>
<th>Expt PZ3</th>
<th>TOS hrs.</th>
<th>Temp</th>
<th>H2/BD</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>99</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>136</td>
<td>16.0</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>e</td>
<td>160</td>
<td>21.0</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>g</td>
<td>232</td>
<td>25.7</td>
<td>1</td>
<td>0.001</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>j</td>
<td>358</td>
<td>30.6</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>k</td>
<td>381</td>
<td>35.3</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>n</td>
<td>455</td>
<td>40.2</td>
<td>1</td>
<td>0.001</td>
<td>n/a</td>
<td>0.001</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>o</td>
<td>480</td>
<td>44.8</td>
<td>1</td>
<td>n/a</td>
<td>0.002</td>
<td>n/a</td>
<td>0.003</td>
<td>n/a</td>
</tr>
<tr>
<td>a</td>
<td>40</td>
<td>16.0</td>
<td>1.64</td>
<td>0.003</td>
<td>0.019</td>
<td>0.042</td>
<td>0.073</td>
<td>0.109</td>
</tr>
<tr>
<td>b</td>
<td>65</td>
<td>16.0</td>
<td>1.64</td>
<td>0.010</td>
<td>0.024</td>
<td>0.052</td>
<td>0.080</td>
<td>0.128</td>
</tr>
<tr>
<td>c</td>
<td>92</td>
<td>16.0</td>
<td>1.64</td>
<td>0.020</td>
<td>0.020</td>
<td>0.020</td>
<td>0.091</td>
<td>0.139</td>
</tr>
<tr>
<td>f</td>
<td>187</td>
<td>21.0</td>
<td>1.64</td>
<td>0.005</td>
<td>0.026</td>
<td>0.059</td>
<td>0.079</td>
<td>0.112</td>
</tr>
<tr>
<td>h</td>
<td>284</td>
<td>25.7</td>
<td>1.64</td>
<td>0.004</td>
<td>0.008</td>
<td>0.023</td>
<td>0.048</td>
<td>n/a</td>
</tr>
<tr>
<td>i</td>
<td>335</td>
<td>30.6</td>
<td>1.64</td>
<td>0.002</td>
<td>0.003</td>
<td>0.003</td>
<td>0.024</td>
<td>0.063</td>
</tr>
<tr>
<td>l</td>
<td>407</td>
<td>35.3</td>
<td>1.64</td>
<td>0.026</td>
<td>0.026</td>
<td>0.011</td>
<td>0.027</td>
<td>0.059</td>
</tr>
<tr>
<td>m</td>
<td>432</td>
<td>40.2</td>
<td>1.64</td>
<td>0.002</td>
<td>0.003</td>
<td>0.008</td>
<td>0.018</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Table 24: Comparison of Butane Selectivities (H₂) for CP2 sample PZ3
Dimensionless Selectivities and Comparison of Catalysts with Literature:

Both catalysts were analyzed using a Langmuir-Hinshelwood model modified by the following assumptions: no diffusion limitations, butane forms from 1-butene and butadiene, 2-butenes form from 1-B isomerization BD hydrogenation, the rate dependence on partial pressure is similar for all reactions, and the adsorption and reaction coefficients of the 2-butenes are similar. This method was first used by Boitiaux et al. (25) and leads to the following simplified reaction sequence:

\[
\begin{align*}
Kbd & \xrightarrow{k_1} B1 \\
BD & \xrightarrow{k_1' + k_3} B_a + B_2 \\
Kb1 & \xrightarrow{k_2 + k_4} B1 + B_2
\end{align*}
\]

where \(BD\) = butadiene, \(B_1\) = 1-butene, \(B_2\) = 2-butenes, \(B_a\) = butane, \(k\) = reaction coefficient, \(K\) adsorption coefficients.

The Langmuir rate equations are then:

\[
\frac{dBD}{dt} = \frac{-(k_1 + k_1' + k_3)KbdBD \cdot f(P_{H_2})}{1 + KbdBD + Kb1B1 + Kb2B2}
\]

and

\[
\frac{dB1}{dt} = \frac{k_1 \cdot Kbd \cdot BD \cdot f(P_{H_2})}{1 + Kbd \cdot BD + Kb1 \cdot B1 + Kb2 \cdot B2} - \frac{(k_2 + k_4)Kb1 \cdot B1 \cdot f(P_{H_2})}{1 + Kbd \cdot BD + Kb1 \cdot B1 + Kb2 \cdot B2}
\]

whose ratio becomes:
\[
\frac{dB_1}{dB} = \frac{k_2 + k_4 \cdot k_b}{k_1 + \frac{1}{K_b d \left(1 + \frac{(k_1' + k_3)}{k_1} \cdot K_B D\right)}} - \frac{1}{1 + \frac{(k_3' + k_1')}{k_1}}
\]

or
\[
\frac{dB_1}{dB} = \gamma \frac{B_1}{BD} - \alpha
\]

After Integration one obtains:
\[
B_1 = \frac{-\alpha}{1 - \gamma} A + C \cdot BD^\gamma\text{ Eqn.1}
\]

where C is function of the initial conditions:
\[
C = \left(Bo + \alpha \cdot BD^\gamma \gamma / (1 - \lambda)\right)BD^\gamma\text{ Eqn.2}
\]

From the parameters \(\alpha\) and \(\lambda\) one can calculate the following dimensionless selectivities as previously defined by Boitiaux (25):

Selectivity of direct formation of 1-B from Butadiene \(Sp^{1-2} = \frac{k_1}{k_1' + k_3}\)

Selectivity of 1-4 addition: \(Sp^{1-4} = \frac{k_1'}{k_1}\)

Selectivity of direct formation of butane: \(Sp^{ba} = \frac{k_3'}{k_1}\)

Selectivity of consecutive reactions: \(Sc = \frac{k_1 \cdot K_b d}{k_2 + k_4 \cdot K_b 1}\)

An advantage of using these selectivities is their independence of BD conversion; they depend only on catalyst characteristics and temperature. Using Newton's method, the experimental data were fit to Equations 1 and 2; the results are shown in Figures 60 and 61.
Typical Fitting of Dimensionless Selectivities for PP4 Catalyst

Fit of P(61) Data Prior to Kink Point

Lambda = 7.079e-4

Alpha = 7.3621e-1

Sdev = .02

Pd/Alumina - Boitiaux (25)

% 1-Buten in Product

% BD in Product

Figure 60) Fitting of P(61) Data to L-H model for Calculation of Dimensionless Selectivities

Comparison of CP2 Catalyst with Literature

Fit of CP2 Data

Pd + Promoter, Procatalyse LD 271
Derrien (1)

Pt/alumina with Piperidine
Boitiaux et al. (33)

% 1-B in Product

%BD in Product

Figure 61) Fitting of CP2 Data to L-H model, Comparison with Literature
Data shown for Decrease ◇ and Increase * in Flowrate
The effect of the kink point on these types of theoretical curves was also investigated for the Pd sample (Figure 62). Clearly a fundamental change in the reaction occurs and the L-H model is no longer valid under these conditions. The selectivities calculated prior to the kink point agree well with those of the previous figure.

**Effect of Kinkpoint on L-H Model**

![Graph showing the effect of kink point on L-H model.]

Lambda = 7.079e-4  
Alpha = 7.3621e-1  
Sdev = 0.02

Figure 62) Effect of Kink point P(61) Results

<table>
<thead>
<tr>
<th>Figure #</th>
<th>Sp(ba)</th>
<th>Sp(1-4)</th>
<th>Sp(1-2)</th>
<th>Sc</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(61)</td>
<td>1</td>
<td>0.36</td>
<td>2.79</td>
<td>1040</td>
<td></td>
</tr>
<tr>
<td>P(61)</td>
<td>3</td>
<td>0.35</td>
<td>2.83</td>
<td>1380</td>
<td></td>
</tr>
<tr>
<td>CP2 d</td>
<td>2</td>
<td>0.57</td>
<td>1.75</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>CP2 u</td>
<td>2</td>
<td>0.48</td>
<td>2.08</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>Pd Cat</td>
<td>Boitiaux-1</td>
<td>0</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Pt Cat w/</td>
<td>Boitiaux-2</td>
<td>0.38</td>
<td>0.47</td>
<td>1.18</td>
<td>100</td>
</tr>
<tr>
<td>Piperidine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LD 271</td>
<td>Derrien 2</td>
<td>0</td>
<td>0.4</td>
<td>2.5</td>
<td>165</td>
</tr>
</tbody>
</table>

Table 25) Dimensionless Selectivities of CP2 and P(61) Catalysts
Although the selectivity values obtained by Boitiaux (25,33) and Derrien (1) came from liquid phase hydrogenation experiments, they were similar to those from this work except in the case of the Pd alumina catalyst. Initial selectivities for the P(61) catalyst when compared with those given by Boitiaux et al. (25) differ significantly in both Sp(1-2) and Sc selectivities (Figures 67,68: Table 26). In both cases, selectivities calculated from data prior to the kink point far exceeded those given in literature.

Selectivities for CP2 under our experimental conditions, as shown in Figure 64, were similar to those reported (1) for the Procatalyse catalyst LD271 and better than those for Pt/Alumina treated with piperidine.
Kinetic Results

The kinetics of 1,3-butadiene hydrogenation in the presence of 1-butene were examined for the P(61) and CP2 catalysts. In the case of P(61), the catalyst followed a limiting form of the Langmuir-Hinshelwood equation in which the reaction rate was first order in hydrogen and zero order in butadiene. For the CP2 catalyst, however, the rate exhibited a negative order dependence on butadiene as well as a first order dependence on hydrogen. Measurements were taken under plug flow conditions with constant temperature and inlet partial pressures. BD conversions were varied in the plug flow reactor by changing the total flow rate of the gasses.

Langmuir-Hinshelwood:

The modified Langmuir-Hinshelwood equation (Eqn. 1) was derived using the following assumptions: non-competitive adsorption between hydrocarbons and hydrogen, the rate controlling step is the reaction of the surface species, rate is first order in hydrogen, butenes and butadiene are competing for the same sites, and no diffusion limitations. We have made no assumptions as to whether hydrogen adsorption is associative of dissociative.

\[ r_{BD} = \frac{-k_aK_{BD}P_{BD}K_{H2}P_{H2}}{1 + k_{BD}P_{BD} + K_{1B}P_{1B}} \]  

\[ r_o = kP_{H2} \quad \text{where} \quad k = k_aK_aK_{H2} \]

We can then calculate the observed reaction coefficients from the following equation calculated for the plug flow reactor.
\[
\ln \left( \frac{P_{H_2o}}{P_{H_2o} - P_{BD}X_{BD}} \right) = \frac{W_{PD}V_{BED}k_{wobs}}{FR} \quad \text{equation A}
\]

\[FR = \text{Total Flow Rate of Gases}\]
\[V_{BED} = .55 \text{ CC for all samples}\]

Analysis of P(61):

Effect of Kink point on Activities:

As discussed previously, the selective hydrogenation of butadiene for this catalyst has been hampered by the sudden loss of catalyst selectivity at an intermediate BD conversion. Figure 63 shows the effect of this phenomenon on the average \(K_{obs}\) (or \(K'_{obs}\)) calculated as a function of butadiene conversion in the following manner:

One can rewrite equation A:

\[Y = k'_{obs} \cdot X\]

where \(Y = \ln(\cdot) = \ln \left( \frac{P_{H_2o}}{P_{H_2o} - P_{BD}X_{BD}} \right)\) and \(X = \frac{1}{FR}\)

Then by linear regression one obtains:

\[k'_{obs} (BD Conv.) = \frac{\sum_{i=0}^{n} X_i \cdot Y_i}{\sum_{i=0}^{n} X_i \cdot X_i}\]

where \(n\) increases stepwise from 1 to the number of data points taken in a run.

for \(k'_{obs}\) based on hydrogen removal we used the same calculation method but \(\ln(\cdot) = -\ln(1 - x_{H_2})\) in this case.
In this figure, we compare the average observed reaction coefficients of BD with that of hydrogen in order to compare the total hydrogenation with that of the butadiene. It is clear that $K_{obs}'$ of butadiene hydrogenation changes little, although the rate of butene hydrogenation suddenly increases at this point.

**Effect of Kinkpoint on Catalyst Activity - Typical PP4 Catalyst**

![Graph showing the effect of kinkpoint on Catalyst Activity](image)

Figure 63) Effect of Kink point on Kobs for Butadiene Hydrogenation

$k_{wobs}$ and $E_{app}$ Calculations:

For each sample $k_{wobs}$ was calculated between flow rates of 110 and 45 SCCM which proved to be linear in all cases. Figure 64 and Table 26 show all the data and calculation for each PP4 run.
Calculation of 1'st Order Kwobs for PP4

Figure 64) Calculations for K_{wobs} of PP4 Sample

<table>
<thead>
<tr>
<th>Run</th>
<th>TOS (min.)</th>
<th>Temp. K</th>
<th>H2/BD</th>
<th>Kwobs</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>63</td>
<td>289</td>
<td>1.64</td>
<td>9.15</td>
</tr>
<tr>
<td>F</td>
<td>115</td>
<td>298.7</td>
<td>1.64</td>
<td>27.69</td>
</tr>
<tr>
<td>G_H</td>
<td>136</td>
<td>293.6</td>
<td>1.64</td>
<td>13.64</td>
</tr>
<tr>
<td>I</td>
<td>148</td>
<td>298.7</td>
<td>1.64</td>
<td>25.29</td>
</tr>
<tr>
<td>J</td>
<td>165</td>
<td>299.7</td>
<td>1.64</td>
<td>23.78</td>
</tr>
<tr>
<td>K</td>
<td>235</td>
<td>298.7</td>
<td>1.64</td>
<td>20.78</td>
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<tr>
<td>L</td>
<td>279</td>
<td>293.8</td>
<td>1.64</td>
<td>11.80</td>
</tr>
<tr>
<td>M</td>
<td>306</td>
<td>293.8</td>
<td>3.3</td>
<td>10.76</td>
</tr>
<tr>
<td>O</td>
<td>359</td>
<td>298.8</td>
<td>1.1</td>
<td>17.45</td>
</tr>
<tr>
<td>P</td>
<td>380</td>
<td>303.6</td>
<td>1.1</td>
<td>29.20</td>
</tr>
<tr>
<td>Q</td>
<td>401</td>
<td>303.7</td>
<td>1.64</td>
<td>28.93</td>
</tr>
<tr>
<td>R</td>
<td>423</td>
<td>303.6</td>
<td>2</td>
<td>26.25</td>
</tr>
<tr>
<td>S</td>
<td>448</td>
<td>308.3</td>
<td>1.64</td>
<td>37.64</td>
</tr>
<tr>
<td>T</td>
<td>473</td>
<td>308.3</td>
<td>1.1</td>
<td>66.04</td>
</tr>
<tr>
<td>U</td>
<td>497</td>
<td>308.3</td>
<td>1.1</td>
<td>47.25</td>
</tr>
<tr>
<td>W</td>
<td>545</td>
<td>308.3</td>
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<td>37.92</td>
</tr>
<tr>
<td>X</td>
<td>570</td>
<td>313.3</td>
<td>1</td>
<td>64.81</td>
</tr>
<tr>
<td>Y</td>
<td>597</td>
<td>317.9</td>
<td>1</td>
<td>89.29</td>
</tr>
</tbody>
</table>

Table 26) K_{wobs} for P(61) Catalyst Runs
K_{wobs} units = 1/(g Pd * minutes)
From the reaction coefficients above we calculated the apparent activation energy of the catalyst (Figure 65).

**Calculation of $E_{app}$ for PP4 Catalyst**

$E_{app} = 14.9 \pm 0.2$ kcal/mol

- Slope = -7487.04
- Intercept = 28.0845
- Correlation = 0.9636
- Sdev = 0.167

Figure 65) Calculation for $E_{app}$ of P(61) Catalyst
Analysis of CP2 Catalyst:

A kinetic analysis of the CP2 catalyst proved to be difficult. Instead of following the same rate equation for BD hydrogenation this catalyst exhibited a negative order behavior with respect to BD pressure. One CP2 experiment was plotted in the same manner as Figure 66 for P(61). It is obvious from this figure that butadiene hydrogenation over the Cu/Pd:2/1(at) catalyst is strongly dependent on BD pressure.

**Example of Attempt to Fit 1'st Order Rate Constant to CP2 Catalyst**

![Graph](image)

**Figure 66** Comparison of PZ3 Results with 1'st order H2 rate model.

Due to time constraints further analysis of PC2 kinetics will be continued elsewhere.
Summary of Results

Prior to the Kink Point:

1) Selectivities remained virtually constant preceding the kink point.
2) Trans/Cis ratios during "SS" appeared to decrease with increasing temperature and increasing H₂/BD ratio; average values were 3.33 and 5.19 for P(61) and CP2 respectively.
3) Both catalysts were highly selective for butene formation.
4) P(61) was more selective than CP2 for 1-B formation.
5) Sc values for the P(61) catalyst were more than 100 times that reported in literature for liquid phase hydrogenation with a typical Pd/alumina catalyst.
6) CP2 was superior to a Pt + piperidine catalyst and similar to the Procatalyse LD271 catalyst in terms of selectivity.
7) Activity for BD hydrogenation of the P(61) catalyst was first order in hydrogen and zero order in BD, while the CP2 catalyst had a strong negative order dependence on BD.

Both catalysts showed ≈100% selectivity for the formation of butenes prior to the kink point. The P(61) catalyst had a higher selectivity for 1-B production while the Trans/Cis ratio of CP2 was higher. Table 27 compares reported gas phase selectivities with P(61) and CP2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp</th>
<th>1-B</th>
<th>t-2B</th>
<th>c-2B</th>
<th>Trans/Cis</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03wt%Pd</td>
<td>308</td>
<td>0.53</td>
<td>0.42</td>
<td>0.05</td>
<td>8.75</td>
<td>11</td>
</tr>
<tr>
<td>5 mol% Pd</td>
<td>316</td>
<td>0.59</td>
<td>0.37</td>
<td>0.04</td>
<td>9.70</td>
<td>13</td>
</tr>
<tr>
<td>P(61)</td>
<td>289-313</td>
<td>0.72</td>
<td>0.22</td>
<td>0.07</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>CP2</td>
<td>289-313</td>
<td>0.62</td>
<td>0.32</td>
<td>0.06</td>
<td>5.20</td>
<td></td>
</tr>
</tbody>
</table>

Table 27) Comparison of Literature Selectivities with P(61) and CP2
Selectivities based on BD.

Selectivities found for P(61) in the "SS" are quite different from selectivity values of Pd/alumina given in the literature for liquid hydrogenation of BD. The Sc value for P(61) was 100x the reported value, suggesting that the gas phase adsorption is more than just a simple competition for sites.

\[
Sc = \frac{k_1}{k_2 + k_4} \frac{Ka}{Kb_1}
\]

Perhaps BD adsorption with a stabilized monolayer of BD follows a similar mechanism as recently described by Cider (117) in the cross-desorption of CO and acetylene. According to the proposed mechanism, gas phase BD adsorbs very close to an already adsorbed species causing a local disturbance in the electronic state of the surface which might speed hydrogenation of the previously adsorbed molecule. In this way 1-B would be absent from the surface while BD is present and hydrogen pressure is low.

Figure 64 compares CP2 selectivities with published values for promoted catalysts in liquid phase BD hydrogenation. Selectivities for the CP2 catalyst (which where stable up to \(\approx\)100% BD conversion) far exceeded those of Pt + piperidine and were comparable to those of the Procatalyse promoted Pd catalyst LD271. Unfortunately, since we have no information on the performance of our catalyst under liquid phase conditions, we cannot make any definite conclusions about its usefulness in an industrial situation.

Hydrogenation of BD over P(61) is first order in hydrogen and zero order in BD. CP2, though, showed a definite negative order dependence on BD pressure. Boitiaux, et al. found a negative order dependence on BD hydrogenation for Pt and Rh, but not for Pd. They explained (23) this negative order dependence by the complexation of metal sites with 2 BD species, rendering the site inactive. The surface equilibrium constant between the "complexed" and active BD species, called \(K'\), was a function of dispersion for the catalysts.
$$r_{BD} = -k \frac{KC_{by}}{1 + KC_{by}(1 + K'C_{by}) + K_oC_o}$$

They found (19,20,33) that adding ligand promoters (e.g. piperidine, Group Ib metals) decreases complexation and increases the rate of BD hydrogenation (although it was still dependent on dispersion). The Pd-BD system did not follow this hypothesis, showing a simultaneous BD TOF dependence on dispersion and independence of butadiene pressure (as shown in this work). In our system, addition of a ligand promoter (Cu) to our Pd catalyst caused a change in reaction rate from zero to negative order in BD. According to their theory, negative order dependence implies that the BD can "complex" on the CP2 catalyst where it could not do so on the P(61) catalyst. Boitiaux et al (32) also reported a similar, although only slightly, negative BD dependence on hydrogenation rate using a Pd/alumina catalyst modified with piperidine. This seeming contradiction will be examined elsewhere.

Kink Point or "acceleration point":

1) There was a substantial decrease in 1-B selectivity as 1-B was both hydrogenated and isomerized.

2) Trans/Cis dropped suddenly from its "SS" value of near 3.5 to near 2 (equilibrium in this case was ≈3.1).

3) The 2-B/nB also dropped with the sudden formation of n-B and continued to decrease until a value of around 5.

4) The position and character of the curve following the kink point was highly dependent on the H2/BD ratio, temperature, and catalyst history. At low temperatures and hydrogen pressure the stability of the "SS" region reached
higher BD conversions. In some cases (high temp. and H₂/BD) the so called "SS" was never reached.

5) Little change in the rate of BD conversion occurred after the kink point, but while it maintained a near 1'st order dependence on H₂, butane formed quickly.

6) All samples showed an hysteresis when the total gas flow rate was lowered and raised again. The high selectivities experienced under "SS" conditions did not return immediately but required a few hours of re-exposure to BD.

A similar kink point was also observed in the case of the CP2 catalyst although it did not represent as drastic a change:

1) The Trans/Cis ratio decreased from near 6 at "SS" to about 3.5 in the presence of BD and continued to decrease with contact time until reaching about 1.6 in the absence of BD in the product. The thermodynamic equilibrium value for this sample was near 3.2.

2) The 2-B/nB ratio also decreased and at 99.9% BD conversion was near 3 and continued to decrease to near 1.6 in the absence of BD in the product.

3) Selectivity for 1-B production improved slightly after returning from low flow rates (high conversions) to higher flowrates.

Discussion of Kink point:

The curious behavior found during hydrogenation of BD over palladium is not without precedent in literature. In 1963, Meyer and Burwell (11) described that the
reaction was almost 100% butene selective until a BD conversion was reached at which the following occurred: butane formed, 1-B selectivity dropped rapidly, 2-butene selectivities increased, and Trans/Cis 2-butene ratio decreased.

More recently, Leviness (44) reported a similar phenomenon ("acceleration point") during the selective hydrogenation of acetylene over Pd/alumina catalysts. He surmised that the sudden loss in ethylene selectivity at low acetylene concentrations was caused indirectly by acetylene diffusion limitations in the catalyst pores. According to Leviness, the acetylene partial pressure must exceed a critical measurable value for total metal coverage by acetylene. Once ethyne drops below this critical pressure, ethylene competes for surface sites, ethane forms, and ethylene selectivity drops rapidly. In diffusional limited catalysts this occurs first in the catalyst's pores where the ethyne concentration is less than that found near the particles outer surface. Leviness speculated that the production of oligomer/polymers ("green oil") known to occur during this reaction might amplify these problems by introducing a liquid layer through which the acetylene must diffuse to reach Pd sites.

Boitiaux and others, who have completed liquid phase BD hydrogenation studies, have not reported the appearance of a kink point. They did show that BD hydrogenation over supported Pt, Pd, and Rh closely follows a Langmuir-Hinshelwood (BD/butene competition sites) model with less than 0.1% residual 1,3-butadiene present. On the other hand, Boitiaux et al. also reported typical selectivities for Pd/alumina catalysts reacted in the liquid phase that were inferior to those given in this work prior to the kink point.

As did Meyer and Burwell (11), we found that after the kink point the Trans/Cis decreased. Trans/Cis decreased dramatically from 3.5 past the equilibrium ratio (3.1) to near 2.0 for P(61). On the other hand, this ratio decreased slowly for CP2 until BD was absent when it hurried to a value of near 1.6 (equilibrium was 3.2). It is unkown whether
the isomerization occurred on alumina or palladium sites. Boitiaux et al. (30) also found a lower than equilibrium Trans/Cis value of 1.6 for butene isomerization over Pd/alumina in the liquid phase at 20°C. In gas phase studies, Ragaini et al. (1969,45) studied 1-B isomerization over Pd/alumina catalysts at 50°C and found the 2-Bs ratio lower than the equilibrium value of 2.8 and decreasing to unity with decreasing H₂ pressure. Riley (2) also reported trans/cis ratios near 2 for the gas phase hydrogenation of BD which he attributed to the isomerization of 1-B on Pd. Hightower and Hall (46) have shown that aluminas characteristically yield Trans/Cis ratios of much less than unity for 1-Butene isomerization.

To my knowledge, no one has reported the strange hysteresis which we have found for product selectivities and activities during an increase and then decrease in the PFR's space time, although, at the same time, we have not seen any papers in which this type of analysis was run.

How do we explain this observed behavior?

As in the case of catalytic acetylene hydrogenation, polymerization occurs during reaction of 1,3-butadiene with hydrogen. We have no information on the quantity of this material produced, composition, or its position on the catalysts surface. We do know that a volatile portion of this oligomer can desorb from the surface (From the Activation/Deactivation section), indicating that during BD hydrogenation an equilibrium is established between the formation and desorption of these species. Other higher molecular weight polymers are also produced during BD hydrogenation. Sarkany et al. (6) showed these polymers are mainly formed from whichever (labeled or unlabeled)
butadiene that the catalyst sees first. We surmise that these polymeric products might cause increased diffusion limitations and loss of reaction sites.

Thiele Moduli ($\phi_s$) and Efficiency factors ($\eta_{\text{eff}}$) were estimated for the reaction of a particular P(61) hydrogenation run during which a kink point occurred (Appendix). Assuming no polymeric influence, we found that diffusion limitations are unlikely ($\phi_s \approx 0.47$) and yet many of our observations do not support this conclusion (e.g. kink point decreases with increasing temperature and hydrogen pressure; these changes would increase the reaction rate and thus diffusion limitations). We suspect that formation of polymer could decrease the catalyst's average pore radius and/or form a liquid barrier between the diene reactant and Pd surface. We calculated $\phi_s$ and $\eta_{\text{eff}}$ values for a variety of situations of reduced pore radius and diffusion through a liquid phase (estimated to be n-octane) and found the following results:

1) It is not likely that a reduction of pore radius alone could cause diffusion limitations in these catalysts. A large decrease in radius (from 115Å to 10Å) would be required (see Figure 70, Appendix).

2) For BD diffusion through a liquid phase (n-octane), on the other hand, we have estimated the Thiele moduli to be 7.6 and 10.2, for effective pore radii of 115Å and 50Å, respectively. BD concentration profiles for a spherical pellet with these values of the $\phi_s$ are given in Figure 71, Appendix).

After the kink point, the following occurred for the P(61) catalyst: 1-B selectivity rapidly decreased, butane formed, Trans/Cis dropped to 2, 2-B/nB dropped to 5, BD hydrogenation activity remained the same, and 1-B isomerization/hydrogenation became significant. We have shown that these occurrences cannot be explained by a simple L-H competition for sites. Instead the following possibilities are considered.
1) Additional sites (Pd and/or alumina) for hydrogenation and isomerization become available after the kink point. This opening of sites may be due to: the desorption of oligomer/polymer (in the absence of large amounts of BD) which may open up previously filled pores; the desorption of oligomer from Pd sites (assuming an equilibrium between the formation of oligomer from BD and its desorption); the removal of strongly adsorbed slow-reacting BD species from Pd sites; and/or the successful competition of 1-B for alumina sites previously blocked by BD.

2) A change in the adsorption mechanism of BD may occur. BD adsorption prior to the kink point may proceed via cross-desorption in which an attempted BD adsorption aids hydrogenation of a nearby adsorbed species. We surmise that this would only occur under hydrogen deficient conditions with local BD coverage; once 1-B begins to compete for sites it may start a chain of events that destroys the stability of this BD layer and allows further adsorption of 1-B.

Finally, we have to explain the hysteresis observed in all P(61) samples. If diffusion effects were the only explanation for the observed results and the reaction was merely a L-H competition for adsorption sites, then we would expect that raising the flowrate would follow back along the same curve seen for lowering the flowrate. The first possibility is that it was merely a temperature effect. Since additional hydrogenation reactions occurred after the kink point, the catalyst sample might have experienced a temperature runaway which required some recovery time. However, this does not seem likely for the following reasons: the alumina catalyst has only 0.5wt%Pd and is further diluted by a 1/1 weight ratio of additional alumina, the reactant gasses are diluted with a typical value of 95% N₂, and the rate of BD hydrogenation does not increase after the kink point. The reactor's flow characteristics were also examined and we concluded that
the hysteresis could not be caused by the transition between laminar and turbulent flow (see Appendix for calculations of Reynold's number). Another explanation may be the slow reformation of oligomer or strongly adsorbed BD species which either blocks 1-B adsorption sites or causes a change in the Pd surface energies and consequently the surface adsorption characteristics, again in favor of BD. In 1989, Ouchaib et al. (29) measured the relative adsorption coefficients of BD and 1-B on a fresh and stabilized Pd/alumina catalyst with the following results: $\frac{Abd}{Ab} = 2.9$ and 12 for the fresh and stabilized catalyst respectively.
V. Conclusions and Recommendations

Temperature Programmed Reduction (TPR):

Hydrogen consumption in great excess of values predicted for metal reduction hindered quantitative measurements of the reductions. The "fresh" P(61) catalyst, in particular, consumes 11 times the hydrogen expected for metal reduction, clearly indicating partial decomposition/hydrogenation of the Pd precursor. Whether this reaction gives methane or some other product, however, is unknown and should be investigated using mass spectrometry. Only catalysts Red(750°C)/ Ox(400°C,10min) had "clean" TPR profiles.

Palladium oxide reduces below room temperature. During temperature programmed reduction in 10%H2/Ar decomposition of the palladium/hydride phase occurs near 369K (96°C). Unsupported copper oxides reduce near 620K (347°C). After high temperature reduction (750°C) and calcination (400°C,10min), copper containing alumina supported catalysts reduce below 523K (250°C). This indicates the existence of copper as Cu2+ ions with surface interaction instead of copper oxide.

Catalysts Red(750°C)/Cal(400°C,10min)/Red(250°C,10min) are fully reduced and ready for use in hydrogenation.

Activation/Deactivation:

Activation and deactivation of the CP2 and P(61) catalysts were studied under plug flow conditions. Both catalysts suffered rapid deactivation (≈95% activity loss in < 6 hours) attributable to polymer buildup covering the Pd surface and filling some alumina
pores. Evacuation or N₂ purging restored most of the P(61) catalyst's activity. Moreover, the selectivity of this regenerated catalyst was similar to that of a "fresh" catalyst. When deactivated again under constant plug flow conditions, this catalyst behaved similarly to the fresh catalyst. The trans/cis ratio remained relatively low (≈unity for P(61) and ≈3 for CP2) until stability was reached, after which it increased and stabilized at a value somewhat above equilibrium.

During deactivation, the hydrogenation and isomerization reactions consume net 1-B until BD conversion drops below 80% and 10% for CP2 and P(61), respectively. Catalyst treatment in hydrogen (250°C) or oxygen (400°C) modifies the beneficial interaction between Cu and Pd in CP2.

**BD Hydrogenation over Stabilized Catalysts:**

The bimetal catalyst (CP2) is more active and selective than palladium alone (P(61)) for the hydrogenation of BD. Although both catalysts were prepared and pretreated under exactly the same conditions, P(61) cannot prevent 1-B consumption at high BD conversions. On the other hand, CP2 removes virtually all BD present (≈100% conversion), without significant butane production or butene isomerization. Selectivities for CP2 under our experimental conditions were similar to literature values for an industrial catalyst (Procatalyse LD271). It is unknown, however, whether CP2 would react as well under the industrial situations in which the Procatalyse catalyst was tested.

Kinetics of BD hydrogenation are different for the two catalysts. Rate dependence on BD pressure (in the low conversion range) is zero order for palladium alone P(61) and becomes negative order with copper addition (CP2). The rate varies linearly with
hydrogen pressure over both catalysts. Activation energy for BD hydrogenation over P(61) is 14.9 ± 0.4 kcal/mol.

For stabilized catalysts, BD conversion could be increased in the plug flow reactor by decreasing the gas space velocity. At low conversions P(61) is highly selective (Sc ≈ 1000) with virtually no butane formation and high 1-B selectivity (>70%). Beyond a certain BD conversion (≈ 40% for the 9%BD/1-B mixture) this high selectivity is lost and 1-B quickly isomerizes and hydrogenates. The reason for this change is unclear and cannot be explained merely by a L-H competition for sites between 1-B and BD. This type of event is sometimes attributed to diffusion limitations, and although we have calculated \( \eta_{\text{eff}} \) (Appendix) to be greater than 99% for the fresh catalyst, the formation of oligomer/polymer could create diffusional problems by decreasing the effective diffusion coefficient.

When the space velocity is again increased (to decrease BD conversion), rather than following the same selectivity curve, a hysteresis is found. Several possibilities are considered for this phenomenon, though additional experiments have to be made before any conclusions can be drawn. One likely explanation is that additional sites become open to 1-B adsorption and reaction (on Pd and/or alumina) at low partial pressures of BD due to the desorption of oligomer.

We recommend gravimetric analysis of the P(61) catalysts. This technique may detect whether massive desorption of oligomer occurs at the kink point. Also, temperature programmed oxidation (TPO) on the spent catalysts may determine the extent of oligomer/polymer covering the Pd surface rather than the alumina. Finally, an examination of oligomer content versus time would reveal the relative amount of butadiene oligomerized versus hydrogenated.
Finally, more information is needed on the effects of copper addition to Pd and the effect of pretreatment on bimetal interaction. Hydrogenation studies should continue with analysis of the remaining Cu-Pd catalysts (PC5 and CP1) and also analysis of all palladium containing catalysts using different pretreatments. Bimetal interactions may be detected from hydrogen titration experiments using small aliquots of 10%H2/Ar. Since Pd-hydride decomposes in 10%H2/Ar near 96°C, titrations should be performed first at 110°C then at room temperature to separate adsorbed and absorbed hydrogen. A decrease in either of these quantities would be a strong indication of Pd-Cu interaction.
V. Literature Cited


8) Sárkány, A., Hightower, J.W., Steffler, G., Furlong, B., and Gučzi, L., ?


VI. Appendix

Calculations of Effectiveness Factor, Thiele Modulus, and Reynolds Number

Calculation of the Effectiveness Factor and Thiele Modulus

The nominal properties of the catalyst are:

Pellet Radius (R) ≈ 0.3 mm. (used largest pellet size, see Figure 7)

Average Pore Radius ≈ 115 Å (Figure 6)

Specific Surface Area ≈ 61 m²/g

Specific Pore Volume (\(V_g\)) is estimated from the average pore radius and specific surface area assuming all pores were one continuous cylinder \(L_g\) long with a radius of \(r_{avg}\).

\[
V_g = S_g \cdot \frac{\pi \cdot r_{avg}^2 \cdot L_g}{2 \pi \cdot r_{avg} \cdot L_g} = S_g \cdot r_{avg}/2 ≈ 0.35 \text{ cc/(g catalyst)}
\]

The true density (\(\rho_t\)) of alumina will be assumed similar to the value given by Ritter and Drake\(^1\)

\[\rho_t = 3.675 \text{ g/cc}\]

The bed density (\(\rho_b\)) for all plug flow reactions was ≈ 0.73 g/cc

The pellet density (\(\rho_p\)) ≈ 1/(\(V_g + 1/\rho_t\)) = 1.61 cc/g

The pellet porosity (\(e_p\)) ≈ \(\rho_p \cdot V_g = 0.56\)

We will calculated the effectiveness factor for a particular P(61) hydrogenation experiment PP4I (shown in figure 56) in which the kink point occurred.

Initial butadiene pressure (\(P_{BD}\)) ≈ 0.004 atm

The total pressure (\(P\)) ≈ 1 atm

The rate constant \(k_{W obs}\) (from Table 27) ≈ 25.29 (g Pd*min\(^{-1}\))

\[ k_h = k_{\text{wobs}} \times (\text{wt Pd}) = 0.44 \text{ (1/s)} \]

Reaction Temperature \( T = 25.6^\circ \text{C} = 298.8 \text{ K} \)

\( D_{\text{eff}} \) was then calculated:

\[
D_k = \frac{2r_{\text{seg}}}{3} \sqrt{\frac{8k_B \cdot T}{\pi \cdot M}} \approx 0.0261 \frac{\text{cm}^2}{\text{s}}
\]

\( k_B \) is Boltzmann's constant and \( M \) is the weight of one molecule of BD in grams.

\[ D_B \approx \frac{1}{3} v \cdot \lambda = 0.114 \frac{\text{cm}^2}{\text{s}} \]

where \( v = \sqrt{\frac{8k_B \cdot T}{\pi \cdot M}} \) and \( \lambda \approx \frac{10^{-5}}{P} \)

\[
D = \frac{1}{(1/D_B - 1/D_k)} = 0.0213 \frac{\text{cm}^2}{\text{s}}
\]

\[ D_{\text{eff}} = \frac{D \cdot \varepsilon_T}{\tau} \approx 4.0 \times 10^{-3} \frac{\text{cm}^2}{\text{s}} \], where the tortuosity \( \tau = 3 \).

As a first estimate set the efficiency factor \( \eta \approx 1 \) we get: \( k_{\text{vc}} = k_h \frac{\rho_\text{c}}{\rho} \eta_{\text{eff}} \approx 0.97 \text{ (1/s)} \)

The Thiele modulus (\( \phi_b \)) and Efficiency factor (\( \eta_{\text{eff}} \)) for spherical pellets are calculated from the following equations using an iterative method:

\[ \phi_b = R \sqrt{\frac{k_{\text{vc}}}{D_{\text{eff}}}} = 0.47 \]

\[
\eta_{\text{eff}} = \frac{3}{\phi_b} \left( \frac{1}{\tanh(\phi_b)} - 1 \right) = 0.986
\]

From these calculations we can conclude that diffusional limitations are not significant for the fresh catalyst. However, after some time on stream this reaction is known to produce polymer/oligomer material which might effectively cause a decrease in
pore diameter or, if the BD were forced to diffuse through a layer of liquid material to reach Pd sites, cause $D_{\text{eff}}$ to decrease considerably.

Calculation of $D_{\text{eff}}$ for Diffusion of a small concentration of BD in n-octane at 298K:

The following nominal properties of n-octane (o) and butadiene (BD) were used:

The "association parameter" $\psi_o = 1.0$ for octane

The molecular weight of octane $M_o = 114.23$ g/mol$^3$

The viscosity of the solution was assumed pure octane, $\mu = 0.574$ cp at 15°C$^2$

The molar density of liquid butadiene, $V_{BD} = 87.09$ cc/mol$^3$

$$D^3 \approx 7.4e^{-8} \cdot \frac{(\psi_o \cdot M_o)^{1/2} \cdot T}{\mu \cdot V_{BD}} = 2.72e^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$D_{\text{eff}} = \frac{D \cdot \varepsilon_f}{\tau} \approx 6.7e^{-6} \text{ cm}^2 \text{ s}^{-1}, \text{ where the tortuosity } \tau = 3.$$
BD concentration is still considerable for the calculated value of 7.6 (Figure 68) and so we cannot rule out diffusion limitation if a liquid phase is involved.

**Calculated Variation in Thiele Modulus and Efficiency Factor with Pore Radius**

![Graph showing variation in efficiency factor and Thiele modulus with pore radius](image)

Figure 67) Calculated Variation in Efficiency Factor and Thiele Modulus with Pore Radius

**Concentration Gradient of a Spherical Particle**

![Graph showing concentration gradient inside a spherical particle](image)

Figure 68) Calculated BD Concentration Gradients inside a Spherical Particle.
Calculation of Reynolds Number for PFR.

The Reynolds number can be estimated from the following equations\(^4\):

Flow rates in the plug flow reactor were varied from 12 to 110 SCCM.

Viscosity of N\(_2\), \(\mu = 178.1\) micro-poise\(^5\)

The void fraction of the bed \(\varepsilon_b \approx 1 - \rho_b/\rho = 0.58\)

The Diameter of the Tube \(D \approx 1\) cm.

The gas velocity \(<v> \approx \frac{4}{\pi \cdot D^2} \cdot \frac{F \cdot R}{\varepsilon_b}\)

\[ \text{Re} = \frac{D \cdot \langle v \rangle \cdot \rho}{\mu} = 6.5 \text{ to } 32.6 \] for the flowrates used in the experiment.

Therefore the gasses remained in the laminar flow regime throughout these experiments.

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