INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Rd, Ann Arbor, MI 48106-1346 USA
313/761-4700  800/521-0600
The selective hydrogenation of 1,3-butadiene in the presence of n-butenes over supported palladium catalysts

Riley, Mark G., Ph.D.
Rice University, 1989
RICE UNIVERSITY

THE SELECTIVE HYDROGENATION OF 1,3-BUTADIENE IN THE PRESENCE
OF N-BUTENES OVER SUPPORTED PALLADIUM CATALYSTS

By

MARK G. RILEY

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE;

Joe W. Hightower, Professor,
Department of Chemical Engineering,
Director

Ka-Yiu San, Assistant Professor,
Department of Chemical Engineering

Kenton H. Whitmire, Associate
Professor, Department of Chemistry

Houston, Texas
February, 1989
The Selective Hydrogenation of 1,3-Butadiene in the Presence of n-Butenes Over Supported Palladium Catalysts

by

Mark G. Riley
ABSTRACT

The Selective Hydrogenation of 1,3-Butadiene in the Presence of n-Butenes Over Supported Palladium Catalysts

by

Mark G. Riley

The selective hydrogenation of 1,3-butadiene in the presence of n-butenes over supported palladium catalysts, an industrially important reaction, was investigated at atmospheric pressure between 308K and 393K. The study included measuring the reaction kinetics both in the presence and absence of CO, examining of the differences between palladium supported on six different carriers, testing for the effects of hydrogen spillover, and investigating the catalyst's aging behavior. Isotopic tracers (single \( ^{13}C \) labeled 1-butene) provided direct information about the reaction network.

The kinetics of butadiene hydrogenation were measured on a 0.02% Pd/alumina catalyst. Reaction orders were one in hydrogen and zero in butadiene. Addition of CO decreased the rate of butadiene hydrogenation; the reaction rate was proportional to the negative one-half power of the CO pressure in the range of 25 to 145 ppm CO. CO affects the hydrogenation rate by reducing the surface concentration of hydrogen. Activation energies for butadiene hydrogenation were 13.3 \( \pm \) 0.8 kcal/mole in the absence of CO and increased to 15.5 \( \pm \) 0.5 kcal/mole with the addition of 40 ppm CO.

Six supports were tested to determine what effect the support might have on the catalytic properties of the supported palladium catalyst. The six materials tested were: activated carbon, alumina,
barium carbonate, barium sulfate, silica gel, and titania. Alumina, silica, and titania all displayed approximately the same behavior; barium carbonate and sulfate supported catalysts exhibited significantly higher production of butane than those supported on refractory oxides. High palladium loading (all catalysts were 5 weight percent palladium) may have obscured real differences between alumina, silica, and titania.

The presence of support activity induced by spiltover hydrogen was also investigated. Blending the supported Pd catalyst with additional support containing no Pd usually caused some increase in both hydrogenation and isomerization activity, but the results were not sufficiently reproducible to provide conclusive evidence for hydrogen spillover effects. The variability in the results, probably caused by the low reduction temperatures used.

Through the use of $^{13}$C labeled 1-butene, n-butane was observed to come from the hydrogenation of both 1-butene and 2-butene during the selective hydrogenation of 1,3-butadiene in the presence on n-butenes.
Acknowledgements

The author wishes to acknowledge the support of the following people:

Professors Ka-Yiu San and Kenton H. Whitmire who served as members of the Thesis Committee and provided many helpful suggestions.

Professor Joe W. Hightower who served as Chairman of the Thesis Committee.

The National Science Foundation for their financial support of this work.

The Exxon Chemical Company for financial aid.

Mr. Vince Brogan of Engelhard Corporation for supplying numerous catalyst samples.

Mr. Richard Chronister for his assistance and suggestions in electronics.

Dr. Laszlo Guczi of the Hungarian Institute of Isotopes for thoughtful suggestions and advice during the course of this thesis.

Dr. Steve LeViness who was always ready to discuss ideas and results.

Special thanks are due the following people:

My classmates whose friendship is greatly appreciated.

Dr. Michael B. Hodges of the Savannah River Laboratory who taught me much of what know today about conducting research.

Dr. Rayford G. Anthony of Texas A&M University who first stirred my interest in catalysis research.

My parents, for their constant support during my graduate studies.
I am a part of all that I have met;
Yet all experience is an arch wherethrough
Gleams that untraveled world whose margin fades
Forever and forever when I move.

from Ulysses
TABLE OF CONTENTS

I. INTRODUCTION ......................................................... 1

II. LITERATURE REVIEW
A. Hydrogenation of 1,3-Butadiene Over Transition Metal ........ 6
   Catalysts
B. Adsorption and Additive Effects ................................. 17
C. Industrial Selective Hydrogenation and Catalyst ............. 22
   Deactivation
D. Hydrogenation of Similar Compounds and Butene ............. 28
   Isomerization
E. Structure Sensitivity and Catalyst Pretreatment ............. 37
F. Hydrogen Spillover and Carrier Effects ....................... 43

III. APPARATUS AND PROCEDURE
APPARATUS ............................................................. 48
PROCEDURE ............................................................ 54

IV. RESULTS AND DISCUSSION
A. Kinetics of Butadiene Hydrogenation and the Role of CO
   Results .......................................................... 59
   Discussion ...................................................... 72
B. Support Material Effects on the Catalytic Properties of
   Supported Pd Catalysts
   Results .......................................................... 81
   Discussion ...................................................... 88
C. The Role of Hydrogen Spillover in the Selective
   Hydrogenation of Butadiene in the Presence of 1-Butene
   Results .......................................................... 98
Discussion.............................................. .101
D. Catalyst Aging
Results..................................................... .107
Discussion................................................... .110
E. Labeled 1-Butene Studies
Results....................................................... .112
Discussion.................................................... .117
V. SUMMARY................................................... .120
VI. CONCLUSIONS AND RECOMMENDATIONS.............. .124
VII. LITERATURE CITED..................................... .126
VIII. APPENDICES
A. Calculation of Thiele Modulus for 0.5% Pd/AT-9 Catalyst ... 132
B. Sample Results from the Gas Chromatograph and Mass....... 134
   Spectrometer
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>butene</td>
</tr>
<tr>
<td>BD</td>
<td>butadiene</td>
</tr>
<tr>
<td>BMEA</td>
<td>bis-methoxy-ethyl adipate</td>
</tr>
<tr>
<td>C</td>
<td>cis</td>
</tr>
<tr>
<td>CSTR</td>
<td>continuous stirred tank reactor</td>
</tr>
<tr>
<td>D</td>
<td>dispersion</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionization detector</td>
</tr>
<tr>
<td>IFP</td>
<td>Institut Francais du Petrole</td>
</tr>
<tr>
<td>L-H</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>LLDPE</td>
<td>linear low density polyethylene</td>
</tr>
<tr>
<td>MEK</td>
<td>methyl ethyl ketone</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tertiary butyl ether</td>
</tr>
<tr>
<td>S</td>
<td>selectivity</td>
</tr>
<tr>
<td>SMSI</td>
<td>strong metal support interaction</td>
</tr>
<tr>
<td>t</td>
<td>trans</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency (1/s)</td>
</tr>
<tr>
<td>W/F</td>
<td>contact time (mass of catalyst/mass flow rate)</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1. Reactivities of Unsaturated Hydrocarbons ............... 21
2. Microreactor System .................................. 49
3. Variation in BD Hydrogenation Rate With H₂ Pressure .... 61
4. Effects of Temperature on Butadiene Hydrogenation Rate .... 61
5. Effects of CO on Butane Selectivity for 0.5% Pd/AT-9 ........ 65
6. Effects of CO on 2-Butene Selectivity for 0.5% Pd/AT-9 .... 65
7. Effect of CO on Hydrogenation/Isomerization Ratio for 0.5% Pd/AT-9 ........................................... 66
8. Effect of CO on Trans to Cis Ratio for 0.5% Pd/AT-9 ....... 66
9. Butadiene Hydrogenation Rate in the Presence of CO ....... 67
10. Temperature Dependence of Butadiene Hydrogenation Rate ... 69
11. Effect of CO on Butadiene Hydrogenation Rate .............. 69
12. Square Root Dependence of Hydrogenation Rate on CO Pressure. . 71
13. Aging Behavior of 0.5% Pd/AT-2 at 313K ................. 108
14. Aging Behavior During Selective Butadiene Hydrogenation ... 109
15. Hydrocarbon Distribution for Labeled 1-Butene Experiment. . 113
   Using 0.02% Pd/AT-2 Catalyst
16. Butene (56) Distribution for Labeled 1-Butene Experiment. . 113
   Using 0.02% Pd/AT-2 Catalyst
17. Butene (57) Distribution for Labeled 1-Butene Experiment. . 114
   Using 0.02% Pd/AT-2 Catalyst
18. Hydrocarbon Distribution for Labeled 1-Butene Experiment. . 115
   Using 5% Pd/AP-21 Catalyst
   Using 5% Pd/AP-21 Catalyst
20. Butene (57) Distribution for Labeled 1-Butene Experiment. . . . .116

Using 5% Pd/AP-21 Catalyst
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Effects of Sulfur Coverage on Pt(110)</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>Various Hydrocarbon Processes</td>
<td>23</td>
</tr>
<tr>
<td>3.</td>
<td>Turnover Frequencies of Various Hydrocarbons</td>
<td>40</td>
</tr>
<tr>
<td>4.</td>
<td>Ethylene Hydrogenation Over Catalyst Mixtures</td>
<td>44</td>
</tr>
<tr>
<td>5.</td>
<td>Benzene Hydrogenation Over Catalyst Mixtures</td>
<td>45</td>
</tr>
<tr>
<td>6.</td>
<td>Butadiene Hydrogenation on 0.5% Pd/AT-9</td>
<td>59</td>
</tr>
<tr>
<td>7.</td>
<td>Butadiene Hydrogenation on Crushed 0.5% Pd/AT-9</td>
<td>60</td>
</tr>
<tr>
<td>8.</td>
<td>Typical Results with 0.5% Pd/AT-9 Using CO at 313K</td>
<td>64</td>
</tr>
<tr>
<td>9.</td>
<td>Hydrogenation of 1,3-Butadiene on Pd-Alumina</td>
<td>72</td>
</tr>
<tr>
<td>10.</td>
<td>Nominal Catalyst and Support Properties</td>
<td>82</td>
</tr>
<tr>
<td>11.</td>
<td>Butadiene Hydrogenation on 5% Pd/C</td>
<td>83</td>
</tr>
<tr>
<td>12.</td>
<td>Butadiene Hydrogenation on 5% Pd/Alumina</td>
<td>83</td>
</tr>
<tr>
<td>13.</td>
<td>Butadiene Hydrogenation on 5% Pd/BaCO$_3$</td>
<td>84</td>
</tr>
<tr>
<td>14.</td>
<td>Butadiene Hydrogenation on 5% Pd/BaSO$_4$</td>
<td>85</td>
</tr>
<tr>
<td>15.</td>
<td>Butadiene Hydrogenation on 5% Pd/Silica</td>
<td>86</td>
</tr>
<tr>
<td>16.</td>
<td>Butadiene Hydrogenation on 5% Pd/Titania</td>
<td>87</td>
</tr>
<tr>
<td>17.</td>
<td>Results of Hydrogen Spillover Experiments</td>
<td>100</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

C₄ hydrocarbons have numerous uses in the petrochemical industry. 1,3-butadiene is employed to make polybutadiene and styrene-butadiene synthetic rubbers. n-Butenes are utilized for both petrochemistry and gasoline production. 1-Butene is used as a co-monomer with ethylene in the production of linear low density polyethylene (LLDPE). 2-Butenes are more valuable for petrochemistry than 1-butene with the exception of polymerization. 2-Butenes are utilized to produce methyl ethyl ketone (MEK) and 1,3-butadiene; in addition, alkylation of 2-butenes yields a higher octane alkylate than does alkylation of 1-butene. The separation of n-butenes and isobutene (2-methyl-propene) is greatly simplified if the n-butenes are 2-butenes. Isobutene is employed in the production of butyl rubber and methyl tertiary butyl ether (MTBE), and like n-butenes can undergo dimerization.

In 1987, 269 thousand metric tons of synthetic rubber were produced from butadiene (1). The United States production of LLDPE was 9.63 billion pounds in 1987 and is expected to increase (1). MTBE production in the USA was 3.37 billion pounds in 1987 (1). Thus, it is clear that the production of C₄ hydrocarbons and their subsequent uses (synthetic plastics and rubbers, chemicals such as MEK and MTBE, and constituents of the gasoline pool) are essential feedstocks in the petrochemical and refining industries.
Most C₄ hydrocarbons are produced either by steam cracking naphtha or by catalytic cracking of heavier hydrocarbons, although smaller amounts come from fluid coking of pyrolysis naphtha and hydrodealkylation of B.T.X. (benzene, toluene, xylene) streams (2). To improve the octane rating of the gasoline pool, C₄ hydrocarbons produced by catalytic cracking are usually added directly or used in the form of a higher molecular weight compound (optimally isooctane) produced by the alkylation unit. Selective hydrogenation of the alkylation unit feed stream is required to remove the dienes (1,3-butadiene), alkenylaromatics, and dimers which tend to make gasoline gummy.

Unfortunately, increasing the severity of catalytic cracking to improve octane (which is required for heavier crude oils) also increases the amount of butadiene in the C₄ stream sent to the alkylation unit (3). Streams (both C₃ and C₄) produced by catalytic cracking commonly contain higher levels of contaminants (e.g. metals and sulfur) than similar streams produced by steam cracking and are generally unsuitable for petrochemical uses unless further processing is performed. Steam cracking is extensively employed to produce olefins, diolefins, and aromatics for petrochemical manufacturing.

Selective hydrogenation is widely employed after fractionation of the cracked product to remove trace quantities of hydrocarbons with a higher degree of unsaturation than the major component(s) of the cut. This allows for the production of olefin streams free of active impurities for use in polyolefin manufacturing and other demanding petrochemical processes.
Selective hydrogenation catalysts have undergone considerable of evolution in the past forty years (2). The first industrial catalysts were sulfided nickel or nickel tungsten. Some copper based catalysts were also used for vapor phase hydrogenations. Since all these early catalysts had low activities, they required high operating temperatures. In addition to reducing the selectivity, high operating temperatures decrease the cycle time of the catalyst by increasing the rate of polymerization.

Second generation selective hydrogenation catalysts introduced in the late 1960's contained palladium supported on porous oxides (usually alumina) and were the result of extensive fundamental research on group VIII transition metals (2). While palladium based catalysts are very selective and have sufficient activity for operation at low temperatures (10–100 °C), they have several problems. First, they are sensitive to poisoning by mercaptans and sulfides contained in the feed streams; second, they are very active for olefin isomerization; third, they are subject to deactivation caused by polymerization (at least during vapor phase hydrogenation); and fourth, CO addition is often required to maintain selectivity at low acetylene/diolefin concentrations, even though CO addition decreases the catalytic activity and requires higher operating temperatures which in turn lead to greater polymerization and faster deactivation.

A third generation of selective hydrogenation catalysts was introduced in the early 1980's; these are used in state of the art reactors today. While these catalysts contain palladium, they also include a second metal from group 1b (Cu, Ag, Au) both supported on a
refractory oxide. Because of their extremely low metal loadings these catalysts are quite difficult to characterize; fundamental studies involving these materials are only now appearing in the literature (2). At the present time the knowledge of selective hydrogenation catalysts has progressed to the point where each reaction has its own specifically optimized catalyst (2).

1,3-Butadiene hydrogenation on supported palladium catalysts have been conducted in both the vapor and liquid phase. Vapor phase studies have usually been fundamental in nature and conducted at universities, whereas the liquid phase studies have been performed by industrial researchers. A justification for conducting fundamental research in the vapor phase when industrial reaction conditions are the liquid phase lies in the assumption that the same reaction mechanisms occur in both phases. With this in mind the objectives of this research are set forth in the following paragraph.

One objective was to determine the kinetics of vapor phase hydrogenation of 1,3-butadiene in the presence of n-butenes on a palladium-alumina catalyst. Investigating the manner in which small amounts of carbon monoxide affect the hydrogenation of butadiene and the hydrogenation/isomerization of n-butenes was also a goal. Another objective was to determine if the support material has any effect on the behavior of the catalyst. This was motivated by the knowledge that almost all palladium catalysts for the selective hydrogenation of acetylenes or diolefins are supported on low surface area aluminas. A final goal was to investigate what role, if any, hydrogen spillover may
play in decreasing the ability of supported palladium catalysts to selectively hydrogenate 1,3-butadiene in the presence of n-butenes.
Chapter II

Literature Review

A. Hydrogenation of 1,3-Butadiene Over Transition Metal Catalysts

Modern day studies of 1,3-butadiene hydrogenation over supported metal catalysts began in 1963 with Meyer and Burwell (4). They studied the deuteration of 1-butyne, 1,2-butadiene, and 1,3-butadiene in the vapor phase at 40°C on a 0.03% Pd/Al₂O₃ catalyst. Isomerization of 1,3-butadiene did not occur under these conditions and the formation of n-butane was about 0.1% of the total butene formation when the hydrogen/butadiene ratio was less than 0.9. Olefin selectivities were 53.2% 1-butenes, 42.0% trans-2-butenes, and 4.8% cis-2-butenes. These selectivities were the same for hydrogen and deuterium and were invariant when the hydrogen/butadiene ratio was less than 0.9.

With hydrogen/butadiene ratios near unity or above, significant amounts of butane were formed before all the butadiene had disappeared. Furthermore, upon the appearance of butane the amount of 1-butenes decreased sharply and there was a concurrent rise in the formation of cis- and trans-2-butenes. It should be noted that at 40°C, 2-butenes are thermodynamically favored over 1-butenes by about 20:1. By competitively reacting pairs of C₄ diene/alkyne mixtures Meyer and Burwell found the relative reaction rates to be 1,3-butadiene ~ 2-butyne = 1; 1,2-butadiene = 4; and 1-butyne = 11.
Bond and Wells (5) in 1964 reviewed the body of work dealing with the catalytic hydrogenation of unsaturated hydrocarbons over transition metal catalysts. In this review they set the tone for research in selective hydrogenation up until the present time. They state:

"In a 'simple' reaction such as that of hydrogen with ethylene there is a very limited number of things which can be measured: orders of reaction, activation energy, and perhaps the simultaneous para-hydrogen conversion. Activation energies are notoriously capricious, for they (and orders of reaction) are influenced by surface contamination. The secret seems to lie paradoxically in studying more complex reaction systems, namely, those in which the reaction may proceed in two different directions, to yield two or more recognizably different products. In such a system of competitive reactions, certain of the variable and uncontrollable factors seem to influence the alternative paths equally, so that the differences in rates, and hence also in orders and in activation energies, are of greater reproducibility and significance than absolute values."

In 1965 Bond, et al. (6) reported on the gas phase hydrogenation of 1,3-butadiene over group VIII metals. They studied the reactions in a batch reactor using catalysts with loadings of 5 molar percent (Rh, Pd, Ir, Pt) or 1 molar percent (Ru, Os) supported on alpha alumina. For palladium they reported an activation energy \( \Delta H \approx 15.7 \text{ kcal/mol} \) over a temperature range of 20-42°C. The reaction orders for hydrogen and butadiene were 1.7 and -0.7 respectively. Platinum had a hydrogen order of 1.3 and a butadiene order of -0.5 with an activation energy of 19.5 kcal/mol over the temperature range of 0-152°C.

Butane was an initial product with all metals except Pd. Excepting Pd, the product distributions from butadiene hydrogenation depended on the initial hydrogen pressure (for a fixed initial butadiene pressure) and the reaction temperature for each of the other group VIII metals. 1-Butene was the major product during the initial stages of the
reaction for all metals (except Ir when the temperature exceeded 70°C). The butene distribution for Pd, Pt, and Rh depended strongly on the extent of the reaction with trans-2-butene becoming the dominant product as the butadiene conversion approached 100\%.

Bond and co-workers (6) also discussed the reaction mechanism for 1,3-butadiene hydrogenation. The accepted mechanism follows three steps: (1) adsorption of hydrogen and/or butadiene, (2) formation of a half hydrogenated C₄H₇ intermediate species, and (3) hydrogenation of the half hydrogenated species to give the product. Isotopic tracer studies with deuterium have shown that the formation of the half hydrogenated species is reversible. The exact nature of the absorbed butadiene is not known. From this reaction mechanism it is clear that 1-butene is formed by 1:2 addition: the conformation of the adsorbed butadiene species is not important. In contrast, 2-butenes are formed by either 1:4 addition or 1-butene isomerization. In the case of 1:4 addition the conformation of the adsorbed butadiene species determines whether the 2-butene product will be the cis or trans isomer.

In 1968 Wells and Bates (7) studied 1,3-butadiene hydrogenation over Pd, Pt, Rh, and Ir wires. They found that the butene compositions were independent of activity, initial hydrogen pressure, and conversion (0-50\%) but depended on reaction temperature. The product distributions were comparable to those reported by Bond, et al. (6) for the metals supported on alumina. They concluded that the reaction mechanisms appear to be a characteristic of the metal and do not vary much with the physical form of the catalyst, whether supported or bulk metal.
Bates et al. (8) in 1970 examined the deuteration of 1,3-butadiene over Pd, Pt, and Rh supported on alumina. They found that butene isomerization before desorption does not occur even though absorbed butyl groups were found with Pt and Rh. While stepwise addition was the predominant mechanism for butene formation, sites at which fast multiple exchange occurs also exist. In addition, they speculated that butane may be formed at sites distinct from those used for butene formation.

In 1973 Furukawa and co-workers (9,10,11) studied the selective hydrogenation of 1,3-butadiene in a C₄-hydrocarbon fraction over Pd-alumina catalysts in the liquid phase under industrially significant conditions. The studies were conducted in an a stirred autoclave reactor with a gas-liquid separator used to maintain constant reactor pressure. They examined the effects of presulfiding the catalyst, adding H₂S, CO, and other compounds, both organic and inorganic, and reaction conditions on the hydrogenation of butadiene in a C₄ fraction (9). In the absence of sulfur compounds, butadiene was selectively hydrogenated to n-butenes with small n-butene losses when the butadiene content was low (<1%). Hydrogenation of high (1-3%) butadiene content fractions resulted in lower n-butene selectivities and greater losses to n-butane. This result, although somewhat paradoxical considering the results of gas phase studies, was the motivation for studying the effects of additives in order to find some way to handle streams with high butadiene content.

Furukawa, et al. examined the selectivities and activities of supported metal catalysts for selective hydrogenation of 1,3-butadiene in a C₄-hydrocarbon fraction in the presence of carbon monoxide under a
variety of reaction conditions (10). They found that CO would improve the selectivity of hydrogenation (low butane formation) and inhibit the isomerization of 1-butene. They studied ways of selectively producing 1-butene by selective hydrogenation of 1,3-butadiene (11). Using Pd/alumina catalysts and CO as an isomerization inhibitor, they found that hydrogenation of butadiene yielded about 40% 1-butene at greater than 90% butadiene conversion. The reaction was zero order in butadiene when the butadiene concentration was in the range of 5-50 mol%.

In 1983 Boitiaux, et al. (12) began to study the effects of dispersion on the hydrogenation of 1-butene and 1,3-butadiene over Pd/alumina catalysts. The turnover frequency (TOF) for 1-butene hydrogenation was independent of the dispersion, whereas the TOF for butadiene hydrogenation decreases sharply with increasing dispersion. They concluded that butadiene adsorbed more strongly to the smaller Pd particles which caused the TOF to decrease as the dispersion was increased. Their experiments were conducted in a liquid phase batch reactor at 20^°C and 2 MPa. The reaction was zero order with respect to either hydrocarbon, and butane formation was less than three percent for up to ninety percent butadiene conversion. No change in catalytic activity was observed between the first and second batch experiments using the same catalyst without regeneration.

Later that year Boitiaux, et al. (13) reported additional work on the effects of dispersion on the hydrogenation of 1-butyne, 1,3-butadiene, and 1-butene. Using palladium catalysts with dispersions between 9 and 100%, they found that 1-butyne exhibited similar sensitivity to metal dispersion to that observed for butadiene in their
previous study (12). Both alumina and silica were used as supports, and the dispersions were varied by sintering the catalysts at elevated temperatures. The butene selectivities were independent of dispersion for both 1-butyne and 1,3-butadiene.

In 1984 Boitiau, et al. (14) studied the effects of adding piperidine to the reaction mixture. In their previous papers (12,13) Boitiau and co-workers claimed that the hydrogenation rates for 1-butyne and 1,3-butadiene over highly dispersed palladium catalysts were low because the smaller Pd particles bind the hydrocarbon more strongly than larger Pd particles. They observed that adding an electron donating compound, like piperidine, increased the activity of the catalysts for 1-butyne hydrogenation by a factor of four to five, did not change the butadiene hydrogenation activity, and decreased the rate of 1-buten hydrogenation by 40-fold when the Pd catalyst was highly dispersed. However, piperidine had only a negligible effect at low dispersions.

Nagamoto and Inoue (15) examined the hydrogenation of 1,3-butadiene over a Pd membrane. Depending on the temperature and hydrogen pressure, palladium exists as either an alpha phase hydride, a beta phase hydride, or a mixture of the two. The alpha phase hydride is characterized by small amounts of hydrogen absorption and a lattice spacing almost identical to pure palladium. The beta phase hydride exists where the H/Pd ratio is too large for all the absorbed hydrogen to be accommodated in the alpha phase; the lattice expands to relieve the lattice strain. They found that the hydrogenation rate over an alpha phase palladium hydride membrane was first order in hydrogen and
zero order in butadiene. In addition, the reaction proceeded under hydrogen adsorption limitations due to butadiene affecting the rate of hydrogen adsorption.

Some studies of 1,3-butadiene on platinum single crystals have recently been reported. In 1987 Oudar, et al. (16) investigated butadiene hydrogenation and H$_2$-D$_2$ exchange on Pt(110). The kinetics of hydrogenation were found to be dependent on the hydrogen pressure. At high hydrogen pressures (P$_{\text{Hydrogen}}>130$ torr) the reaction was first order in hydrogen and zero order in butadiene, but the selectivity did not depend on hydrogen pressure. Below 125 torr of hydrogen, the hydrogen reaction order changed from first to second order and the selectivity toward butane decreased as the hydrogen pressure decreased. LEED analysis following reaction at high hydrogen pressures revealed a monolayer of randomly oriented butadiene molecules. At lower hydrogen pressures more carbon was deposited on the catalyst than was observed higher hydrogen pressures. They speculated that deactivation occurs by selective poisoning of the hydrogen dissociation sites by some hydrocarbon species.

The reaction mechanism that Oudar and co-workers proposed is based on the formation of a half-hydrogenated butadiene species as the rate determining step. They conclude that hydrogen dissociation is unlikely to be rate limiting since this would give a reaction order of two, which is double the experimentally determined order of unity. They measured an activation energy for butadiene hydrogenation of 39.3 kJ/mol.

Also in 1987 Pradier, et al. (17) studied 1,3-butadiene hydrogenation over Pt(100). They proposed a kinetic model in which
hydrogen is dissociatively adsorbed but does not compete with hydrocarbon adsorption, and where the hydrogenation of a half-hydrogenated C\textsubscript{4}H\textsubscript{7} species is the rate determining step. However, in this model the reaction is 1/2 order with respect to hydrogen, which inexplicably differs with their results for Pt(110) (16). Additionally, they indicate that at zero butadiene conversion n-butane is formed almost exclusively by the hydrogenation of 1-butene. Pradier and co-workers report an activation energy for butadiene hydrogenation of 33 kJ/mol, slightly lower than that of Pt(110). They also examined the role sulfur plays in altering the kinetics of butadiene hydrogenation, finding that the overall reaction order and activation energy varied with the sulfur coverage. The results are shown in Table 1 (17) below.

Additional studies in 1988 by Pradier, et al. (18) compared the results of 1,3-butadiene hydrogenation on Pt(111) with their previous work on Pt(110) and Pt(100). The reaction orders for hydrogen and butadiene were first and zero, respectively. While sulfur is generally a poison for platinum, some promotion was seen at low sulfur coverages (0\textsubscript{s}=0.1). Moreover changes in activation energy or reaction orders were not seen at sulfur coverages of 0.2-0.3, in contrast to the behavior of Pt(110). The most important finding of this work is 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).

Further studies in 1987 by Boitiaux, et al. (19,20,21) examined the liquid phase hydrogenation of 1-butyne, 1,3-butadiene, and 1-butene on Pd, Pt, and Rh catalysts. While the hydrogenation of 1-butene and
1,3-butadiene on both alumina and silica supported Pt could be modeled using Langmuir-Hinshelwood (L-H) kinetics (rate proportional to the surface coverage), 1-butyne hydrogenation exhibited sensitivity to Pt dispersion much like that found for 1-butyne and 1,3-butadiene on Pd (13). The lower activity at high dispersions for 1-butyne hydrogenation is speculated to be caused by an inactive complex formed between a Pt site and two 1-butyne molecules. The inactive complex is assumed to be in equilibrium with an active complex formed by interaction of one 1-butyne molecule with one Pt site. They do not discuss how the inactive complex is related to catalyst deactivation.

### Table 1. Effects of Sulfur Coverage on Pt(110) (18)

<table>
<thead>
<tr>
<th>S Coverage</th>
<th>$E_a$ (kJ/mole)</th>
<th>$\text{Order}/H_2$</th>
<th>$\text{Order}/BD$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>34</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>0.5</td>
<td>44</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

In studying the kinetics of hydrogenation on supported Rh, Boitiaux and co-workers (20) found that of 1-butyne, 1,3-butadiene, and 1-butene only 1-butene was not sensitive to Rh dispersion. A single kinetic model could be used to describe 1-butyne hydrogenation on all three metals studied. The model is essentially a L-H type with a complexation constant (which is not truly a constant because it depends on the metal dispersion and its dispersion) added to account for stronger hydrocarbon-metal bonding at higher dispersions. For hydrocarbon-metal pairs showing no sensitivity to dispersion, the complexation constant is zero and the kinetic expression reduces to the
classical L-H zero order equation. The same is true at very low dispersions where little or no multicomplexation is seen. While this approach worked with butadiene-Rh, it failed for butadiene-Pd.

They also found a correlation between apparent negative orders in hydrocarbon and sensitivity to metal dispersion for all hydrocarbon-metal pairs except butadiene-Pd. Boitiaux and co-workers (20) concluded that negative order in hydrocarbon and sensitivity to metal dispersion occur together and speculated that both phenomena are caused by the same source.

Boitiaux, et al. (21) compared the hydrogenation selectivities of Pt and Rh with previous work on Pd (12,13). Pt and Rh had very similar behavior for the hydrogenation of 1-butyne and 1,3-butadiene. The behavior of Pd was not unlike that of Pt and Rh except that with Pd no butane was formed initially; both Pt and Rh produced significant amounts of n-butane initially. The trans/cis 2-butene ratio was 12 for Pd and about 3.5 for Pt and Rh. They theorized that the initial formation of butane and the trans/cis ratio were related. Citing data on group VIII metals (both homogeneous and heterogeneous catalysts), they observed that when the trans/cis ratio decreased the formation of initial butane increased. From this observation they proposed that butane is formed from a semi-hydrogenated species which originates as a syn-diadsorbed 1,3-butadiene. It is from this syn-diadsorbed 1,3-butadiene that cis-2-butene is formed.

It is clear that the theories of initial butane formation of Boitiaux, et al. (21) and those of Pradier, et al. (17) are at odds. Both authors cite mechanisms proposed by Wells (22) and co-workers as
the source for their theories. In (22) Wells proposed two mechanisms for 1,3-butadiene hydrogenation: (A) is a very general mechanism with almost every step being reversible, (B) is a more restrictive model in which interconversion between syn and anti conformations is not allowed. Thus, in model (B) trans-2-butene comes from 1,4 hydrogenation of an anti-diadsorbed butadiene, while cis-2-butene arises from 1,4 hydrogenation of a syn-diadsorbed butadiene. 1-butene is formed by 1,2 hydrogenation of either conformational form. At the present, no mechanistic studies have conclusively proven either the assertions of Boitiaux (model A) or those of Pradier (model B).
B. Adsorption and Additive Effects

Adsorption phenomena play an important role in selective hydrogenation reactions. Adsorption strengths, in the absence of diffusional limitations, determine the prevalence of each compound on the catalytic surface and thereby control which compounds may react. Bond (23) refers to this as thermodynamic selectivity as opposed to mechanistic selectivity, which is governed by the reaction mechanism. Additives, both in the fluid phase or on the catalyst, are commonly used to alter adsorption behavior to effect some desirable change in the reaction behavior.

Chou and Vannice (24) measured the heat of adsorption of hydrogen on both supported and unsupported Pd. They found $Q_{Ad}$ to be independent of the support with a value of $15 \pm 1$ kcal/mole. $Q_{Ad}$ was invariant at 15 kcal/mole for average crystal sizes between 3 and 1000 nm, but with average crystal sizes below 3nm the value of $Q_{Ad}$ increased sharply as the crystal size decreased reaching values as high as 20 kcal/mole for highly dispersed catalysts. They attributed the crystal size sensitivity of $Q_{Ad}$ to changes in the electronic properties of small Pd crystallites. Boitiaux and co-workers (12,13) have documented a similar phenomenon for the adsorption of CO and 1-butyne on small Pd crystallites citing downward (towards lower frequencies) shifts in the IR bands to indicate stronger metal-adsorbate bonds with highly dispersed catalysts.

The adsorption of CO on transition metals has been a topic of intense study. Queau and Poilblanc (25) examined the infrared spectra
of CO chemisorbed alone and with several Lewis bases on Pd and other transition metal films. They found that CO chemisorbed on the metals to form a σ bond by donating a pair of electrons from the carbon atom to the metal and a π bond by back donation of metal d electrons to the antibonding π* orbital of CO. This adsorption decreases the strength of the carbon-oxygen bond which is seen in the decrease of the vibrational frequency of CO. The frequency shift of coadsorbed CO has been an important tool in studying many reactions on transition metal catalysts. Primet, et al. (26) made similar observations for CO adsorbed on Pt/Al₂O₃.

Chou and Vannice (27) also measured heats of adsorption for CO on Pd. Their findings were similar to those for hydrogen. The value of Q_ads for CO was 22 kcal/mol for crystal sizes between 3 and 1000 nm. Below 3 nm the heat of adsorption increased to a value of 35 kcal/mole on highly dispersed catalysts. The increase in heat of adsorption was higher than that predicted from single crystal studies. This seemed to indicate that changes in the electronic properties of small Pd crystals were primarily responsible for the increase in the Pd-CO bond strength as the crystal size decreased.

Apple and Dybowski (28) have studied the coadsorption of CO and H₂ on Rh/TiO₂. Preadsortion or coadsorption of CO inhibited the adsorption of "spillover" hydrogen. They theorized that CO blocks the pathway for hydrogen to the support.

Boitiaux, et al. (29) reviewed the use of additives in the selective hydrogenation of unsaturated hydrocarbons. They note that most of the research has been conducted with CO, sulfur containing
compounds, and nitrogen containing compounds. These additives are used to alter one or more of the following selectivities: (1) hydrogenation itself, (2) isomerization versus hydrogenation, and (3) hydrogenation versus polymerization. In addition to altering selectivities, these additives may affect the overall activity of the catalyst.

Carbon monoxide is commonly used to inhibit hydrogenation reactions on group VIII metals. By decreasing the reaction rate, carbon monoxide reduces the likelihood that mass transfer limitations will occur and thereby helps to inhibit the hydrogenation of desirable compounds. Bain, et al. (30) observed that 1-butene isomerization was inhibited by CO coadsorption on Pt-alumina but that 1-butene hydrogenation was unaffected under the same conditions. Similar results for 1-butene isomerization have been reported by Furukawa and co-workers (10,11). Pope, et al. (31) reported that ethylene hydrogenation on 1% Pd-charcoal was poisoned by the addition of 0.5 to 2.5 ppm of CO in the reactant stream.

Ratajczykowa and co-workers (32) investigated the effects of CO and Pb on palladium catalysts in the selective hydrogenation of acetylenes. They found that preadsorbed CO blocked the adsorption of hydrogen and ethylene on Pd (100, 110, and 111) single crystals but that acetylene could displace the carbon monoxide. Lead decreased the adsorption strength of 2-butyne, hydrogen, and ethylene on both Pd(111)-Pb and Lindar (Pd₃Pb/CaCO₃) catalysts. Since lead affects the adsorption of acetylenes to a lesser extent than that of olefins, Lindar catalysts are quite effective in promoting selective hydrogenation.
The addition of CO and sulphur compounds have played an important role in selective hydrogenation reactions. Furukawa and co-workers (9) found that H₂S, as well as other mercaptans, would improve the hydrogenation selectivity of Pd-alumina catalysts but would not stop the isomerization of 1-butene, as CO was shown to do. Furthermore, sulfiding the catalysts was not readily reversible (as CO addition was) and S/Pd ~ 35-40 (atomic ratio of S in H₂S to Pd) during presulfiding resulted in a total loss of activity, requiring reactivation with flowing hydrogen. Presulfiding by hydrogen sulfide increased the resistance of the catalyst to other gas phase poisons. Similar results have been seen by Greenfield (33) for 1,3-butadiene hydrogenation on sulfided Pt and Pd supported on alumina.

Oudar, et al. (34) have examined 1,3-butadiene hydrogenation on sulfur poisoned Pt(111) single crystals. Each sulfur atom was found to poison one hydrogen dissociation site but had no effect on neighboring sites. Butadiene was seen to decrease by about 15-20% the binding energy of sulfur to the platinum. They conclude that "the deactivation behavior of sulfur for a catalytic reaction involving unsaturated hydrocarbon depends on the adsorption strength of the hydrocarbon and on its concentration on the surface." This conclusion seems rather sweeping considering the number of hydrocarbons (one) examined.

Boitiaux and co-workers (14) have studied the effects of piperidine on the hydrogenation of 1-butyne, 1,3-butadiene, and 1-butene over highly dispersed Pd catalysts. They found that an electron donating compound like piperidine increased the selectivity towards olefin formation. Figure 1 (14) illustrates how adsorption strengths
and rate constants are related. Electron donating compounds weaken the hydrocarbon-metal bond (decrease the adsorption constant) and shift the relative position of each hydrocarbon to the left along the curve. Thus, depending on the hydrocarbon's initial adsorption strength (position on the curve), an electron donating compound may either increase or decrease the rate constant for that particular hydrocarbon. Addition of piperidine decreased the rate of olefin hydrogenation, increased the rate of 1-butyn hydrogenation, but had no effect on the rate of butadiene hydrogenation. Piperidine also had no effect on the activity of catalysts with dispersions less than 20% for any of these reactions.

Figure 1. Reactivities of Unsaturated Hydrocarbons
C. Industrial Selective Hydrogenation and Catalyst Deactivation

Selective catalytic hydrogenation of multiply unsaturated hydrocarbons has become an integral step in the production of synthetic petrochemicals. With the ever expanding use of plastics, synthetic rubbers, and synthetic fibers, the demand for raw materials from which these petrochemicals are made has also increased dramatically. Olefins are the raw materials for most petrochemicals and are produced, and are primarily produced by various hydrocarbon cracking processes as shown in Table 2 (2).

The first generation selective hydrogenation catalysts contained nickel or copper as the active ingredient and generally had low activity. These catalysts were usually sulfided and operated at high temperature. However, operation at high temperatures leads to an increase in polymerization which causes the activity, selectivity, and cycle length to decrease (2). The next generation of catalysts were based on palladium, which was found by Bond, Wells, and others to be the most selective and active of the group VIII metals for selective hydrogenation of alkynes and alkadienes to alkenes. Palladium has one major drawback: it is very sensitive to poisoning by the sulfur containing compounds which commonly occur in crude oil (2).

The development of selective hydrogenation processes has proceeded as the need for higher purity and a wider range of products has increased. Initially, selective hydrogenation was used in the production of ethylene to remove acetylene from ethylene streams resulting from the steam cracking of ethane. The removal of acetylene
from ethylene streams is still the single most important application of selective hydrogenation; an extensive review of the acetylene hydrogenation has been done by LeViness (35). Derrien (36) has reviewed the literature pertaining to selective hydrogenation (hydrorefining) as applied to products produced by steam cracking.

Table 2. Various Hydrogenation Processes (2)

<table>
<thead>
<tr>
<th>Source</th>
<th>Cut</th>
<th>Impurity</th>
<th>Valuable Product</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Cracking</td>
<td>C2's</td>
<td>Acetylene</td>
<td>Ethylene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>C3's</td>
<td>Propyne/Propadiene</td>
<td>Propylene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>C4's</td>
<td>Butynes</td>
<td>Butadiene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>C4's</td>
<td>Butadiene</td>
<td>Butenes</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>C4's</td>
<td>Butadiene</td>
<td>1-Butene</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Pyrolysis</td>
<td>Dienes</td>
<td>Olefins/Aromatics</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Naphtha</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalytic Cracking</td>
<td>C3's</td>
<td>Propyne/Propadiene</td>
<td>Propylene</td>
<td>1,2</td>
</tr>
<tr>
<td></td>
<td>C3's/</td>
<td>Propyne/Propadiene</td>
<td>Butenes/Propylene</td>
<td>1,2,3,4</td>
</tr>
<tr>
<td></td>
<td>C4's</td>
<td>Butadiene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluid Coking</td>
<td>C3's/</td>
<td>&quot;</td>
<td></td>
<td>1,2</td>
</tr>
<tr>
<td></td>
<td>C4's</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrolysis</td>
<td>Dienes</td>
<td>Olefins</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Naphtha</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B.T.K.</td>
<td>Dienes/Thiophene</td>
<td>Benzene</td>
<td>1</td>
</tr>
</tbody>
</table>

1. Petrochemistry
2. Gasoline Pool
3. Alkylation
4. Oligomerization

In this review we will only cover those selective hydrogenation processes dealing with C4 hydrocarbons. According to Derrien there are four selective hydrogenation processes associated with the C4 cut. The first is the selective hydrogenation of vinylacetylene in streams rich in 1,3-butadiene. The usual catalyst for this reaction is palladium supported on alumina or silica. However, vinylacetylene hydrogenation is very different from other selective hydrogenation reactions in one respect: the vinylacetylene-palladium complex formed at temperatures
less than 100°C is soluble in the hydrocarbon mixture (liquid phase hydrogenation). The formation of this Pd-vinylacetylene complex leads not only to a very selective catalyst but also an unstable one whose activity is constantly decreasing due to elution of Pd. This problem with vinylactylene-Pd complexes is usually solved by operating the reactor at temperatures above 100°C, or by using bimetallic (palladium) catalysts.

The second process is the selective hydrogenation of the butene rich cut. In this process the objective is to remove the butadiene impurities while maximizing the n-butene yield. Again supported Pd is the catalyst of choice owing to its high selectivity for n-butene formation. A third process is the hydrorefining of the 1-butene rich cut. The hydrorefining of the 1-butene rich stream is similar to the second process but has the additional constraint of avoiding loses of 1-butene. This is a very demanding process because palladium is a moderately active catalyst for olefin isomerization and the end use of the 1-butene, LLDPE, requires a quite low butadiene content. The fourth process is hydroisomerization of 1-butene to 2-butenes. Separation of n-butenes and isobutylene is easier if the butenes are 2-butenes, and 2-butenes are more useful than 1-butene in the synthesis of chemical intermediates.

Deactivation is a problem with almost all selective acetylene or diolefin hydrogenation catalysts. The deactivation is caused by the formation and accumulation of coke or polymers, which after a sufficient period of time block the active hydrogenation sites. Catalyst deactivation is only now receiving greater study. Still unknown are:
the nature of polymer deactivation, the kinetics of polymer formation, the role of polymer in hydrogen spillover and surface reactions, and how certain additives can alter the formation of polymers.

Polymer formation in the selective hydrogenation of 1,3-butadiene in butene streams has been known for a long time. In 1963, Kirsch and Shull (37) reported finding vinylcyclohexene, other unsaturated C₈ and C₁₂ hydrocarbons, and higher boiling materials in the reaction mixture after several hundred hours of operation using a cobalt-molybdena catalyst. Also in 1963, Kronig (38) studied the Bayer "cold hydrogenation" process for the selective hydrogenation of acetylenes and diolefins in C₄ streams produced from pyrolysis. He found little or no polymer formation when the "cold hydrogenation" process is used for the hydrogenation of vinlylacetylene or butadiene. The "cold hydrogenation" process is based on a supported noble metal catalyst operating in a trickle bed reactor at 10 - 20°C and a total pressure of 2 - 6 atmospheres. The low operating temperature is claimed to nearly eliminate polymerization.

Several studies have examined the nature of adsorbed olefins and diolefins on supported palladium catalysts. Using infrared spectroscopy, Avery (39) investigated the adsorption of propene, 1-pentene, and 1,3-butadiene on palladium supported on silica. He found that propene and 1-pentene were both strongly adsorbed on the Pd surface with the 1-pentene being the more strongly adsorbed of the two. Avery found this consistent with the general trend of increasing adsorption strength with increasing molecular weight for linear olefins. The differences in the strengths of adsorption between propene and 1-pentene
were attributed to isomerization of the 1-pentene to 2-pentene and to propene having only one methyl group with which to interact with the metal. The adsorption of 1,3-butadiene produced a completely dehydrogenated residue which he inferred from the absence of any alkyl function in the adsorbed molecule. After hydrogenation of the residue, examination by IR spectroscopy indicated a high ratio of methylene groups as compared to methyl groups indicating that the residue was most likely a strongly adsorbed linear C_{4n} species.

Using ^{14}C labeled ethylene and propylene Altham and Webb (40) studied adsorption phenomena on alumina and silica supported platinum catalysts. They found that a large fraction of the adsorbed olefin was held by the catalyst, in agreement with Avery (39). Ethylene was retained to a greater extent than propylene. At first glance this seems to contradict the findings of Avery (39) but acetylene and ethylene with no alkyl groups have irregular adsorption behavior compared to higher molecular weight alpha-acetylenes and alpha-olefins.

The problem of catalyst deactivation by oligomerization is most severe in the hydrogenation of acetylene in ethylene streams. Beginning with the C_{3} cut it is economically feasible to operate liquid phase or trickle bed reactors. It is generally believed that the rate of polymer accumulation on the catalyst when operating in the liquid phase is greatly reduced due the solvent action of the liquid phase on the surface oligomers (in acetylene hydrogenation these oligomers are commonly known as "green oil" and literally drip from the reactor bed). New developments in the field of selective hydrogenation of diolefins and acetylenes have been reported by Boitiaux and co-workers (2) at IFP
(Institut Francais du Petrole). Among these are a liquid phase hydrogenation for acetylene using a solvent that is removed by flashing and recirculated to the reactor. Additionally, they have developed a bimetallic (group 1b) palladium based catalyst which has lower polymerization activity, lower isomerization activity, and higher olefin selectivity than conventional palladium based catalysts. These improvements in the catalyst are attributed to the second metal altering the electronic properties of the palladium.
D. Hydrogenation of Similar Compounds and Butene Isomerization

The study of selective hydrogenation of multiply unsaturated hydrocarbons has until recent times been with few exceptions confined to the study of acetylene hydrogenation in ethylene streams. The attention given to selective acetylene hydrogenation is understandable if for no other reason than ethylene's importance in the petrochemical industry. From an academic point of view choosing the simplest alkyne-alkadiene/alkene pair makes a great deal of sense because no isomers are present. However, the acetylene/ethylene system, like many other "first members" in chemical series, exhibits some unusual behavior not characteristic of the other members of the series. For this reason it is not always possible to extrapolate what is known about acetylene/ethylene selective hydrogenation to the selective hydrogenation of higher molecular weight hydrocarbon pairs. In this section the selective hydrogenation of compounds similar to 1,3-butadiene will be reviewed, as will the isomerization of butenes over palladium and other materials.

Oliver and Wells (41) have studied the hydrogenation of propadiene and 1,2-butadiene with deuterium on palladium-alumina. They noted that during hydrogenation 1,2-butadiene, which has four adsorbed states, shares common adsorbed states with both 1,3-butadiene (two states) and 1-butyne (two states). They felt that these adsorbed intermediates may help explain why 1,3-alkadiene hydrogenations are generally more selective than alkyne hydrogenations. From deuterium distributions in the products they concluded that 1,3-alkadiene hydrogenations are more
selective than alkyne hydrogenations because they do not produce significant amounts of intermediates which are necessary precursors to alkanes. However, their conclusions are open to criticism since they have no direct evidence for the precursor to alkanes. Moreover, their experimental method makes diffusional limitations highly probable. It should be noted that their results are exactly what one would expect if, due to diffusional limitations, the 1,2-alkadiene was unable to cover all the palladium sites.

Khulbe and Mann (42) have also studied the hydrogenation of propadiene using silica supported group VIII metals. They found the reaction orders to be first and zero in hydrogen and propadiene, respectively. With Pd, Pt, and Ru the reaction order increased to between 1.5 and 2 as soon as the "acceleration point" was reached. The acceleration point in the pressure-time plot (which was coined by Bond) is the point where non-linear behavior between pressure drop and time is first observed. The acceleration point is commonly seen in the selective hydrogenation of most alkyne-alkadiene/alkene systems conducted in batch reactors with hydrogen/alkyne-alkadiene ratios greater than one and is due to alkene hydrogenation on metal sites not covered by the alkyne or alkadiene. The apparent activation energies varied between 5.6 and 16 kcal/mole and are in general agreement with values for 1,3-butadiene hydrogenation on Group VIII metals given by Bond and co-workers (6).

The hydrogenation of 1-butyne is of considerable interest since it is a major impurity in 1,3-butadiene rich cuts. The hydrogenation of 1-butyne on supported Pd has been shown (4,13,14) to yield 1-butene almost
quantitatively at low conversions (C₁-Butyne < 20%). Structure sensitivity has been reported for 1-butyne hydrogenation on supported palladium by Boitiaux, et al. (13) and Hub, et al. (43). Boitiaux and co-workers (18,19) have also studied 1-butyne hydrogenation on supported Pt and Rh and have observed sensitivity to metal dispersion similar to that seen for supported Pd. The selectivity was lower for both Pt and Rh, with n-butane being an initial product for both metals.

The hydrogenation of 2-butyne was studied by several groups in the mid 1960's but has had little subsequent attention since 2-butyne is an insignificant impurity in the C₄ cuts from either steam or catalytic cracking. Meyer and Burwell (44) found that the selectivity and stereoselectivity were essentially the same for both hydrogen and deuterium addition to 2-butyne with cis-2-butene constituting more than 95% of the products. Isotopic exchange of hydrogen and deuterium on 0.3% Pd-alumina was strongly inhibited by the presence of 2-butyne, its rate decreasing by at least a factor of 40 with the addition of 2-butyne to the H₂-D₂ mixture. They noted transient behavior during the startup of the reaction. The catalyst was initially unselective for 2-butyne hydrogenation and required approximately 35 seconds to become selective.

Phillipson, et al. (45) examined the hydrogenation of 2-butyne over several alumina supported Group VIII metals and copper. They also found that cis-2-butene was the predominant product, constituting greater than 75% of the products over all metals studied. Phillipson and co-workers noted that hydroisomerization of the alkenes occurred as the 2-butyne was depleted under conditions of high hydrogen partial pressure.
Ryndin and co-workers (46) studied the gas phase hydrogenation of vinylacetylene (C\textsubscript{4}H\textsubscript{4}) on alumina and silica supported palladium. Hydrogenation of vinylacetylene yields both 1,3-butadiene and butenes, with trace amounts of butane at conversions of roughly 10 percent. The selectivity towards butadiene was independent of dispersion on Pd/silica and was 70 to 80 mole percent. Palladium/alumina exhibited similar behavior except for two catalyst samples with very high dispersions. Significantly, they found that the turnover frequency decreased as the dispersion increased in part confirming the findings of Boitiaux and co-workers (13) for 1-butyne and 1,3-butadiene hydrogenation on palladium supported on alumina or silica.

The liquid phase hydrogenation of C\textsubscript{5} hydrocarbons has been studied by Bond and Rank (47) over supported platinum metal catalysts. Studies of 1-pentyne and 2-pentyne showed high selectivity towards 1-pentene and cis-2-pentene, respectively. Olefin selectivities greater than 97% were reported for palladium supported on carbon. The hydrogenation of 1,3-pentadiene was also examined. 1,3-pentadiene exists as both cis and trans isomers with the trans isomer dominating at ambient temperatures (85% trans, 15% cis). Trans-1,3-pentadiene hydrogenation on Pd/C yields approximately 61% trans-2-pentene, 32% 1-pentene, and 7% cis-2-pentene with an olefin selectivity of 0.98. Cis-1,3-pentadiene hydrogenation on Pd/C gave approximately 38% 1-pentene, 22% cis-2-pentene, and 40% trans-2-pentene with an olefin selectivity of 0.99. Meyer and Burwell (44) have examined the liquid phase hydrogenation of 3-hexyne on 13.8% Pd/alumina. They found the initial product to be cis-3-hexene. As the reaction moves towards completion the amounts of trans-3-hexene, trans-
2-hexene, and cis-2-hexene increase as the amount of cis-3-hexene decreases. When all the 3-hexyne has reacted the hexenes isomerize towards the equilibrium composition and hexane formation accelerates.

The C₄ hydrocarbons are the smallest group of hydrocarbons containing all the industrially significant types unsaturation. This makes them an ideal group to study the nature of selective hydrogenation of unsaturated hydrocarbons in general. The C₄ hydrocarbon group contains both terminal and internal acetylenes, a conjugated diene, and isomeric olefins. With the C₄ group one gains an additional reaction (isomerization) with which to study the nature of the selective hydrogenation catalysts. Changes in the isomeric composition of the butenes can be used to infer butene reactions occurring on the metal and the support if one or both are active for isomerization. With this in mind it is appropriate to review the studies of n-butene isomerization on palladium and several support materials.

Wells and Wilson (48) have examined the isomerization of 1-butene over seven platinum metals (including Pd) supported on four types of alumina at 100°C in the absence of hydrogen. They found that Pd was the most active of the seven metals studied for isomerization, yielding almost equilibrium compositions of butenes at both 100 and 150°C. They also note that several of the metals (Os, Ir, Pt, and Rh) have little or no isomerization activity as unsupported powders, indicating that the support must be involved somehow in catalyzing the isomerization reactions. Citing hydrogen atom migration from the support to the metal during H-D butene exchange reaction, Wells and Wilson argue that a good
case can be made for hydrogen atom migration being important in the isomerization reaction.

This conclusion has been substantiated by Holbrook and Wise (49), who studied the role of hydrogen in the isomerization of 1-butene over unsupported Pd and Pd supported on alumina. Palladium supported on alumina had insignificant activity for 1-butene isomerization at 100°C, but upon the addition of hydrogen the catalyst became highly active for isomerization. They observed that the isomerization activity varies linearly with the square root of the hydrogen concentration at low H₂ pressure and becomes first order in hydrogen when the hydrogen pressure is high enough for significant butene hydrogenation (typically greater than 50% 1-butene conversion). Similar results were found for unsupported Pd microspheres. The differences between the results of Wells, et al. and Holbrook, et al. in the absence of hydrogen are probably due to differences in catalyst pretreatment. Wells and Wilson removed hydrogen by evacuation whereas Holbrook and Wise used oxygen treatment at 300 °C for 15 minutes. To reconcile the results of these two studies, one really needs to know if the Pd was oxidized, what were the effects of any water formed, and would evacuating at 200°C remove all of the hydrogen from the catalyst.

Holbrook and Wise also examined the activity of the alumina support and found no activity at 100°C, although a small amount of activity was found at 325°C. In comparing the isomerization activity (at 10⁻² vol % H₂) between the supported and unsupported catalysts, they calculated a value of 0.33 X 10⁻³ moles/m²min for the supported catalyst and 1.9 X 10⁻³ moles/m²min for the microspheres. They note that while
the difference is higher than the estimated error, it does indicate that the alumina is not contributing significantly to the isomerization under their experimental conditions.

Ragaini, et al. (50) have also looked at 1-butene isomerization on an alumina supported palladium catalyst. They found that the trans/cis 2-butene ratio was approximately 2 at 50°C and was independent of contact time except at very low hydrogen pressures, in good agreement with the results of Holbrook and Wise. Ragaini and co-workers indicate that fresh catalyst samples were run for at least four hours with the reaction mixtures to obtain stable catalytic conditions noting that "this procedure guaranteed good reproducibility of the kinetic data." Further discussion of "fresh" and "equilibrated" catalysts can be found in the catalyst pretreatment section of the literature review.

Macnab and Webb (51) have examined the isomerization of 1-butene over alumina and silica supported rhodium catalysts. They found that 2-butene produced between 25 to 75°C were near thermodynamic equilibrium and that the support seemed to have little influence on the results. The support materials were investigated for activity. Silica had no hydrogenation or isomerization activity at temperatures to 154°C for 12 hours. Alumina, on the other hand, showed activity for both hydrogenation and isomerization. At 101°C the butenes reached equilibrium proportions in three hours with approximately 15% of the butene being hydrogenated. The addition of an equal amount of alumina to the supported Rh catalysts had no effect other than lowering specific rates of isomerization and hydrogenation (r_i/r_h unaffected). Macnab and Webb also examined 1-butene isomerization in the absence of hydrogen
(vacuum at 295°C for six hours pretreatment) finding only a trace of isomerization after one hour. They state that the amount of isomerization observed was insignificant when compared with the amount in the presence of hydrogen.

Isomerization of n-butenes catalyzed by metal oxides commonly used as supports is more difficult to generalize than isomerization catalyzed by group VIII metals. There are many differences between common supports materials like alumina, silica, and titania which can affect their isomerization activity, e.g. acidity, surface area, naturally occurring impurities, etc. In addition there can also be differences in activity due to the history (pretreatment) of the support as is commonly seen with titania. For these reasons it is difficult to draw firm conclusions about the isomerization activity of a particular support without knowing about the preparation methods used, the conditions of the pretreatment, and the specific test reaction. Following is a brief summary of n-butene isomerization on alumina, silica, and titania.

Silica is the least active for isomerization of the three supports. The acid catalyzed reactions of hydrocarbons on refractory oxides like alumina are believed to involve carbonium ions produced on the acid sites of the refractory oxide. With silica these acid catalyzed reactions are not possible due to silica’s lack of acidic properties. Silica is well known for its catalytic inactivity at temperatures below 300°C; and consequently, catalytic studies of silica are rare compared to alumina and titania. Macnab and Webb (51), in batch experiments, found no isomerization activity for 1-butene at 154°C in 12 hours. Hall, et al. (52), having measured the rate of $\text{H}_2$-$\text{D}_2$
exchange on alumina, silica, and silica-alumina catalysts, found that gamma-alumina reached a maximum rate of exchange at 250°C whereas silica did not reach a maximum until 610°C and was inactive under 400°C.

Alumina, on the other hand, has considerable catalytic activity at moderate temperatures. Hightower and Hall (53) have reviewed some of the work on 1-butene isomerization on alumina. They reported cis/trans 2-butene selectivities between 1.0 and 6.25 for various aluminas between 23 and 300°C. They cite the following values for the cis/trans ratio: 5.0 at 23°C, 3.37 at 50°C, and 2.17 at 150°C. Similar findings have been reported by Utiyama, et al. (54) who noted that the activity and the cis/trans ratios are very much dependent on the type of alumina. These findings are also supported by MacIver, et al. (55) who reported eta-alumina to be more reactive than gamma-alumina.

The isomerization behavior of 1-butene over titania can best be described as complex. Lemberton, et al. (56) have studied the mechanisms of isomerization of 1-butene on titania and suggested four different routes for the isomerization of butenes. In addition, they found that the behavior of titania (including the cis/trans 2-butene ratio) strongly depends on the pretreatment and reaction temperatures. It should be noted that under all the conditions tested the titania gave cis/trans ratios greater than 1.5.
E. Structure Sensitivity and Catalyst Pretreatment

While the concept of structure sensitive (or demanding) reactions is not new (57), only recently (1983) has this phenomenon been reported for the hydrogenation of C₄ hydrocarbons on supported palladium catalysts (12). In the simplest terms, a structure sensitive reaction is one in which the chemisorptive or catalytic properties of the catalyst increase or decrease with the metal particle size. The role of structure sensitivity in heterogeneous catalysis has been reviewed by Bond (57).

Bond states that "any genuine variation of catalytic activity with particle size will ultimately be traced to one of three factors: (i) a variation in the strengths (or relative strengths) of chemisorption of the reactants; (ii) a change in the structure or surface stoichiometry of the adsorbed intermediates, a consideration not unrelated to the first; and (iii) a difference in the active area during steady-state conditions by reason of the variable formation of unreactive residues of the reactants."

He notes that structure sensitive reactions normally occur on metal particles that are 10 nm in diameter or less, observing that to obtain a 50% dispersion for Pd particles requires a particle size of 2 nm. Bond listed examples of structure sensitive reactions in areas of oxidation, hydrogenolysis, isomerization, exchange, and hydrogenation.

Structure sensitivity in the reaction of 1,3-butadiene hydrogenation on Pd/alumina was first reported by Boitiaux, et al. (12) in 1983. They observed that it was very difficult to make highly dispersed palladium catalysts using low surface area aluminas. While highly dispersed catalysts had been obtained using high surface
aluminas, these catalysts were undesirable since high surface aluminas promote polymerization reactions. Boitiaux and co-workers developed a method to prepare highly dispersed palladium catalysts. In measuring the dispersion by CO chemisorption they observed large shifts (40 cm\(^{-1}\)) in the IR spectra of the adsorbed CO with increasing dispersion. They examined the effects of dispersion on the turnover frequency (TOF) of 1,3-butadiene and 1-butene hydrogenations. Boitiaux and co-workers found the turnover frequency for 1-butene hydrogenation to be independent of metal dispersion. The hydrogenation of 1,3-butadiene was very sensitive to metal dispersion with the TOF decreasing from a high of about 160 s\(^{-1}\) at 20% dispersion to about 10 s\(^{-1}\) at 100% dispersion. They attribute the decrease in activity at high dispersions to stronger adsorption of butadiene on small metal particles.

In further studies (13,19,20,21) Boitiaux and co-workers have examined alumina and silica supported Pd, Pt, and Rh for structure sensitivity in the hydrogenation of 1-butene, 1,3-butadiene, and 1-butyne. All three metals were structure sensitive for the hydrogenation of 1-butyne, but were insensitive for the hydrogenation of 1-butene. Butadiene was structure sensitive on all metals except Pt. In another publication (14) Boitiaux and co-workers show that the hydrogenation activity of Pd/alumina for 1-butyne and 1,3-butadiene can be increased by adding an electron donating compound like piperidine to the reaction mixture. The piperidine reduces the bond strength (Boitiaux refers to this as decomplexation) of the hydrocarbon-Pd complexes formed on catalysts with high dispersions, allowing the 1-butyne or butadiene to turn over faster on the Pd sites.
Hub, et al. (43) also examined the effect of particle size on the hydrogenation of 1-butyne and 1-butene on palladium catalysts. They found that the TOF for 1-butene was higher on highly dispersed catalysts than on poorly dispersed catalysts; but the behavior was just the opposite for 1-butyne. The highly dispersed catalysts were also slightly more selective for olefin formation than were the poorly dispersed catalysts. One might challenge these conclusions since the authors used only three catalyst samples (D=97%, D=26%, and D>80%) to draw these conclusions. In contrast, Boitiaux and co-workers used as many as 14 catalyst samples (9% ≤ D ≤ 100%) in their studies, which would seem to be the only prudent method for establishing such a trend when one considers the experimental uncertainties involved in measuring TOF and dispersion.

The sensitivity of vinylacetylene hydrogenation to palladium particle size has been investigated by Ryndin, et al. (46). They found that the TOF for vinylacetylene varied linearly with the particle size up to a particle size of about 40 angstroms after which it became constant. They concluded that the low TOF of highly dispersed palladium catalysts was attributable to the stronger chemisorption of vinylacetylene on electron deficient small palladium particles. Table 3 compares TOF (maximum values for structure sensitive compounds) that have been observed for several unsaturated hydrocarbons on Pd-alumina.

The structure sensitivity observed in the hydrogenation of some unsaturated hydrocarbons on supported palladium catalysts depends strongly on the pretreatment conditions. The pretreatment conditions, specifically oxidation and reduction temperatures, govern the metal
dispersion of the support and influence the electronic properties of the crystallites. Investigations of the role of pretreatment conditions on supported palladium catalysts have been conducted by Leonte, et al. (58) and Vannice and Chou (59).

Table 3. Turnover Frequencies of Various Hydrocarbons

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>TOF (1/sec)</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>105</td>
<td>20</td>
<td>20</td>
<td>(12)</td>
</tr>
<tr>
<td>Butadiene</td>
<td>160</td>
<td>20</td>
<td>20</td>
<td>(12)</td>
</tr>
<tr>
<td>1-Butyne</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>(13)</td>
</tr>
<tr>
<td>Vinylacetylene</td>
<td>0.15</td>
<td>20</td>
<td>0.2</td>
<td>(46)</td>
</tr>
</tbody>
</table>

Leonte and co-workers studied the effects of oxidation and reduction conditions on dispersion and particle size distributions of 0.5% Pd/Al₂O₃ catalysts. They found that redispersion of palladium crystallites occurred when fresh, regenerated, or sintered catalysts were treated in hydrogen at 800°C for 10 hours, and when sintered reduced catalysts were oxidized in air at 500°C for 24 hours. Leonte and co-workers theorize that the lattice strains induced upon going from Pd to PdO and Pd changing from the beta to alpha phase hydride cause particle cleavage. They note that sintering of palladium catalysts can occur in several ways. Some sintering can be induced by the reaction of unsaturated hydrocarbons on the catalyst. The regeneration of spent catalysts by oxidation in air at 500°C also produces sintering as does high temperature reduction in hydrogen. Leonte and co-workers reported that sintering, of palladium in hydrogen atmospheres can occur even at room temperature but does not become significant until temperatures
reach 650°C. The crystallite size distributions indicate that redispersion was significant only for Pd crystallites larger than 8 nm; apparently these phenomena play little role in highly dispersed palladium catalysts.

Vannice and Chou have investigated the effect of reduction temperature on the rate of hydrogenation of benzene on supported palladium catalysts. They found that after high temperature reduction the turnover frequencies for palladium supported on all the carriers except carbon were in good agreement with values reported by other researchers. The turnover frequencies for silica-alumina and titania were found to be strongly dependent on the reduction temperature. Vannice and Chou do not have an adequate explanation for the variation of activity with reduction temperature and are tentatively proposing special sites near the metal-support interface for both silica-alumina and titania. In their model hydrogen migrates to these special sites and makes them active for hydrogenation. This dependence on reduction temperature was not found for silica or alumina.

Since deactivation is a problem with selective hydrogenation catalysts, measuring the kinetics of a given reaction is not a trivial matter. In some studies (12,20) of butadiene hydrogenation, mostly liquid phase, no catalyst deactivation was observed between the first and second runs. However, Furukawa, et al. (9) in a long run (480 hours) did observe a decrease in activity and changes in selectivities due to carbon deposition on the catalytic surface. Several researchers (44,50) have commented that aging of the catalysts as a part of the pretreatment process was necessary to obtain reproducible kinetic
results. Oudar, et al. (16) observed deactivation of Pt(110) single crystals during butadiene hydrogenation and related it to the formation of partially dehydrogenated butadiene molecules. In 2-butyne hydrogenation, Meyer and Burwell (44) observed an initial decrease in activity that reached a steady state activity in about 10 minutes in a batch reaction. Catalyst aging was required to achieve reproducible kinetic results for hydroisomerization of 1-butene on Pd-alumina (50). From these studies it is clear that there is some danger in trying to draw conclusions from data taken on "fresh" catalysts (at least for studies in the vapor phase). It should be noted that the use of "aged" or "equilibrated" catalysts in hydrocarbon catalysis is not an uncommon practice.
F. Hydrogen Spillover and Carrier Effects

The spillover of adsorbed species from one phase to another of a supported metal catalyst is one of the more controversial and least understood phenomena in the field of heterogeneous catalysis. In simple terms spillover is the migration of a molecule adsorbed on one phase to another (either metal to support or support to metal). A general review of spillover phenomena has been compiled by Dowden (60). Although spillover has been observed for many species, it is the spillover of hydrogen onto irreducible oxides like alumina, silica, and titania, facilitated by a platinum metal, that is of special interest to this work. Hydrogen spillover has been reviewed by Bond (61) who notes that there has long been qualitative evidence (including reactions which were believed not to require a bifunctional catalyst) that the catalytic behavior of supported metal catalysts was dependent on the support even when correcting for differences in dispersion. Although several experimental artifacts could produce such effects, in Bond's words there is... "a growing realisation that the support may frequently play a far more important part in the total reaction than has usually been imagined in the past."

Carter, et al. (62) were among the first to propose the hydrogenation of ethylene on alumina by "spillover" hydrogen. They diluted Pt-SiO₂ with SiO₂ and Al₂O₃ at a dilution rate of 1:9 and measured catalytic activity for ethylene hydrogenation of each of the mixtures as shown in Table 4 (62). Although they did not run a blank to determine how much SiO₂ enhances the activity of Pt-SiO₂ when the two
are mixed, they do state that both the alumina and silica by themselves had insignificant hydrogenation activity compared to the Pt-SiO₂. This work is important because it demonstrates that catalytic activity can be induced into a support which is normally not active for that reaction. It should be stressed that not all supports are equally capable of achieving this induced activity.

Table 4. Ethylene Hydrogenation Over Catalyst Mixtures (62)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>#Conv. (100°C)</th>
<th>#Conv (153°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-silica + silica</td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Pt-silica + alumina (1)</td>
<td>2.1</td>
<td>39</td>
</tr>
<tr>
<td>(2) simple mixture</td>
<td>0.5</td>
<td>14</td>
</tr>
<tr>
<td>Pt-silica contained 0.05% Pd by wt.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst charges were 0.05 gm catalyst + 0.45 gm diluent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sancier (63) has also demonstrated that a support can become active for hydrogenation. He examined benzene hydrogenation on Pd-Al₂O₃ catalysts which were diluted with Al₂O₃. Sancier found a maximum increase in rate of three times at a dilution of 1:200 or more. At the reaction temperature of 150°C the alumina was found to have insignificant hydrogenation activity for benzene. Results of these experiments are given in Table 5.

The conclusion that hydrogen spillover was responsible for the increase in activity of diluted catalyst mixtures has been challenged by Schlatter and Boudart (64) and by Vannice and Neikam (65). Schlatter and Boudart (who saw no evidence for spillover of hydrogen in a similar study of ethylene hydrogenation) claimed that the increase in activity that Carter, et al. (62) observed upon diluting the catalyst with
alumina was due to scavaging of poisons by the alumina. Vannice and Neikam made similar poisoning claims about the data of Sancier (63) for benzene hydrogenation and in addition criticized his use of a pulse reactor for these experiments. Sancier (66) rebutted the criticisms of Vanice and Neikam, claiming that there was no deactivation even when the hydrogen flowed continuously over the catalyst for many hours and that a pulse reactor was ideal for spillover studies because the catalyst, the support, and the diluent have time between pulses of benzene to become re-populated with hydrogen.

Table 5. Benzene Hydrogenation Over Catalyst Mixtures (63)

<table>
<thead>
<tr>
<th>Pd-alumina (mg)</th>
<th>Alumina (mg)</th>
<th>Alumina/Pd-alumina (mg/mg)</th>
<th>Hydrogenation (vol% / mg Pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>55</td>
<td>0</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>100</td>
<td>900</td>
<td>9</td>
<td>31</td>
</tr>
<tr>
<td>50</td>
<td>475</td>
<td>19</td>
<td>37</td>
</tr>
<tr>
<td>25</td>
<td>975</td>
<td>19</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>995</td>
<td>40</td>
<td>46</td>
</tr>
<tr>
<td>1.5</td>
<td>1000</td>
<td>200</td>
<td>67</td>
</tr>
<tr>
<td>0</td>
<td>1000</td>
<td>undefined</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

Teichner and co-workers are among the most active researchers in the area of hydrogen spillover. In Lacroix, et al. (67) they show that silica aerogel can be activated by hydrogen spillover into a catalyst that was active for hydrogenation, hydrogenolysis, and cracking of hydrocarbons at moderate temperatures. In their experiments the silica was contacted with a Pt-Al₂O₃ catalyst in the presence of hydrogen at 430°C for several hours. The platinum catalyst is then removed and the silica cooled to the reaction temperature. Silica treated in this manner was found to be active for ethylene hydrogenation at temperatures
from 170 to 230°C. The first dose of ethylene experienced an induction period not seen with subsequent doses. Silica pretreated in the same manner except not contacted with the platinum catalyst exhibited no ethylene hydrogenation activity for temperatures as high as 430°C.

Campagnon, et al. (68) have studied the effect of the carrier on the hydrogenolysis of cyclopropane and methylcyclopropane on supported platinum catalysts. They found a significant increase in catalytic activity when the Pt-alumina catalyst was diluted with alumina. This finding is consistent with the alumina dilution studies previously mentioned. The hydrogenation of methylcyclopropane on Pt/silica-alumina produced very interesting results. Both the metal and the support were active when the Pt content was below 1%. Above one percent Pt the iso/n-butane selectivity remained constant, indicating that the reaction occurs almost exclusively on the metal. Dilution of Pt/silica-alumina with silica-alumina also produced greater hydrogenation activity and decreased the iso-/n-butane ratio. It should be noted that silica-alumina is active for the isomerization of methylcyclopropane to n-butenes at room temperature; and to this author the invariance in the iso-/n-butane ratio for Pt/silica-alumina catalysts with Pt greater than 1% may well be due to the rate of hydrogenation on the metal being much greater than the rate of isomerization on the support. Campagnon and co-workers imply that the invariance in the iso-/n-butane ratio is due to there being enough Pt atoms to interact with the isomerization sites and somehow render them inactive.

Just as the support can influence the behavior of a catalyst by becoming active through hydrogen spillover, it can also influence the
adsorptive and catalytic properties of the catalyst. This phenomenon is known as strong metal support interaction (SMSI) (69). Although not particularly significant to the work presented in this thesis, it is nevertheless discussed for the sake of completeness. Titania is the support most often cited when discussing SMSI. In SMSI the small metal particles are strongly influenced by the metal oxide, and the chemisorptive and catalytic properties of the metal particles show a great sensitivity to the reduction temperature. Little, et al. (69) has studied nickel supported on both alumina, titania, and mixtures of the two. They report finding SMSI in nickel catalysts supported on a mixture of alumina and titania. Anderson, et al. (70) have studied titania and silica supported Ni, Pd, and Ir catalysts for SMSI. While they found normal adsorptive and catalytic properties for the silica supported catalysts, the titania supported catalysts exhibited catalytic and adsorptive properties that were sensitive to reduction temperature. Since alumina and silica are accepted as not exhibiting SMSI and the reduction temperature used in this work was not high enough to induce SMSI in the titania supported catalyst, SMSI will not be further discussed in this thesis.
CHAPTER III

APPARATUS AND PROCEDURE

APPARATUS

A microreactor system constructed of glass and stainless steel was employed in this study. It was designed for vapor phase kinetic studies at low pressures (0-1000 torr) and moderate temperatures (35-150°C) using small catalyst samples and low gas feed rates. For convenience of discussion the microreactor system can be divided into its constituent parts: the microreactor, gas feed system, analytical system, vacuum system, and temperature control system.

Microreactor

The microreactor (about 1 cc volume) was constructed of Pyrex glass, stainless steel, and Teflon. The reactor system (see diagram in Figure 2) was designed to be capable of operating under CSTR, batch, and plug flow conditions depending on the system valving. While operating in CSTR and batch modes, mixing was achieved using a Teflon recirculation pump, which had a maximum output of seven liters per minute at atmospheric pressure. The system pressure was measured using a stainless steel Heise gauge (0-1000 torr) and a Leybold-Heraeus TM113 thermocouple gauge (10^-3 to 1 torr) which was also constructed of stainless steel. All of the bellows valves (stainless steel) and stopcocks (teflon plug and glass body) which might contact the reaction mixture were capable of obtaining pressures below 10^-3 torr. Both of these pressure gauges could be isolated from the recirculation loop to
avoid "dead end" effects that could result in imperfect mixing. The catalyst samples were held in place in the U-tube reactor either by glass beads in the case of pelletized catalysts or by glass wool in the case of powdered catalysts. Catalyst samples were situated as close to the reactor thermowell as was possible.

Figure 2. Microreactor System
Feed System

Gas flow rates and composition were regulated using electronic mass flow controllers (MKS model 1259B). Each mass flow controller (MFC) was calibrated for a different gas and could be operated alone or in combination with one or more of the other three MFCs to obtain the desired gas mixtures for reaction, oxidation, reduction, and purging. Since more than four gases were used during the course of this study, a gas manifold was constructed to enable several gases to be connected to the same mass flow controller. One MFC was factory calibrated for 0-100 standard cubic centimeters per minute (sccm) of nitrogen and was used to control both air and nitrogen flow rates. Another MFC was factory calibrated 0-100 sccm hydrogen but was used for both hydrogen and a mixture of 15% hydrogen/85% nitrogen. There was no need to recalibrate the controller since the calibration factors for both hydrogen and nitrogen are the same. A third controller was factory calibrated for 0-50 sccm of a 15% H₂/85% N₂ mixture but was used for a hydrocarbon mixture of approximately 9% 1,3-butadiene and 91% 1-butene. The fourth MFC was factory calibrated for 0-20 sccm of a hydrocarbon mixture containing 9% butadiene and 91% 1-butene; however, this flow range proved to be too low, forcing a change to the higher flow rate controller. A mixture of 500 ppm CO in nitrogen was metered using the fourth controller. Correct sccm readings for the third and fourth controllers were obtained by changing the calibration factors on the setpoint and display module for those two controllers.
A single setpoint and display module allowed each controller to be independently set; the actual flow rate of each controller was displayed in sccm. Gas streams were mixed in a cross before entering the inlet sample loop where the gas feed could be sampled and sent to the gas chromatograph for analysis. The flow rate out of the reactor was monitored using a soap bubble meter.

Analytical System

Gases were analyzed with a Varian 3700 gas chromatograph equipped with both a flame ionization detector (FID) and a thermal conductivity detector (TCD). The gases were separated on a 30 foot, 3/16" stainless steel column packed with bis-methoxy ethyl adipate (BEMA). Hydrogen and carbon monoxide are not retained by the BMEA column and eluted before the hydrocarbons. The detectors were arranged in series with the gases passing through the TCD first. Hydrogen was measured on the TCD and gave negligible response on the FID. Carbon monoxide was analyzed with the FID after being converted to methane using a methanation catalyst (nickel on chromosorb packing, from Varian) at 360°C. The methanation unit was located between the TCD and FID and was bypassed when CO was not present. CO was present on the order of 100 ppm and was not detectable with the TCD when using nitrogen as the carrier gas. Hydrocarbons were measured with the FID and were eluted from the column in the following order: n-butane, 1-butene, trans-2-butene, cis-2-butene, and 1,3-butadiene. Two HP 3390A recording integrators were used to record and integrate the output from the two detectors.
Isotopic analysis was conducted with a small quadrapole mass spectrometer (UTI 100C, 1-300 amu range). A sample would be taken from the reactor using a sampling valve (2 ml sample loop) and injected into the gas chromatograph. Since no online mass spectrometer was available, each hydrocarbon (or peak) was trapped after passing through the TCD in a U-tube emersed in liquid nitrogen. The hydrocarbon samples were then taken to the mass spectrometer for analysis.

The U-tube used for trapping the hydrocarbons was approximately ten inches long and was connected a stopcock with one straight and one oblique bore. On the other side of the stopcock were connected two standard taper fittings, a 12/30 taper on the straight bore and a 10/20 taper on the oblique bore. Depending on the position of the stopcock, either one or both sides of the U-tube were open. One position allowed gas to flow freely through the U-tube during the trapping phase; a 180° rotation allowed the carrier gas to be evacuated before the frozen hydrocarbon was evaporated and admitted into the mass spectrometer.

Vacuum System

A turbomolecular pumping system was employed to obtain a "hydrocarbon free" vacuum since catalyst contamination by either diffusion pump or mechanical pump oil could prove to be troublesome. The microreactor system was evacuated using a Balzers turbomolecular pump (model TPH 050) which was capable of providing a vacuum on the order of $10^{-8}$ torr and pumping speeds of 50 liters per minute. An Edwards High Vacuum mechanical pump, capable of pumping 150 liters per minute, was used to back the turbomolecular pump. The pumps were
electronically interlocked with an electronic vent valve to insure proper venting of the system in case of power failure. Proper venting was necessary to prevent the mechanical pump oil from being sucked up into the microreactor system during a power failure.

Temperature Control System

The catalyst temperature was regulated with a Lindberg furnace and a Leeds & Northrup PID temperature controller. A small fan blew air over the glass reactor in the furnace to increase heat transfer and improve temperature control. Catalyst temperature was measured with a J type (iron-constantan) thermocouple placed in a thermowell in contact with the catalyst.
PROCEDURE

Catalyst Pretreatment

After being weighed, catalyst samples were placed as close to the U-tube thermowell as was possible. Pelletized samples, which were used for the kinetic studies, were held in place with glass beads. Powdered samples were suspended in glass wool. Catalyst pretreatment consisted of oxidation in a flowing stream of air (40 sccm) at 473K for two hours followed by flushing with nitrogen and subsequent reduction in a stream of 11 percent hydrogen and 89 percent nitrogen at 548K for two hours. The catalyst was then cooled to reaction temperature under a 2.5 percent hydrogen in nitrogen stream.

Start-up Procedure

Prior to starting a reaction the entire reactor system (including the catalyst) was purged with nitrogen for 20 minutes to remove all the hydrogen. Nitrogen purging was chosen over evacuating the system because evacuation was likely to introduce some air into the system which might affect catalyst behavior. This method yielded reproducible results for the kinetic studies; however, it may responsible for some of the difficulties encountered during the spillover experiments.

After the microreactor was purged of hydrogen, the mass flow controllers were set to the desired flow rate and turned on. Immediately after the flow controllers were activated the valves located after the flow controllers were opened, allowing the gases to mix in a cross before passing through the inlet sample loop and into the reactor.
Placing valves on the outlet side of the flow controllers was necessary to prevent any back-mixing of the gases and to provide a positive shut-off for each gas.

The first sample from the microreactor would be taken about thirty minutes after starting the reaction. Thirty minutes was approximately five residence times, which was long enough for the reactor to reach steady state for a step change in the inlet concentration. After about thirty minutes a pseudo steady-state was established where the rate of deactivation was fairly small compared with the reaction rate. It was during this pseudo steady-state period that the reaction data were taken.

In experiments where aged catalysts were used, the catalyst would be regenerated using the same pretreatment conditions as for a fresh catalyst. All of the kinetic experiments were conducted using aged catalysts; in general, the aged catalysts gave more reproducible results than did fresh catalyst samples.

For batch experiments, the U-tube containing the catalyst under a nitrogen atmosphere was first isolated from the rest of the microreactor system. The mixing loop was evacuated and gases were introduced to the mixing loop one at a time. Butadiene was the first gas admitted to the reactor to the desired pressure; it was subsequently condensed into a cold finger using liquid nitrogen. Labeled 1-butene (1-butene-4-\(^{13}\)C \& 99 atom%, Icon Services, Inc.) was introduced to the desired pressure and also frozen into the same cold finger. The mixing loop section of the microreactor and the cold finger (still at liquid nitrogen temperature) were then evacuated to a pressure of 10\(^{-2}\) torr to remove
any non-condensable gases. Next, the cold finger was warmed to room
temperature, and the degassed hydrocarbons were expanded into the mixing
section. Hydrogen and nitrogen (a diluent) were next introduced to the
reactor to a total pressure near 1 atmosphere. The gases were allowed
to mix for approximately one hour before the reaction was started. Just
prior to starting the reaction the pressure gauges were isolated from
the rest of the system to remove dead volume. The reaction was started
by opening the U-tube reactor to the rest of the microreactor system.

Analytical Procedure - Gas Chromatography

Analysis of either the inlet or reactor gas composition was
accomplished by injecting a gas sample into the gas chromatograph with
either of two (inlet and outlet) six-way sample valves. The inlet
stream had a 250 microliter sample loop, while the reactor stream was
sampled using a 500 microliter sample loop. The size of the sample loop
is limited by the concentration of the largest hydrocarbon in the
stream. If one injects too large a sample, the FID will have
insufficient oxygen to ionize (burn) the largest hydrocarbon peak and
the response will become non-linear. In this thesis, the FID analytical
methods used were optimized to measure 1,3-butadiene. Trying to
optimize 1-butene analysis was deemed impractical since it would involve
measuring a small change in a large peak.

Hydrogen was measured using the TCD with nitrogen as the carrier
gas. Because of their relative thermal conductivities, nitrogen and
argon are the only reasonable choices for a carrier gas with which to
measure the hydrogen concentration.
Carbon-monoxide was the most difficult component to analyze. Above 25 ppm CO analysis was rather simple. Below 25 ppm the hydrogen peak resulted in interference. Hydrogen gave a very weak response on the FID and was never seen when using the electrometer settings that were appropriate for measuring the C₄ hydrocarbons. But at the same electrometer settings required to measure ppm quantities of methane, hydrogen produced a measurable response on the FID. With samples containing more than 25 ppm CO, reproducibility was good and hydrogen interference was small.

Analytical Procedures - Mass Spectroscopy

Before a trapped hydrocarbon sample could be analyzed, the nitrogen and any other non-condensible gases present were removed by evacuating the U-tube while it was still at liquid nitrogen temperature. After the U-tube was allowed to warm to room temperature, the gas was admitted to a large sample vessel (approximately 200 cc). The sample vessel was then isolated from the gas inlet by means of a high vacuum valve. The sample vessel was connected to the mass spectrometer by a capillary tube which allowed the sample to bleed into the mass spectrometer at a fairly constant rate. This inlet system was necessary because the scan rate had to be slow enough (7.5 s/amu) so that the electrometer output could be recorded by a chart recorder.

The hydrocarbons were analyzed using a nominal electron ionization energy of 22.5 eV; scanning covered the range 46 to 62 m/e to measure the parent peaks. Using a moderately low ionization energy minimized the amount of fragmentation, which simplified measurement of the parent
peaks. The measured ratio of the parent peak to the parent peak minus one were: n-butane (1/0.21), 1-butene (1/0.27), and both cis and trans 2-butene (1/0.20). After correcting for the natural occurrence of $^{13}$C and the fragmentation due to loss of hydrogen, one obtained the true isotopic composition of the hydrocarbon. The isotopic composition was used to determine approximately how much of each hydrocarbon (trans-2-butene, cis-2-butene, and n-butane) came from $^{13}$C labeled 1-butene.

Mass spectrometers equipped with computers for data acquisition are capable of at least three orders of magnitude faster scan rates. Very fast scan rates are necessary when transient measurements are made, such as in GC-MS applications. Online GC-MS analysis was originally planned for in this thesis, and the separation methods developed with this in mind. Once the mass spectral data have been acquired by the computer, baseline corrections for tailing peaks and background can be easily made. Trapping the peaks as they elute from TCD has the major disadvantage of not allowing any baseline or tailing peak corrections. For this reason some of the early samples where the 2-butene peaks were small compared to the 1-butene tail are not particularly useful.
CHAPTER IV
RESULTS and DISCUSSION

A. Kinetics of Butadiene Hydrogenation and the Role of CO

Results

The kinetics of 1,3-butadiene hydrogenation in the presence of large excesses (typically ~ 10:1) of 1-butene were examined on two palladium-alumina catalysts. One catalyst was a 0.5% (wt.) Pd/AT-9 (a 4 m²/gm alumina); the other was a 0.02% (wt.) Pd/AT-2 (a 90 m²/gm alumina) with an eggshell (peripheral) metal distribution. Since most industrial selective hydrogenation catalysts use low surface area aluminas for supports, the 0.5% Pd/AT-9 (1/8" pellets) was chosen as the base catalyst against which most others were compared. Typical results are shown in Table 6. Butane selectivity is defined as the rate of butane formation divided by the rate of butadiene consumption.

| Catalyst | Temp. | Inlet \(P_{\text{butadiene}}\) | \(H_2/BD\) | \(F/C\) | \(S_{\text{butane}}\) | Conv. (BD)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 wt% Pd</td>
<td>308K</td>
<td>9.23 torr</td>
<td>0.75</td>
<td>0.65</td>
<td>0.87</td>
<td>0.25</td>
</tr>
<tr>
<td>&quot;</td>
<td>308K</td>
<td>7.25 torr</td>
<td>2.72</td>
<td>1.85</td>
<td>2.78</td>
<td>0.35</td>
</tr>
<tr>
<td>&quot;</td>
<td>338K</td>
<td>9.29 torr</td>
<td>0.76</td>
<td>0.91</td>
<td>0.45</td>
<td>0.34</td>
</tr>
<tr>
<td>&quot;</td>
<td>338K</td>
<td>7.24 torr</td>
<td>1.56</td>
<td>1.24</td>
<td>0.94</td>
<td>0.35</td>
</tr>
<tr>
<td>&quot;</td>
<td>338K</td>
<td>7.15 torr</td>
<td>2.78</td>
<td>1.73</td>
<td>2.24</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The butane selectivities reported in Table 6 were unexpectedly high. The catalyst was tested for diffusional limitations by crushing the pellets to a fine powder and measuring the selectivity under reaction conditions similar to those of the pelletized catalyst (using
the same amount of catalyst in both cases). The results of experiments on crushed 0.5% Pd/AT-9 are presented in Table 7.

Table 7. Butadiene Hydrogenation on Crushed 0.5% Pd/AT-9

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp.</th>
<th>Inlet P (BD)</th>
<th>H₂/BD</th>
<th>t/C</th>
<th>S₄Butane</th>
<th>Conv (BD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pellet</td>
<td>308</td>
<td>9.23</td>
<td>0.75</td>
<td>0.65</td>
<td>0.87</td>
<td>0.25</td>
</tr>
<tr>
<td>crushed</td>
<td>308</td>
<td>10.0</td>
<td>0.69</td>
<td>0.75</td>
<td>0.36</td>
<td>0.38</td>
</tr>
<tr>
<td>pellet</td>
<td>308</td>
<td>46.1</td>
<td>0.79</td>
<td>0.79</td>
<td>1.23</td>
<td>0.17</td>
</tr>
<tr>
<td>crushed</td>
<td>308</td>
<td>46.7</td>
<td>0.66</td>
<td>1.05</td>
<td>0.27</td>
<td>0.22</td>
</tr>
</tbody>
</table>

It was quite clear from the increased butadiene conversion and the decreased in butane selectivity that, at least under the conditions of these experiments, rates over the pelleted catalyst were diffusionaly limited. Measurements under diffusionaly limiting conditions are less than ideal for determining the kinetics of a reaction since such limitations often mask the intrinsic behavior. For this reason, an eggshell metal deposition catalyst was selected for further kinetic studies.

A series of kinetic experiments were conducted using an aged 0.02% Pd/AT-2 catalyst to determine the reaction orders in both hydrogen and butadiene. Operating the reactor in CSTR mode, the rate of butadiene hydrogenation was directly measured (as a result of measuring the inlet and outlet compositions and flow rate). Several researchers have found the hydrogenation of butadiene zero order in butadiene and first order in hydrogen; these same reaction orders held in this study.
Butadiene Hydrogenation at 348K

\[ Y = (\text{BD Hydrogenation Rate / Activity}) \times 1000 \]
Rate (mole/s/gmPD)

Figure 3. Variation In BD Hydrogenation Rate With H₂ Pressure

Butadiene Hydrogenation 328K to 368K

\[ \ln k = 13.3 \pm 0.8 \text{ kcal/gmole} \]
0.02% Pd/AT-2 Eggshell 90 m²/gm alumina

Figure 4. Effects of Temperature on Butadiene Hydrogenation Rate
The variation of butadiene hydrogenation rate with the hydrogen pressure is shown in Figure 3. An Arrhenius plot using a first order hydrogen, zero order butadiene power law model is shown in Figure 4. The activation energy for butadiene hydrogenation on the 0.02% Pd/AT-2 catalyst was measured to be 13.3 ± 0.8 kcal/mole (56 ± 3 kJ/mole).

Corrections were made for deactivation of the catalyst. The activity at one hour after starting the reaction was arbitrarily defined to be unity. The feed conditions were changed and the rate measured again some thirty minutes or more later (at time 1 + A hours). The feed conditions were then returned to those used initially and the rate (activity) measured after about thirty minutes (at time 1 + B hours). The activity, a, at time 1 + A was calculated assuming an exponential decay \[ a = a_0 \exp(-t/T) \] in activity between time 1 and 1 + B. The initial activity is defined by \( a_0 \); in this case unity at one hour time on stream. \( T \) is a time constant which relates how quickly the catalyst deactivates; \( t \) is the time on stream minus one hour.

The power law rate model used in this thesis is a limiting case of a Langmuir-Hinshelwood model. The \( L-H \) model assumes: (1) adsorption of hydrogen and hydrocarbons is non-competitive, and (2) that the rate controlling step is the hydrogenation of a half-hydrogenated absorbed butadiene molecule. With these two assumptions, one obtains the \( L-H \) model shown in equation A. Equation A reduces to the power law model, Equation B, when the term \( K_{H2}P_{H2} \) is sufficiently large compared to \( 1 + K_{H2}P_2 \) so that the denominator of Equation A is not appreciably different from \( K_{H2}P_{H2} \).
Carbon monoxide decreases the catalytic activity of supported palladium catalysts for the hydrogenation of acetylenes and diolefins. This makes it an ideal additive to moderate the activity of the catalyst in cases of high reaction temperatures and/or high hydrogen/acetylene-diolefin feed ratios. CO has also been reported to inhibit the isomerization of 1-butene during the selective hydrogenation of butadiene in 1-butene rich streams under industrial conditions (10,11). Based on these observations, the role that CO plays in improving selectivity and inhibiting isomerization was investigated. The effects of added CO on the hydrogenation of butadiene were examined on both the 0.5% Pd/AT-9 catalyst, which suffered from diffusional limitations, and on the 0.02% Pd/AT-2 eggshell catalyst. Typical results for the 0.5% Pd/AT-9 catalyst are given in Table 8. Additional results with the 0.5% Pd/AT-9 catalyst at a temperature of 313K are shown in Figures 5, 6, 7, and 8.

Figure 5 shows that the ratio of butane formation to butadiene consumption falls from an approximate value of 2.4 when no CO was present to a value of 0.4 at 200 ppm CO concentration (about 0.15 torr). From Figure 5 it is also clear that the addition of CO improves the selectivity of a diffusionaly limited catalyst. This is significant,
since all palladium selective hydrogenation catalysts become
diffusionally limited at some point as the acetylene or diolefin
centration approaches the impurity specification. Figure 6
illustrates the effect of carbon monoxide on the ratio of 2-butene
formation to butadiene consumption which indicates the degree to which
CO suppresses the isomerization of 1-butene to 2-butenes.

Table 8. Typical Results With 0.5% Pd/AT-9 Using CO at 313K

<table>
<thead>
<tr>
<th>Time (hr.)</th>
<th>CO (ppm)</th>
<th>C4H10 (torr)</th>
<th>1-C4H8 (torr)</th>
<th>t-C4H8 (torr)</th>
<th>c-C4H8 (torr)</th>
<th>C4H6 (torr)</th>
<th>H2 (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet 4.55</td>
<td>nil.</td>
<td>0.26</td>
<td>213.2</td>
<td>nil.</td>
<td>nil.</td>
<td>21.53</td>
<td>41.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.36</td>
<td>186.0</td>
<td>21.06</td>
<td>10.49</td>
<td>15.67</td>
<td>21.67</td>
</tr>
<tr>
<td>inlet 1.13</td>
<td>48.6</td>
<td>0.26</td>
<td>211.6</td>
<td>nil.</td>
<td>nil.</td>
<td>21.32</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.59</td>
<td>194.8</td>
<td>15.18</td>
<td>7.22</td>
<td>16.79</td>
<td>31.6</td>
</tr>
<tr>
<td>inlet 99.5</td>
<td>0</td>
<td>0.24</td>
<td>209.9</td>
<td>nil.</td>
<td>nil.</td>
<td>21.18</td>
<td>40.53</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3.13</td>
<td>195.9</td>
<td>13.69</td>
<td>6.52</td>
<td>16.94</td>
<td>33.73</td>
</tr>
<tr>
<td>inlet 149.3</td>
<td>2.92</td>
<td>0.25</td>
<td>208.7</td>
<td>nil.</td>
<td>nil.</td>
<td>21.06</td>
<td>39.26</td>
</tr>
<tr>
<td></td>
<td>2.07</td>
<td>199.2</td>
<td>10.11</td>
<td>5.02</td>
<td>17.26</td>
<td>34.74</td>
<td></td>
</tr>
<tr>
<td>inlet 196.8</td>
<td>2.05</td>
<td>0.25</td>
<td>207.4</td>
<td>nil.</td>
<td>nil.</td>
<td>20.91</td>
<td>40.48</td>
</tr>
<tr>
<td></td>
<td>1.68</td>
<td>199.7</td>
<td>9.18</td>
<td>4.60</td>
<td>17.35</td>
<td>34.90</td>
<td></td>
</tr>
</tbody>
</table>

*The first row indicates the inlet composition. The reactor composition (and
effluent) is given in the following row.

The effect of CO pressure on the rate ratio of butane formation to
2-butene formation (essentially the hydrogenation/isomerization rate
ratio for 1-butene) is shown in Figure 7. Figure 7 shows that the rate
of 1-butene hydrogenation is inhibited to a greater degree than the rate
of 1-butene isomerization, which concurs with the findings of Furukawa,
et al. (10,11). The trans/cis 2-butene ratio was found to be
independent of the amount of carbon monoxide added to the feed stream as
shown in Figure 8. The trans/cis ratios (approximately 2) seen in
Figure 8 were below the equilibrium ratio for 2-butenes at the reaction
temperature of 343K; indicating that butenes were adsorbing on the palladium sites and isomerizing since one would not expect butadiene hydrogenation alone to produce trans/cis ratios near two, based on the initial selectivities reported by others (4,6).

Selectivity Towards n-Butane

\[ S = \frac{\text{rate of butane formation}}{\text{rate of butadiene conversion}} \]

Figure 5. Effect of CO on Butane Selectivity for 0.5% Pd/AT-9

Selectivity Towards 2-Butene

\[ S = \frac{\text{rate of 2-butene formation}}{\text{rate of butadiene conversion}} \]

Figure 6. Effect of CO on 2-Butene Selectivity for 0.5% Pd/AT-9
Figure 7. Effect of CO on Hydrogenation/Isomerization Ratio for 0.5% Pd/AT-9

Figure 8. Effect of CO on Trans to Cis Ratio for 0.5% Pd/AT-9
Carbon monoxide, unlike hydrogen sulfide, is a reversible inhibitor for selective hydrogenation reactions. Since CO is reversibly adsorbed on the palladium, temperature has a strong effect (through $K_{\text{CO}}$) on the degree of inhibition. The lower the reaction temperature the more strongly CO adsorbs to the palladium; CO in high enough concentrations effectively kills all the catalytic activity. The kinetic effects of carbon monoxide on butadiene hydrogenation have been investigated using the 0.02% Pd/AT-2 eggshell catalyst. The hydrogenation of butadiene at constant CO pressure was studied to determine if the reaction order of hydrogen changed upon the addition of CO. In Figure 9, the rate of butadiene hydrogenation is seen to vary linearly with hydrogen pressure at a CO concentration of 40 ppm.

![Graph](image)

**Figure 9.** Butadiene Hydrogenation Rate in the Presence of CO
Since the power law model for the rate used in the absence of CO also holds when 40 ppm of CO was added to the feed, the kinetic measurements were conducted on the 0.02% Pd/AT-2 catalyst with 40 ppm CO added to the feed stream. The rate constants measured over the temperature range of 333K to 373K are shown in Figure 10. The activation energy for butadiene hydrogenation in the presence of 40 ppm CO was determined from the slope of the line to be 15.5 ± 0.5 kcal/mole (65 ± 2 kJ/mole). As previously stated, the activation energy in the absence of CO over the same catalyst and the temperature range of 328K to 368K was 13.3 ± 0.8 kcal/mole. A comparison of the two Arrhenius plots is given in Figure 11. The addition of carbon monoxide appears to increases the activation energy for butadiene hydrogenation by approximately 2 kcal/mole.

The reaction order with respect to CO was also investigated. Studies (28,32) which have looked at the co-adsorption of hydrogen and carbon monoxide have generally shown that CO is more strongly adsorbed than hydrogen. For the purposes of modeling it was useful to consider two types of sites, one type on which hydrocarbons (mainly butadiene) adsorb and another type on which hydrogen and carbon monoxide compete for adsorption. It is important to stress that these two sites are not truly different sites but are artificially created because the packing density of butadiene on a palladium crystallite is lower than the packing densities of either CO of H₂ due to its large physical size. Thus, even when one monolayer coverage of butadiene is reached, there are still sites available to small molecules, like CO and H₂, which are
Figure 10. Temperature Dependence of Butadiene Hydrogenation Rate

Figure 11. Effect of CO on Butadiene Hydrogenation Rate
unavailable to butadiene or n-butenes which are too large to be accommodated in the small interstices.

This also explains how butadiene can dominate the surface sites while hydrogen still adsorbs and reacts. Using this conceptual model and with the further assumption that an adsorbed CO occupies two Pd atoms (bridged adsorption), a L-H rate equation for butadiene hydrogenation in the presence of CO was derived and is given in equation C.

\[
I_{BD} = \frac{kP_{H2}}{1 + (K_{CO}P_{CO})^{0.5}} 
\]

(C)

The validity of this model was tested by rewriting the rate model (equation C) to make \((K_{CO}P_{CO})^{0.5}\) an independent variable as shown in equation D.

\[
(K_{CO}P_{CO})^{0.5} = \frac{kP_{H2}}{I_{BD}} - 1 
\]

(D)

From the results shown in Figure 12, over the range of CO pressures tested the rate equation accurately models the data. Since the exact state of adsorbed CO (bridged, linear, or mixed) in this study is unknown, there are probably other more reasonable explanations than bridged CO adsorption that could account for the negative half order rate dependence on CO.
Figure 12. Square Root Dependence of Hydrogenation Rate on CO Pressure
Discussion

Comparison of this work with other vapor phase studies was limited to Meyer and Burwell (flow) and Bond, et al. (batch) with butadiene and hydrogen being the initial reactants in both studies. Meyer and Burwell (4) reported finding only traces of butane and no product (butene) isomerization when \( H_2/C_4H_6 \leq 0.9 \); however, both butane formation and butene isomerization occurred when \( H_2/C_4H_6 > 0.95 \). Bond, et al. (6) also reported the reaction to be completely selective initially but noted that butane formation and butene isomerization increased as the butadiene was consumed. Table 9 gives the results of these two studies.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp.</th>
<th>l-R</th>
<th>t-2-R</th>
<th>c-2-R</th>
<th>t/c</th>
<th>S_{Butene}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 wt% Pd</td>
<td>308K</td>
<td>0.532</td>
<td>0.42</td>
<td>0.048</td>
<td>8.75</td>
<td>0.999</td>
<td>Meyer</td>
</tr>
<tr>
<td>5 mol% Pd</td>
<td>316K</td>
<td>0.594</td>
<td>0.37</td>
<td>0.038</td>
<td>9.7</td>
<td>1.0</td>
<td>Bond</td>
</tr>
</tbody>
</table>

Initial selectivities, mole %

From the results listed in Tables 6 and 7, two conclusions can immediately be drawn. First, even in cases where there was insufficient hydrogen to react with all of the butadiene, there was significant formation of butane, contrary to the findings of Meyer and Burwell (4). Second, the butene distributions definitely indicated that isomerization had occurred. It has been established by both Meyer and Burwell (4) and Bond, et al. (6) that the hydrogenation of 1,3-butadiene at a temperature near 313K yields 2-butenes with initial trans/cis ratios in excess of 8.0. Moreover, Bond, et al. (6) and Wells and Wilson (48)
have shown that in the absence of butadiene Pd/alumina catalysts
isomerize n-butenes to their equilibrium composition. Of course, how
close the butenes are to their equilibrium composition depends on the
degree of isomerization. The trans/cis 2-butene ratios listed in Table
6 were below the thermodynamic equilibrium ratio (5 at 296K and 3.4 at
323K (53)) indicating that either some of the isomerization must have
occurred on the alumina support or in a non-equilibrium manner on the
palladium. Aluminas have been shown by Hightower and Hall (53) to
classically yield trans/cis 2-butene ratios < 1 for 1-butene
isomerization. Non-equilibrium 2-butene ratios for 1-butene
isomerization on palladium have been reported by Holbrook and Wise (49)
and by Ragaini, et al. (50). Holbrook and Wise have shown that, at low
hydrogen pressure (less than 2 torr), the isomerization of 1-butene on
both supported (alumina) and unsupported palladium spheres yields
trans/cis ratios less than one. Ragaini, et al. have obtained similar
results, finding trans/cis ratios less than equilibrium at low hydrogen
pressures (how low depends on the contact time) with the ratio tending
toward unity (or slightly less than unity) as the hydrogen pressure
tends toward zero.

The results in Table 6 show that the trans/cis 2-butene ratios
increased toward equilibrium values as the hydrogen/butadiene inlet feed
ratios increased. Increasing the hydrogen/butadiene ratio seemed to
increase the amount of hydroisomerization (Pd catalyzed) taking place on
the catalyst. One would not expect n-butene isomerization on alumina to
be particularly sensitive to the hydrogen pressure. This lead to the
conclusion that the low trans/cis ratios are primarily due to 1-butene isomerization on palladium under conditions of low hydrogen pressure.

A third (and arguably most significant) conclusion drawn from the results presented in Table 7 is that the reaction was controlled by diffusion, not by intrinsic chemical kinetics. In Appendix A the Thiele modulus of the catalyst was calculated to be approximately 10 under the reaction conditions indicating severe diffusional limitations. Thus, the catalyst may be conceptually divided into two regions, the first (or outer) region where butadiene hydrogenation takes place and the second (or inner) region where little or no butadiene and n-butene hydrogenation and isomerization occurs. The size of each of these regions depends on the hydrogen/butadiene feed ratio with the thickness of the outer region decreasing as the hydrogen/butadiene feed ratio increases. Larger hydrogen to butadiene feed ratios produce more exposed (those not covered by butadiene) Pd sites. This result in larger butane selectivities (which is undesirable) and trans/cis ratios closer to equilibrium. This model qualitatively explains why the n-butane selectivity and the trans/cis ratio increase as the hydrogen/butadiene feed ratio increases as shown in Table 6. Crushing the catalyst to a fine powder and repeating the reaction under similar conditions (Table 7) confirmed that the catalyst was diffusionaly limited at the reaction conditions of Table 6.

The experiments conducted on the 0.5% Pd/AT-9 catalysts demonstrated how easily mass transfer problems could develop on selective hydrogenation catalysts and emphasize the importance of proper catalyst design. Each incremental increase in olefin selectivity is
worth millions of dollars in the production of ethylene and propylene. Even if the metal loading on this catalyst were reduced one order of magnitude to 0.05% Pd (common industrial loadings are near 0.04% Pd), the Thiele modulus would still be close to unity. While such a catalyst may not present any danger of the reaction running away, it would hardly be a commercial success. It should be noted that both Meyer and Burwell (4) and Bond, et al. (6) in their studies of butadiene on palladium supported on alumina always used powdered catalysts and neither mentioned encountering any diffusional resistances. One can only wonder if they tried pelletized catalysts and abandoned them due to mass transfer limitations.

Since the reaction was diffusionaly limited on the 0.5% Pd/AT-9 catalyst, it was necessary to select a catalyst which would be unlikely to present diffusional problems. A 0.02% Pd/AT-2 (1/8" pellets) with eggshell metal deposition was found to be quite satisfactory. The rate of butadiene hydrogenation at nearly constant hydrogen pressure was found to be unaffected by the butadiene pressure when the butadiene pressure was above a certain critical value. Although this critical butadiene pressure (or acceleration point as Bond, et al. (6) refer to it) was not investigated in detail, it depends on both the hydrogen/butadiene feed ratio and on the actual butadiene pressure in the reactor; it represents the pressure at which butenes start competing for surface sites.

The reaction order with respect to hydrogen was determined to be 1.0 over the temperature range from 328K to 368K. The variation of butadiene hydrogenation rate (corrected for deactivation) with hydrogen
pressure is shown in Figure 3. The rate varied linearly with the hydrogen pressure over the entire range of pressures examined in this thesis. As shown in the Arrhenius plot in Figure 4, the activation energy for butadiene hydrogenation was determined to be 13.3 ± 0.8 kcal/mole (56 ± 3 kJ/mole) using a power law model for the rate with butadiene and hydrogen orders being 0 and 1, respectively.

The reaction orders are in good agreement with the most recent studies of butadiene hydrogenation on supported palladium. Zero order kinetics with respect to butadiene concentration have been reported by Furukawa, et al. (11), Boitiaux, et al. (12), and Nagamoto and Inoue (15) for Pd and by Oudar, et al. (16), Pradier, et al. (17,18), and Boitiaux, et al. (13) for Pt. First order hydrogen dependence was observed by all of the above except Pradier, et al. (17), who reported 1/2 order, and Furukawa, et al. (11), who did not report the hydrogen dependence. The activation energy for butadiene hydrogenation of 13.3 ± 0.8 kcal/mole compares favorably with the value of 16.7 kcal/mole reported by Bond, et al. (6).

Further studies by Boitiaux and co-workers have found that butadiene hydrogenation is more appropriately described by a modified Langmuir-Hinshelwood model. This L-H model assumes that adsorption of hydrogen and hydrocarbons are non-competitive and that the hydrogenation of a half-hydrogenated adsorbed butadiene species is the rate limiting step. In addition, the authors introduce a "complexation constant" which has the effect of making the butadiene adsorption equilibrium constant dependent on the metal dispersion. For a given catalyst (and therefore a fixed dispersion) the reaction model proposed by Boitiaux,
et al. (21) reduces to equation (A) (see p. 63). When the butadiene pressure is large enough that \( K_{BD}P_{BD} \) dominates the denominator of equation (A), the equation reduces to the power law model used in this thesis, equation (B).

An attempt was made to model this work with Langmuir-Hinshelwood kinetics by neglecting butene adsorption. While this allowed \( K_{BD} \) to be calculated, the results were unsatisfactory. Estimates of the error in \( K_{BD} \) were the same order of magnitude as \( K_{BD} \), making it impossible to calculate any meaningful temperature dependence of \( K_{BD} \). It is not possible to use data taken under conditions where the reaction follows power law kinetics, as were the data on the 0.02% Pd/AT-2 catalyst, and calculate the parameters of a Langmuir-Hinshelwood model. In order to see L-H kinetic behavior, one would have to take data under conditions where the n-butene selectivity was just starting to decrease (near the acceleration point). However, measuring the kinetics under these conditions would be difficult. One would be unable to determine if the butane formation was the result of thermodynamic competition between butadiene and butenes or was a manifestation of diffusional limitations; slight fluctuations in either the hydrogen or butadiene pressures may cause large swings in the rate of butane formation.

Carbon monoxide is commonly used to inhibit hydrogenation reactions on palladium catalysts in industrial reactors. In addition, CO has been shown by Furukawa, et al. (10,11) to inhibit the isomerization of 1-butene during the selective hydrogenation of trace amounts of butadiene in 1-butene rich streams under industrial conditions. Bain, et al. (30) have observed a similar effect (CO
suppression of isomerization) for 1-butene hydrogenation on Pt-alumina. Most researchers (10,11,31,32), excepting Bain, et al. (30) who found that the rate of 1-butene hydrogenation on Pt-alumina was unaffected by the CO surface coverage, have reported olefin hydrogenation on palladium catalysts to be poisoned by the addition of CO.

The effects of added CO on the hydrogenation of butadiene were examined on both the 0.5% Pd/AT-9 catalyst, which was influenced by diffusional limitations, and the 0.02% Pd/AT-2 eggshell catalyst. Typical results for the 0.5% Pd/AT-9 are given in Table 8. As expected, there was considerable butane formation in the absence of carbon monoxide. Addition of CO dramatically decreased the butane selectivity as shown in Figure 5. CO's effect on butene isomerization was small as illustrated in Figures 6 and 8. Since the isomerization was less than 15% even in the absence of CO, drawing any conclusion about the suppression of isomerization by CO under these conditions would be unwise. These results are consistent with the findings of the researchers previously cited.

Measuring the kinetics of butadiene hydrogenation in the presence of CO presented several problem. Obtaining data at low CO concentrations was as difficult as obtaining data at low butadiene pressure, although for different reasons. Sample analysis became difficult when the CO concentration dropped below about 25 ppm. Also, selecting a temperature where there was measurable conversion of butadiene at 140 ppm CO limits how little CO one could use and not have the reaction go to completion (or have a hydrogen pressure too small to accurately measure). Due to these limitations it was not possible to
lower the CO concentration continuously to zero in order to verify that equation C reduces to equation B at zero CO concentration.

From equation C it is clear that the addition of CO should increase the activation energy of butadiene hydrogenation. The apparent rate constant has the form of $k_0 \exp\left(-E_A/RT\right)$ and $K_{CO}$ has the apparent form of $K_0 \exp\left(Q_{ad}/RT\right)$. Thus, if CO adsorption has no effect on the adsorption constants for either hydrogen or butadiene or on the surface rate constant, from equation C one would expect the activation energy to increase by $0.5Q_{ad}$. The values of $Q_{ad}$ for CO given by Chou and Vannice (27) would indicate an increase in $E_A$ of between 11 and 17.5 kcal/mole. The work of Palczewska, et al. (32) shows that CO may indeed affect the hydrogen adsorption in a manner other than simple blocking (at least on Pd(111)). The IR frequency shifts of CO when coadsorbed on transition metals with an unsaturated hydrocarbon indicate a net flow of charge towards or away from the metal crystallite. Primet, et al. (26) have seen a net flow of charge towards platinum crystallites on the coadsorption of benzene and CO. Since the electronic nature of the crystallites can be changed by the coadsorption of an unsaturated hydrocarbon and CO, it is not unreasonable, considering that the bonds are electronic, that this might affect the surface reaction rate constant and the adsorption constant for butadiene. Consequently, predicting how much the activation energy should increase upon the addition of CO is not a trivial matter. The fact that the activation energy did increase (from $13.3 \pm 0.8$ to $15.5 \pm 0.5$ kcal/mole) in the presence of 40 ppm CO is consistent with the rate model (Equation C),
although the extent of the increase is considerably less than might have been expected.
B. Support Material Effects on the Catalytic Properties of Supported Pd Catalysts

Results

Since the selective hydrogenation of unsaturated hydrocarbons on group VIII metals has been extensively investigated over the past forty years, only a small part of this body of work (that dealing with butadiene hydrogenation) has been reviewed in this thesis. The role of support material in the catalytic properties in selective hydrogenation catalysts, in contrast, has received little attention (at least on the academic level). Almost all commercial acetylene/diolefin selective hydrogenation catalysts are Pd supported on alumina (36) with high surface area aluminas seldom used due to their promotion of polymerization reactions (12). This leads one to ask the following questions: Why are low surface area aluminas almost a universal choice for the support? What characteristics of alumina make it a good support? Finally, are there any other suitable supports? It was with these questions in mind that butadiene hydrogenation in the presence of n-butenes was studied using six different palladium catalysts, each with a different support.

The six support materials investigated are alumina, silica, titania, carbon, barium carbonate, and barium sulfate. The supported catalysts were obtained from Engelhard; nominal properties are listed in Table 10. Each catalyst was evaluated to determine its catalytic activity and selectivity both in presence and absence of CO.
Evaluations were made on catalysts which had been aged by reaction and then regenerated.

Table 10. Nominal Catalyst and Support Properties

<table>
<thead>
<tr>
<th>Support</th>
<th>Loading (Pd wt%)</th>
<th>Surface Area (BET, m²/gm)</th>
<th>Mean Particle Size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>5</td>
<td>1600</td>
<td>30</td>
</tr>
<tr>
<td>Alumina</td>
<td>5</td>
<td>125</td>
<td>35</td>
</tr>
<tr>
<td>Barium Carbonate</td>
<td>5</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>5</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>5</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Titania</td>
<td>5</td>
<td>50</td>
<td>na</td>
</tr>
</tbody>
</table>

As a practical matter, carbon is a poor support for an industrial selective hydrogenation catalyst since it is not easy to regenerate (without burning some of the support) and has poor mechanical strength. The carbon supported palladium catalyst used in this study had a nominal surface area of 1600 m²/gm and eggshell metal deposition. The results for 5% Pd/C are given in Table 11.

Alumina, the most common industrial support for selective hydrogenation catalysts, was studied in much greater detail. The alumina support had a surface area of 125 m²/gm which is higher than the alpha aluminas commonly used industrially but lower than gamma aluminas used for reforming catalysts. The amount of isomerization activity that this particular alumina support might display is difficult to estimate not knowing its preparation method. However, samples of the alumina
Table 11. Butadiene Hydrogenation on 5% Pd/C

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Time hr</th>
<th>n-B torr</th>
<th>1-B torr</th>
<th>t-B torr</th>
<th>c-B torr</th>
<th>BD torr</th>
<th>H₂ torr</th>
<th>CO ppm</th>
<th>T/C</th>
<th>Sₐ-B mol/s/gm Pd</th>
<th>kₓ mol/s/gm Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.31</td>
<td>259 nm</td>
<td>nm</td>
<td>26.0</td>
<td>22.5</td>
<td>0.0</td>
<td>3.82</td>
<td>2.5%</td>
<td>3.1E-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.17</td>
<td>0.81</td>
<td>263 7.07</td>
<td>1.85</td>
<td>5.12</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.33</td>
<td>257 nm</td>
<td>nm</td>
<td>25.9</td>
<td>30.7</td>
<td>0.0</td>
<td>2.24</td>
<td>17.3</td>
<td>1.5E-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>4.37</td>
<td>257 10.1</td>
<td>4.51</td>
<td>2.55</td>
<td>3.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>29.9</td>
<td>23.0</td>
<td>0.0</td>
<td>3.82</td>
<td>5.24</td>
<td>8.5E-6</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.94</td>
<td>8.52 5.87</td>
<td>1.54</td>
<td>12.0</td>
<td>5.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>26.1</td>
<td>36.0</td>
<td>0.0</td>
<td>3.24</td>
<td>20.1</td>
<td>7.0E-6</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td>4.08</td>
<td>8.46 8.18</td>
<td>2.52</td>
<td>5.77</td>
<td>7.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>inlet</td>
<td>0.22</td>
<td>260 nm</td>
<td>nm</td>
<td>26.1</td>
<td>35.0</td>
<td>0.0</td>
<td>1.40</td>
<td>24.1</td>
<td>1.5E-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>6.34</td>
<td>237 20.5</td>
<td>14.7</td>
<td>1.02</td>
<td>3.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>363</td>
<td>inlet</td>
<td>0.30</td>
<td>257 nm</td>
<td>nm</td>
<td>25.8</td>
<td>37.1</td>
<td>131</td>
<td>1.54</td>
<td>7.72</td>
<td>3.0E-6</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td>1.769</td>
<td>232 20.5</td>
<td>13.3</td>
<td>6.75</td>
<td>13.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight = 30.7 mgm
Flow Rate 46-47 cc/min.
nm = none detected

Table 12. Butadiene Hydrogenation on 5% Pd/Alumina

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Time hr</th>
<th>n-B torr</th>
<th>1-B torr</th>
<th>t-B torr</th>
<th>c-B torr</th>
<th>BD torr</th>
<th>H₂ torr</th>
<th>CO ppm</th>
<th>T/C</th>
<th>Sₐ-B mol/s/gm Pd</th>
<th>kₓ mol/s/gm Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.32</td>
<td>261 nm</td>
<td>nm</td>
<td>26.2</td>
<td>22.0</td>
<td>0.0</td>
<td>2.21</td>
<td>3.5%</td>
<td>9.7E-6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.93</td>
<td>264 6.20</td>
<td>2.081</td>
<td>8.50</td>
<td>4.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>28.3</td>
<td>22.0</td>
<td>0.0</td>
<td>3.96</td>
<td>1.4%</td>
<td>7.9E-6</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.23</td>
<td>10.6 5.50</td>
<td>1.39</td>
<td>12.2</td>
<td>5.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.36</td>
<td>259 nm</td>
<td>nm</td>
<td>26.1</td>
<td>30.2</td>
<td>0.0</td>
<td>1.09</td>
<td>28%</td>
<td>5.7E-6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>5.45</td>
<td>249 12.5</td>
<td>11.5</td>
<td>7.98</td>
<td>8.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>25.6</td>
<td>32.7</td>
<td>0.0</td>
<td>2.73</td>
<td>25%</td>
<td>6.9E-6</td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>4.77</td>
<td>5.16 9.89</td>
<td>3.63</td>
<td>6.83</td>
<td>7.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>inlet</td>
<td>0.35</td>
<td>256 nm</td>
<td>nm</td>
<td>25.8</td>
<td>33.7</td>
<td>0.0</td>
<td>1.11</td>
<td>29%</td>
<td>1.4E-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.83</td>
<td>194 45.6</td>
<td>410</td>
<td>0.29</td>
<td>3.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>inlet</td>
<td>0.32</td>
<td>253 nm</td>
<td>nm</td>
<td>25.4</td>
<td>36.2</td>
<td>139</td>
<td>1.74</td>
<td>12%</td>
<td>4.1E-6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>2.86</td>
<td>206 44.3</td>
<td>25.4</td>
<td>5.05</td>
<td>10.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>33.2</td>
<td>33.6</td>
<td>0.0</td>
<td>2.12</td>
<td>14%</td>
<td>1.0E-4</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.71</td>
<td>3.60 14.5</td>
<td>6.82</td>
<td>0.33</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>inlet</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>38.4</td>
<td>35.6</td>
<td>124</td>
<td>2.77</td>
<td>1.6%</td>
<td>6.1E-6</td>
</tr>
<tr>
<td></td>
<td>1.83</td>
<td>0.51</td>
<td>10.5 7.60</td>
<td>2.74</td>
<td>7.11</td>
<td>11.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight 31.3 mgm
Flow rate 46-47 cc/min.
nm = none detected
without the palladium were obtained from Engelhard and showed no measurable isomerization activity at either 313K or 433K under reaction conditions similar to those listed in Table 12.

Palladium supported on barium carbonate was studied for two reasons. Barium carbonate is chemically similar to calcium carbonate, which is the support used in making Lindlar catalyst (Pd-Pb/CaCO₃). Secondly, palladium supported on barium sulfate was available from Engelhard allowing a comparison between barium carbonate and sulfate supported catalysts to be made. No information concerning the purity or activity of the support was available. The results of butadiene hydrogenation on palladium supported on barium carbonate are presented in Table 13.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Time</th>
<th>n-B</th>
<th>1-B</th>
<th>t-B</th>
<th>c-B</th>
<th>BD</th>
<th>H₂</th>
<th>CO</th>
<th>T/C</th>
<th>Sₙ-B</th>
<th>kₑp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>hr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>ppm</td>
<td>mol/s</td>
<td>gms Pd</td>
</tr>
<tr>
<td>313</td>
<td>0.32</td>
<td>4.384</td>
<td>237</td>
<td>11.2</td>
<td>11.7</td>
<td>14.9</td>
<td>7.7</td>
<td>0.0</td>
<td>0.95</td>
<td>36%</td>
<td>3.6E-6</td>
</tr>
<tr>
<td>313</td>
<td>3.51</td>
<td>1.67</td>
<td>225</td>
<td>17.1</td>
<td>16.5</td>
<td>14.7</td>
<td>11.4</td>
<td>0.0</td>
<td>2.41</td>
<td>32%</td>
<td>3.2E-6</td>
</tr>
<tr>
<td>313</td>
<td>0.38</td>
<td>8.98</td>
<td>255</td>
<td>28.7</td>
<td>22.9</td>
<td>8.58</td>
<td>0.0</td>
<td>1.04</td>
<td>78%</td>
<td>2.2E-6</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.0</td>
<td>6.63</td>
<td>1.31</td>
<td>30.8</td>
<td>33.3</td>
<td>0.0</td>
<td>1.04</td>
<td>78%</td>
<td>2.2E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.31</td>
<td>11.2</td>
<td>252</td>
<td>36.8</td>
<td>28.9</td>
<td>12.4</td>
<td>10.2</td>
<td>0.0</td>
<td>2.64</td>
<td>47%</td>
<td>2.5E-6</td>
</tr>
<tr>
<td>363</td>
<td>0.30</td>
<td>6.74</td>
<td>203</td>
<td>25.0</td>
<td>36.4</td>
<td>133</td>
<td>1.27</td>
<td>85%</td>
<td>2.7E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>6.74</td>
<td>249</td>
<td>34.1</td>
<td>15.9</td>
<td>18.2</td>
<td>1.17</td>
<td>70%</td>
<td>1.1E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>2.25</td>
<td>2.33</td>
<td>26.4</td>
<td>17.7</td>
<td>21.3</td>
<td>2.18</td>
<td>26%</td>
<td>9.2E-7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight 31.4 mgm
Flow rate 46-48 cc/min.
nm = none detected
Barium sulfate supported palladium was tested primarily to compare with barium carbonate supported palladium. Barium sulfate is not used commercially as a support for palladium selective hydrogenation catalysts; however, it was tested as a comparison with barium carbonate. The results of butadiene hydrogenation on Pd/BaSO$_4$ are presented in Table 14.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Time</th>
<th>n-B</th>
<th>l-B</th>
<th>t-B</th>
<th>c-B</th>
<th>BD</th>
<th>H$_2$</th>
<th>CO</th>
<th>T/C</th>
<th>S$_{n-B}$</th>
<th>k$_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>hr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>torr</td>
<td>ppm</td>
<td></td>
<td>mol/s/gm Pd</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.33</td>
<td>266</td>
<td>nm</td>
<td>nm</td>
<td>26.7</td>
<td>22.6</td>
<td>0.0</td>
<td>6.8%</td>
<td>3.4E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>267</td>
<td>4.78</td>
<td>2.60</td>
<td>14.0</td>
<td>9.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>25.9</td>
<td>22.4</td>
<td>0.0</td>
<td>9.2%</td>
<td>6.7E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.03</td>
<td>7.86</td>
<td>5.94</td>
<td>1.91</td>
<td>12.7</td>
<td>5.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.35</td>
<td>263</td>
<td>nm</td>
<td>nm</td>
<td>26.4</td>
<td>30.4</td>
<td>0.0</td>
<td>69%</td>
<td>2.3E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>223</td>
<td>28.6</td>
<td>21.0</td>
<td>15.0</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>26.7</td>
<td>33.2</td>
<td>0.0</td>
<td>64%</td>
<td>6.4E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>5.87</td>
<td>8.39</td>
<td>3.24</td>
<td>7.50</td>
<td>7.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.35</td>
<td>264</td>
<td>nm</td>
<td>nm</td>
<td>26.5</td>
<td>32.9</td>
<td>0.0</td>
<td>46%</td>
<td>6.4E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>194</td>
<td>49.9</td>
<td>40.2</td>
<td>7.08</td>
<td>6.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.31</td>
<td>264</td>
<td>nm</td>
<td>nm</td>
<td>26.3</td>
<td>34.5</td>
<td>136</td>
<td>0.9%</td>
<td>8.0E-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>262</td>
<td>2.86</td>
<td>0.86</td>
<td>17.8</td>
<td>24.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>25.1</td>
<td>33.8</td>
<td>0.0</td>
<td>21%</td>
<td>1.0E-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>4.36</td>
<td>10.9</td>
<td>4.77</td>
<td>3.90</td>
<td>4.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>30.8</td>
<td>33.9</td>
<td>129</td>
<td>9.9%</td>
<td>3.9E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.42</td>
<td>2.06</td>
<td>5.44</td>
<td>3.50</td>
<td>10.0</td>
<td>12.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight = 30.2 mgm
Flow rate = 45-46 cc/min.
nm = none detected

Pd/silica was, like Pd/alumina, a catalyst of great interest in this study because of its industrial potential. Silicas are generally less active than aluminas (e.g. for butene isomerization) and tend have greater surface areas than aluminas. The vast majority of selective hydrogenation catalysts used in industrial processes cite alumina as the support (36); silica has also been used as a support (71). The results
of butadiene hydrogenation of palladium supported on silica gel are presented in Table 15.

Table 15. Butadiene Hydrogenation of 5% Pd/Silica

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Time hr</th>
<th>n-B torr</th>
<th>l-B nm</th>
<th>t-B torr</th>
<th>c-B nm</th>
<th>BD torr</th>
<th>H₂ torr</th>
<th>CO ppm</th>
<th>T/C</th>
<th>Sₙ-B mol/s/gm Pd</th>
<th>kₑ mol/s/gm Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>1.00</td>
<td>0.32</td>
<td>258</td>
<td>nm</td>
<td>25.9</td>
<td>23.2</td>
<td>6.78</td>
<td>3.73</td>
<td>0.0</td>
<td>5.86</td>
<td>0.4%</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.39</td>
<td>262</td>
<td>6.34</td>
<td>1.08</td>
<td>6.78</td>
<td>3.73</td>
<td>0.0</td>
<td></td>
<td>1.3E-5</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>27.3</td>
<td>22.6</td>
<td>3.89</td>
<td>0.0</td>
<td>5.21</td>
<td>1.8%</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.32</td>
<td>11.1</td>
<td>6.41</td>
<td>1.23</td>
<td>9.60</td>
<td>3.89</td>
<td>0.0</td>
<td></td>
<td>1.2E-5</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.72</td>
<td>0.32</td>
<td>257</td>
<td>nm</td>
<td>25.8</td>
<td>31.8</td>
<td>4.18</td>
<td>7.25</td>
<td>0.0</td>
<td>2.73</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td>2.59</td>
<td>258</td>
<td>8.79</td>
<td>3.22</td>
<td>4.18</td>
<td>7.25</td>
<td>0.0</td>
<td></td>
<td>7.6E-6</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>4.30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>30.1</td>
<td>33.4</td>
<td>4.28</td>
<td>5.87</td>
<td>0.0</td>
<td>2.79</td>
<td>17%</td>
</tr>
<tr>
<td></td>
<td>5.96</td>
<td>10.8</td>
<td>3.87</td>
<td>4.28</td>
<td>5.87</td>
<td>0.0</td>
<td>3.97</td>
<td>0.0</td>
<td></td>
<td>1.1E-5</td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.32</td>
<td>260</td>
<td>nm</td>
<td>26.2</td>
<td>34.1</td>
<td>1.07</td>
<td>3.04</td>
<td>1.62</td>
<td>25%</td>
<td>1.8E-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.66</td>
<td>16.3</td>
<td>10.1</td>
<td>0.67</td>
<td>3.04</td>
<td>1.62</td>
<td>3.04</td>
<td>1.82</td>
<td>25%</td>
<td>1.8E-5</td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.31</td>
<td>258</td>
<td>nm</td>
<td>25.8</td>
<td>36.6</td>
<td>132</td>
<td>4.46</td>
<td>0.1%</td>
<td>1.6E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.47</td>
<td>0.33</td>
<td>254</td>
<td>5.05</td>
<td>1.23</td>
<td>9.60</td>
<td>19.8</td>
<td>4.46</td>
<td>0.1%</td>
<td>1.6E-6</td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight = 30.6 mgm
Flow rate = 45-46 cc/min.
nm = none detected

Palladium supported on titania completes the six supported catalysts studied in this thesis to investigate support effects. Like alumina and silica, titania is a refractory oxide that possesses the physical and mechanical properties necessary to be a good support for noble metal catalysts in industrial reactors. As was discussed in the literature review, titania supported noble metal catalysts have received considerable attention in recent years due to a phenomenon known as Strong Metal Support Interaction (SMSI). The pretreatment conditions required to induce SMSI have been clearly documented, and under the conditions used for experiments in this thesis, SMSI almost certainly does not occur. A sample of the titania support was tested for
catalytic activity: none was observed. The results of butadiene hydrogenation on Pd/titania are given in Table 16.

Table 16. Butadiene Hydrogenation of 5% Pd/Titania

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>Time hr</th>
<th>n-B torr</th>
<th>l-B torr</th>
<th>t-B torr</th>
<th>c-B torr</th>
<th>BD torr</th>
<th>H₂ torr</th>
<th>CO ppm</th>
<th>T/C</th>
<th>S₀-B mcl/s/gm Pd</th>
<th>X_mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>0.32</td>
<td>261</td>
<td>nm</td>
<td>nm</td>
<td>26.1</td>
<td>22.2</td>
<td>0.0</td>
<td>0.0</td>
<td>3.01</td>
<td>1.3%</td>
<td>2.9E-5</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.59</td>
<td>273</td>
<td>7.14</td>
<td>2.36</td>
<td>5.42</td>
<td>1.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>28.2</td>
<td>21.5</td>
<td>0.0</td>
<td></td>
<td>5.13</td>
<td>0.0%</td>
<td>1.7E-5</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.0</td>
<td>12.9</td>
<td>6.18</td>
<td>1.20</td>
<td>9.38</td>
<td>2.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.32</td>
<td>260</td>
<td>nm</td>
<td>nm</td>
<td>25.9</td>
<td>30.5</td>
<td>0.0</td>
<td></td>
<td>1.05</td>
<td>27%</td>
<td>1.8E-5</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td>6.45</td>
<td>265</td>
<td>15.3</td>
<td>14.6</td>
<td>3.58</td>
<td>3.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>29.0</td>
<td>33.6</td>
<td>0.0</td>
<td></td>
<td>2.58</td>
<td>23%</td>
<td>2.3E-5</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>5.89</td>
<td>3.73</td>
<td>12.2</td>
<td>4.71</td>
<td>3.87</td>
<td>2.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.31</td>
<td>262</td>
<td>nm</td>
<td>nm</td>
<td>26.3</td>
<td>33.4</td>
<td>0.0</td>
<td></td>
<td>1.18</td>
<td>35%</td>
<td>4.1E-5</td>
</tr>
<tr>
<td></td>
<td>1.10</td>
<td>8.72</td>
<td>233</td>
<td>28.9</td>
<td>26.3</td>
<td>1.07</td>
<td>1.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.35</td>
<td>258</td>
<td>nm</td>
<td>nm</td>
<td>25.9</td>
<td>35.2</td>
<td>128</td>
<td></td>
<td>1.93</td>
<td>9.3%</td>
<td>2.1E-6</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
<td>1.46</td>
<td>253</td>
<td>14.1</td>
<td>7.30</td>
<td>10.3</td>
<td>16.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>29.5</td>
<td>33.1</td>
<td>0.0</td>
<td></td>
<td>2.27</td>
<td>19%</td>
<td>1.6E-4</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>5.35</td>
<td>2.76</td>
<td>15.5</td>
<td>6.84</td>
<td>0.93</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>28.7</td>
<td>35.0</td>
<td>123</td>
<td></td>
<td>2.17</td>
<td>11%</td>
<td>1.4E-5</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td>2.97</td>
<td>3.47</td>
<td>14.6</td>
<td>6.74</td>
<td>2.80</td>
<td>4.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst weight = 30.0 mgm
Flow rate = 45-46 cc/min.
nm = none detected
Discussion

From Table 11 one can see that 5% Pd/C is fairly selective towards olefin formation under hydrogen deficient (inlet H₂/BD < 1) conditions. The presence or absence of a large excess of 1-butene seems to have little or no effect on either the trans to cis-2-butene ratio or the butane selectivity. As stated previously, butadiene hydrogenation on palladium at temperatures near 40°C typically yields trans/cis ratios greater than eight and possibly as high as twelve (4, 6, 11).

Isomerization of the butenes either on the support or on the metal will, given sufficient time, eventually produce the equilibrium trans/cis ratio of about 3.4 (323K). Carbon does not catalyze the isomerization of n-butenes under the given reaction conditions unless some impurity is present to give it activity. Unfortunately, due to the lack of complete catalyst and support characterization, one cannot rule out the possibility of support activity for n-butene isomerization for this catalyst.

The results of butadiene hydrogenation under conditions of excess hydrogen also support the supposition that some palladium sites are open for butene hydrogenation and isomerization. From Table 11 one observes that increasing the hydrogen to butadiene ratio in the inlet stream increases the rate of butane formation and decreases the trans/cis ratio. The trans/cis ratio is higher in the absence of a large excess of 1-butene. Both of these observations are consistent with butene adsorption and reaction on palladium. The addition of CO was observed to reduce the rate of hydrogenation, both of butadiene and n-butene, but had little effect on the trans/cis ratio. This conclusion is in
agreement with the findings of Furukawa, et al. (10,11) that CO affects hydrogenation to a much greater extent than isomerization.

The results for butadiene hydrogenation of alumina supported palladium are given in Table 12. Butadiene hydrogenation under hydrogen deficient conditions shows a low selectivity for butane both in the presence and absence of a large excess of 1-butene. The trans/cis ratio is about thirty five percent higher (3.96 vs 2.21) when no 1-butene is in the feed stream and is nearly equal to the equilibrium value at the reaction temperature of 313K. With an excess of hydrogen the butane selectivity increases and the trans/cis ratio decreases in both cases. Results of butadiene hydrogenation on Pd/alumina in the presence of CO show the same trends as those seen on Pd/C. Both hydrogenation of butadiene and n-butene were inhibited by the addition of CO with the isomerization being affected to a much smaller extent. The presence of a large excess of 1-butene increased the rate of butene hydrogenation and isomerization.

All of the butadiene hydrogenation experiments (Table 13) using palladium supported on barium carbonate exhibited unacceptably high butane selectivities. The butane selectivity was high under hydrogen deficient conditions and relatively low butadiene conversions. It was high even when using CO. These were rather unexpected results. While barium sulfate supported palladium (Table 14) showed butane selectivities which were a little higher than one might expect under hydrogen deficient conditions, they followed the expected trends of increasing under conditions of hydrogen surplus and of decreasing upon the addition of CO.
When the hydrogen/butadiene ratio in the inlet stream was less than unity, the butane selectivity over Pd/silica was very low. Low alkane selectivity is one of the requirements for a good acetylene/diolefin selective hydrogenation catalyst. The trans/cis ratios were also closer to the values of 8 to 9 reported by previous researchers (4,6). The presence of a large excess of 1-butene seems to make little difference. Under excess hydrogen conditions, as expected, the butane selectivities increased and the trans/cis ratios decreased. The addition of CO had a large effect on both the butane selectivity and trans/cis ratio. Butane selectivity was reduced to near zero and the trans/cis ratio increased by almost a factor of three. A sample of the silica gel support was obtained from Engelhard and tested for catalytic activity. As expected, none was observed.

Low butane selectivities were observed for Pd/titania under hydrogen deficient inlet conditions. Some isomerization is inferred from the lower trans/cis ratio seen in the 1-butene rich case as compared to the 1-butene free (in the feed) case. At higher hydrogen pressure, the selectivities characteristically increase and the trans/cis ratios decrease. While addition of CO produces the expected result of increasing the trans/cis ratios and decreasing the butane selectivities, the extent of these changes is smaller than those observed with some of the other catalysts.

Some variation in the first order rate constant was observed. While a part of the variation may be attributed to catalyst deactivation, most of the variation results from the first order kinetic model not holding over the entire range of reaction conditions. When
comparing rate constants between runs for a given catalyst, one observes that there is good agreement in the rate constants when the butadiene pressure is higher that six torr. Below a butadiene pressure of six torr there is significant deviation in the value of the first order rate constant. The first order rate law, as previously discussed, was not expected to hold at lower butadiene pressures due to the non-linearity of the L-H kinetics.

The butane selectivities for these six supported catalysts were higher than expected, especially under hydrogen deficient conditions. The trans/cis ratios were also quite low compared to previously published work (4,6). Since these were common to all the catalysts tested (varying only in degree), it is convenient to discuss possible causes for these results for all the catalysts as a group rather than to discuss each catalyst separately. In the following analysis I will assume that butene isomerization can occur on either the support or the metal; butene hydrogenation occurs only on the palladium.

In considering possible causes for high butane selectivities, it is useful to consider two separate cases. The first case is the hydrogen deficient one. In previously published work, both Bond, et al. (6) and Meyer and Burwell (4) found the hydrogenation of butadiene to have an olefin selectivity of unity. All three of the refractory oxide supported catalysts gave low butane selectivities under hydrogen deficient conditions. The second case deals with hydrogen in excess of butadiene. Under these conditions, olefin selectivities are less than unity (4). The butane selectivities increased for all six supported catalysts under excess hydrogen conditions, as was expected. However,
the reactors were never operated under conditions where all the butadiene was converted. In all the experiments except those with barium carbonate supported palladium, the butadiene pressure was low enough to suggest that butene could compete with butadiene for adsorption on the palladium. The rate of butadiene diffusion within the pores of the catalyst may also contribute to the increase in butane selectivity under excess hydrogen. However, given that these catalysts were fine powders, it is unlikely that mass transfer limitations are responsible for the butane selectivity increases. Rather, they are simply the consequence of increased butene adsorption and hydrogenation due to lower butadiene pressures.

In discussing possible reasons for the low trans/cis ratios observed in this work, it is convenient to begin with those dealing with support activity for butene isomerization. Of these six supports, they can be divided into three groups: those known to isomerize butene (alumina and titania), those thought not to isomerize butene (carbon and silica), and those whose isomerization properties are unknown (barium carbonate and barium sulfate). Ample literature citations clearly indicate that alumina (53) and titania (56) both isomerize n-butenes. However, when samples of both supports were contacted with the BD/1-B/H₂ reactant stream, neither hydrogenation nor isomerization was observed. But one should not completely discount the possibility of support activity since the metal impregnation method may have altered the support in some manner (eg. Cl⁻) that could have induced some activity for butene isomerization. For example, Wells and Wilson (48) reported that alumina that was inactive for butene isomerization on its own
"actively assisted isomerization" on supported noble metal (Os, Ir, Pt, and Rh) catalysts.

Under the conditions of these experiments one would not normally expect either a carbon or a silica support to have any butene isomerization activity. Webb and MacNab (71) observed the isomerization of 1-butene attributable to the silica in a Rh/silica catalyst due to activity induced by hydrogen spillover. For reasons discussed in the next section, likelihood of induced activity from hydrogen spillover is not great. The carbon and silica supported catalysts had the highest trans/cis ratios of the six catalysts lending weight to the supposition that they (carbon and silica) are inactive for butene isomerization.

As for barium carbonate and barium sulfate, little is known about their isomerization activity. While one or both of them may have some activity, one hesitates to draw any strong conclusions; lacking information on the catalyst and any possible support activity, there is really not much that can be resolved. No samples of the supports by themselves were available for testing.

The second possibility (and the more probable) why the trans/cis ratios are lower than those previously reported (4,6) is related to butene isomerization under conditions of low hydrogen pressure and possibly short contact times. As previously noted, under excess hydrogen conditions butene can compete with butadiene for adsorption on the palladium. When the butadiene pressure was low enough for significant butene adsorption, the hydrogen pressure generally tended to be five torr or lower. Holbrook and Wise (49) have shown that, at low hydrogen pressure (less than 2 torr), the isomerization of 1-butene on
both supported (alumina) and unsupported palladium yields trans/cis ratios less than one. Ragaini, et al. (50) have obtained similar results finding trans/cis ratios less than equilibrium at low hydrogen pressures (how low depends on the contact time) with the ratio tending towards unity (or slightly less than unity) as the hydrogen pressure tends toward zero.

Ragaini, et al. (50) conducted their study at a temperature of 323K using contact times (W/F) of between 7.9 X 10⁻² and 3.4 X 10⁻³ gm Pd-hr/mole 1-butene. Calculations in a like manner from the data in Table 11 show that the contact time of 1-butene is about 3.6 X 10⁻² gm Pd-hr/mole. But if one considers that only ten percent of the Pd sites are available for butene adsorption due to competition with butadiene, one obtains a contact time of 3.6 X 10⁻³ gm Pd-hr/mole, which is slightly shorter than the contact times used by Ragaini, et al. These contact time calculations are only put forth to demonstrate the plausibility of the argument since any proper comparison of these catalysts should be based on the actual number of Pd sites available for isomerization. Thus, trans/cis ratios less than those normally observed (9-11,36) for butadiene hydrogenation in the presence of a large excess of 1-butene can be satisfactorily explained even in the absence of support isomerization activity. In fact, under the proper conditions, one theoretically could obtain a trans/cis ratio from just under unity to about 12 depending on the extent of the butene isomerization and butadiene hydrogenation.

As for Pd/BaCO₃, I am forced to conclude that the unusual catalytic behavior of is probably due either to activity attributable
to the support or to a change in the catalytic properties of palladium induced by the support. I tend to favor the former based on the fact that in the Lindlar catalyst, lead is used to enhance the selectivity of the Pd/CaCO₃ (32). The resulting Pd-Pb/CaCO₃ catalyst is very selective for the hydrogenation of alkyl acetylenes to cis-olefins. The lead may poison any active sites which may exist on the support; however, without catalyst and support characterization this is just speculation.

Before comparisons among the catalysts are made, a few points should be considered. The first point is that 5 wt% Pd catalysts are a poor choice for determining if any support effects might be present. Cost is not the only reason that selective hydrogenation catalysts for industrial use are typically 0.04 wt% Pd; low metal loadings produce more selective hydrogenation catalysts than those with higher loadings. Additionally, high metal loadings are likely to mask whatever differences which may exist among the supports, especially if they are subtle differences. Second, even a well-planned study using catalysts with more realistic metal loadings would require extensive catalyst and support characterization to validate claims attributable to the supports. Finally, even though no catalyst or support characterization was available during this study, there were sufficiently large differences between some of the catalysts that a few conclusions can be drawn.

It is best to view these experiments as support screenings for palladium. In a way they are analogous to the group VIII metal screening experiments conducted by Bond and co-workers during the 1960's using 5 wt% metal supported on alumina. From the results presented in
Tables 11-16, it is clear that barium carbonate and barium sulfate are not good supports for a palladium selective hydrogenation catalyst. Both have butane selectivities higher than the other catalysts under hydrogen deficient conditions; however, it is unlikely that mass transfer limitations could be responsible for all of the butane formation, especially for the two catalysts with low surface areas. It is likely that one (BaCO₃), and perhaps both of these supports may have some activity of their own, but this was not tested.

All three refractory oxides (alumina, silica, and titania) would make good palladium supports. In terms of activity and selectivity the performance of all three catalysts were for all practical purposes the same. I believe that this is simply a result of the metal loading being two orders of magnitude higher than is commonly used in this type of reaction. Perhaps if lower metal loadings had been used, some significant differences would have been observed.

It is important to keep in mind that there are many other factors in addition to selectivity and activity that one would want to consider in selecting a support for a selective palladium hydrogenation catalyst. Does the support affect the aging behavior of the catalyst by promoting or retarding polymerization reactions? How well does the support stabilize the palladium dispersion, and does it prevent sintering upon regeneration? How well does the support adsorb poisons and protect the palladium activity? While important in industrial applications, these are all questions that, at the present time, are not of great academic interest. To quote Bond (61) again, there is "a growing realisation
that the support may frequently play a far more important part in the
total reaction than has usually been imagined in the past."
C. The Role of Hydrogen Spillover in the Selective Hydrogenation of Butadiene in the Presence of 1-Butene

Results

Hydrogen spillover has been an active area of debate in supported metal catalysis since the 1960's (72). It is not a debate over whether hydrogen spillover occurs; over 400 papers on the subject have been published since the phenomenon was first reported. In his review of hydrogen spillover, Bond (61) states,

It has to be admitted at the outset that it is at the same time a phenomenon of wide if not universal occurrence with supported metal catalysts, and one of the least well understood effects in this complex field. Its importance cannot however be over-emphasized. There has for a long time been evidence of a qualitative kind that the catalytic behaviour of a supported metal was not totally independent of the support, even in the case of reactions which were not thought to require a bifunctional catalyst, and even after allowing for differences in metal dispersion.

The case that hydrogen spillover may play in the selective hydrogenation of butadiene in the presence of n-butenes over supported palladium catalysts is set forth in this section.

First let me describe the experiments. The experiments designed to study hydrogen spillover consist of three types. The first is a support only experiment. A support (alumina, silica, or titania) is placed in the reactor and tested for catalytic activity. No palladium is present during a support experiment. The second type of experiment is a supported catalyst experiment. It involves measuring the catalytic activity of a supported metal catalyst (Pd/alumina, Pd/silica, or Pd/titania) under the same conditions as those used to test the support.
The third type of experiment is a mixed catalyst consisting of one part supported metal catalyst (same amount as previously tested) and two parts of the support material. The mixed catalyst is prepared by physically mixing (in a gentle manner) the supported metal catalyst with the support. The mixed catalyst is then measured for catalytic activity under the same conditions as the support and the supported catalyst. If the support showed no activity by itself in the first type of experiment, it should behave simply as a diluent in the mixed catalyst experiment. However, in the event that the supported catalyst and mixed catalyst behave differently, one may be able to attribute the differences to catalytic activity of the support induced by hydrogen spillover. One must hasten to add that hydrogen spillover is not the only phenomenon which can cause such a result.

The results of the experiments designed to test for the signs of hydrogen spillover are presented in Table 17. Although not explicitly stated in the table, none of the support materials were catalytically active by themselves.
Table 17. Result of Hydrogen Spillover Experiments

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Cat.</th>
<th>Sup.</th>
<th>Time</th>
<th>n-B</th>
<th>i-B</th>
<th>t-B</th>
<th>c-B</th>
<th>BD</th>
<th>H₂</th>
<th>S_Hexane</th>
<th>T/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.3</td>
<td>0.0</td>
<td>1.00</td>
<td>204</td>
<td>nm</td>
<td>3.46</td>
<td>nm</td>
<td>0.34</td>
<td>6.29</td>
<td>7.53</td>
<td>3.6%</td>
</tr>
<tr>
<td>2</td>
<td>27.0</td>
<td>50.4</td>
<td>1.00</td>
<td>205</td>
<td>nm</td>
<td>10.7</td>
<td>nm</td>
<td>10.4</td>
<td>10.4</td>
<td>9.48</td>
<td>71%</td>
</tr>
<tr>
<td>3</td>
<td>29.1</td>
<td>0.0</td>
<td>1.00</td>
<td>244</td>
<td>nm</td>
<td>13.8</td>
<td>nm</td>
<td>19.3</td>
<td>6.11</td>
<td>2.57</td>
<td>12%</td>
</tr>
<tr>
<td>4</td>
<td>26.1</td>
<td>52.2</td>
<td>1.00</td>
<td>241</td>
<td>nm</td>
<td>24.2</td>
<td>nm</td>
<td>21.6</td>
<td>9.10</td>
<td>3.48</td>
<td>35%</td>
</tr>
<tr>
<td>5</td>
<td>27.9</td>
<td>55.0</td>
<td>1.00</td>
<td>248</td>
<td>nm</td>
<td>25.0</td>
<td>nm</td>
<td>20.6</td>
<td>3.64</td>
<td>5.14</td>
<td>60%</td>
</tr>
<tr>
<td>6</td>
<td>28.7</td>
<td>0.0</td>
<td>1.00</td>
<td>243</td>
<td>nm</td>
<td>24.6</td>
<td>19.3</td>
<td>19.3</td>
<td>6.26</td>
<td>38%</td>
<td>1.00</td>
</tr>
<tr>
<td>7</td>
<td>27.8</td>
<td>56.7</td>
<td>1.00</td>
<td>241</td>
<td>nm</td>
<td>24.5</td>
<td>19.3</td>
<td>10.5</td>
<td>6.86</td>
<td>24%</td>
<td>0.95</td>
</tr>
<tr>
<td>8</td>
<td>28.0</td>
<td>50.9</td>
<td>1.00</td>
<td>263</td>
<td>nm</td>
<td>24.9</td>
<td>19.3</td>
<td>10.5</td>
<td>6.86</td>
<td>24%</td>
<td>0.95</td>
</tr>
<tr>
<td>9</td>
<td>28.2</td>
<td>53.1</td>
<td>1.00</td>
<td>266</td>
<td>nm</td>
<td>26.8</td>
<td>nm</td>
<td>20.8</td>
<td>6.82</td>
<td>5.96</td>
<td>4.6%</td>
</tr>
<tr>
<td>10</td>
<td>27.8</td>
<td>54.5</td>
<td>1.00</td>
<td>260</td>
<td>nm</td>
<td>26.1</td>
<td>nm</td>
<td>19.9</td>
<td>6.85</td>
<td>10%</td>
<td>0.71</td>
</tr>
<tr>
<td>11</td>
<td>29.9</td>
<td>56.5</td>
<td>1.00</td>
<td>263</td>
<td>nm</td>
<td>26.3</td>
<td>18.0</td>
<td>19.9</td>
<td>20.9</td>
<td>6.85</td>
<td>10%</td>
</tr>
<tr>
<td>12</td>
<td>27.8</td>
<td>54.0</td>
<td>1.00</td>
<td>264</td>
<td>nm</td>
<td>26.6</td>
<td>15.6</td>
<td>15.6</td>
<td>4.90</td>
<td>71%</td>
<td>0.76</td>
</tr>
</tbody>
</table>

nm = none measured
Reactions Temperature = 313K
Flow rate = 46 cc/min.
A = alumina, S = silica, and T = titania
* = Hydrocarbons introduced 1 minute before hydrogen
** = Hydrogen introduced 1 minute before hydrocarbons
Discussion

Generally, it is much easier to see the effects that "spillover" hydrogen produces than it is to observe spillover hydrogen directly. The evidence for the occurrence of hydrogen spillover presented in this thesis is qualitative in nature. For this reason in discussing the results of this present work it is useful to discuss the conditions under which hydrogen spillover is likely to occur and what one might expect to observe if spillover does occur.

The three obvious conditions for hydrogen spillover are a source (group VII metal), an acceptor (the support), and hydrogen. Several factors influence hydrogen spillover. Conner, et al. (72) list the following factors:

The range of the temperatures of hydrogen adsorption (below room temperature or significantly above); the possible necessity of a co-catalyst such as water or other proton acceptor; the amount and the percentage dispersion of the source of hydrogen spillover; the nature of the contact between the source and the acceptor; the specific areas of the coupled source-acceptor; the possibility of migration through the gas phase and not exclusively on the surface; the role of the partial pressures of \( \text{H}_2 \); the strength of the bond between spillover hydrogen and acceptor sites; the chemical nature of the acceptor and source; the presence of chlorine and sulfur ions; the duration of chemisorption; the effects of \( \text{O}_2 \) and \( \text{CO} \); and the nature of the spillover hydrogen.

Among this long list of factors affecting hydrogen spillover, several stand out and may have bearing on this thesis. The reduction temperature seems to be fairly important. Most studies of group VIII metal supported on alumina or silica use a reduction temperature in excess of 430°C (61,72). A temperature of 430°C or higher insures that the alumina or silica is fully demethoxylated. The demethoxylation and
induction of catalytic activity on the support are not very fast processes and require as much as 12 hours at 760 torr hydrogen at 430°C (72). The type of metal also affects the temperature at which spillover occurs. With Ni, spillover occurs on alumina at 300°C but not at 430°C, whereas Pt give exactly the opposite behavior (61,72). In this work, the supported palladium catalyst were reduced at 275°C for two hours before being cooled to the reaction temperature of 40°C.

Other factors such as the presence of oxygen and water may also have some importance to this work. The microreactor system used in this thesis was not capable of holding (or even achieving) the kinds of vacuums normally used (10⁻⁵ torr or better) by others in hydrogen spillover experiments. Given that oxygen might be present, one can also assume that the catalyst might be exposed to water during reduction of any oxides that might be formed. Although the effects of oxygen and water on hydrogen spillover are not well understood, it has been reported that oxygen and water that could be formed from the oxygen are detrimental to hydrogen spillover, while water by itself is either a promoter or has no effect (72).

Experiments very much like the ones described in this thesis have been done for ethylene and benzene hydrogenation. Carter, et al. (62) found that diluting Pt-SiO₂ with alumina increased the rate of ethylene hydrogenation by about a factor of twenty (see Table 4., page 44). Using Pd/alumina, Sancier (63) saw an increase in benzene hydrogenation of three times at a dilution (alumina) of 1:200 or more (see Table 5, page 45). Both Carter and Sancier concluded that the increases in catalytic activity were due to support activity induced by hydrogen
spillover. However, these conclusions were challenged by others who were unable to reproduce their results, ethylene by Schlatter and Boudart (64) and benzene by Vannice and Neikam (65). To this day the conflict has not been resolved. In other studies under different conditions, Teichner and co-workers (72) observed ethylene and acetylene hydrogenation on silica activated by hydrogen spillover. Webb and MacNab (72) have observed the isomerization of 1-butene attributable to the silica in a Rh/silica catalyst, the silica having been activated by spillover hydrogen.

The hydrogen spillover experiments presented in this thesis were modeled along the lines of Carter, et al. (62) and Sancier (63) but with one important difference. In this work, mixtures of 1-butene, 1,3-butadiene, and hydrogen were passed over the catalyst or support, whereas both of the other studies used only a single hydrocarbon. By using two hydrocarbons additional chemistry comes into play. Three reactions can occur in the butadiene/1-butene system: namely, butadiene hydrogenation, butene hydrogenation, and butene isomerization. As long as the experiments are conducted in a kinetically controlled regime (i.e. no diffusional limitations) and under high enough butadiene pressures where one can be fairly certain that butadiene prevents the butene from adsorbing on the palladium, any isomerization must then come from the support. It also follows that the amount of butene hydrogenation from the palladium should be small. If a large amount of butane is formed then, either our assumptions about diffusion and/or butene adsorption are wrong or the support is active for butene hydrogenation. This conclusion is based on the assumption that the
support may become active for either butene isomerization, butene hydrogenation, or both.

Experiments 1, 2, and 5 would seem to present clear cases of hydrogen spillover induced support activity. The dilution of the palladium-silica catalyst with silica or alumina caused a dramatic increase in both butene isomerization and hydrogenation.

In experiment 1 there is no evidence of diffusional limitation; in fact, the catalyst behaved very much like the aged palladium/silica catalyst discussed in the previous section. One possible reason for the increase in activity is that the added silica or alumina serves as a scavenger for palladium poisons. This is the explanation put forth by Schlatter and Boudart (64) to account for the results of Carter and co-workers (62). But would a more active palladium explain the high butane selectivity and low trans/cis ratio? In comparing the results in Table 15 for the aged palladium-silica catalyst, it is difficult to imagine that the differences in catalytic behavior are solely due to diffusional effects. Diffusional effects might be seen if the catalytic activity is significantly increased (because the palladium sites are no longer being poisoned). But diffusion is deemed unlikely in a powdered catalyst such as this one. If the palladium activity increases and there are no diffusional limitations, then one would expect to see higher butadiene conversions. However, lower butadiene conversions were observed in experiments 2 and 5. Butene competition with butadiene on the palladium also provides an unsatisfactory explanation for these results, since the butadiene concentration in the reactor was higher in experiments 2 and 5.
than it was in experiment 1. Thus, poison scavenging by the support would not satisfactorily account for the observed differences.

While experiments 3 and 4 present a much weaker case, the support does show some increase in hydrogenation activity but none in isomerization. The increase in hydrogenation activity may be within the limits of experimental error, however.

Experiments 6 through 12 demonstrate some of the experimental difficulties involved with these experiments (vide infra). That reproducibility was a large problem can be seen by comparing experiments 8 and 12. A comparison of experiments 10-12 with experiments 6-9 would lead one to believe that there is a real increase in both butene hydrogenation and isomerization activity. This appears to be limited evidence of support activity induced by hydrogen spillover.

The results presented in Table 17 fail to resolve clearly the conflicting results raised by the work of Carter, et al. (62), Sancier (63), Schlatter and Boudart (64), and Vannice and Neikam (65). While there is some evidence that support activity was induced by hydrogen spillover, there is no way to exclude the possibility that the activity increase was not the result of poison scavenging by the added support. In any case, I am convinced that the evidence for at least limited spillover effects is strong enough to warrant further investigation under more controlled conditions than were possible in this laboratory.

As for the problems with reproducibility, several comments should be made. The amount of hydrogen spillover appears to depend in a very sensitive way on the degree of hydroxylation of the support (61). In all our experiments reduction was carried out at 275°C, which is well
below the reduction temperature of 430°C where demethoxylation occurs. It is thus impossible to know how much hydroxylation (which requires even higher temperatures than demethoxylation) had taken place on the alumina or silica and whether or not it varied from experiment to experiment. This could explain why increased activity was seen in some cases but not in others. It is also interesting to note that Sancier (63) reduced his catalysts at 200°C and claimed to have evidence of hydrogen spillover. The method of admitting the reactants to a pretreated catalyst also was seen to have a strong impact on the performance. Leading with hydrogen before hydrocarbons produced results consistent with what one would expect for hydrogen spillover (however, the increases in butene hydrogenation and isomerization rates may also be due to higher activity as a result of lower initial rates of coking). On the other hand, leading with the hydrocarbons before the hydrogen gave no indication of hydrogen spillover. Thus, it is very clear that the surface structure of the support plays a very important role in hydrogen spillover phenomena (as was already known) and warrants further investigation.
D. Catalyst Aging

Results

Catalyst deactivation is a common problem in the selective hydrogenation of acetylenes and diolefins (29,38). Even in the absence of any poisons (S, metals, etc.), palladium catalysts undergo deactivation due to the build-up of surface oligomers (35,38). In industrial reactors, selective butadiene hydrogenation is carried out in the liquid phase. This tends to minimize the build-up of surface oligomers due to the solvent action of the liquid hydrocarbons (29,38). Many published gas phase butadiene hydrogenation studies (4,6) have not reported catalyst deactivation; but since these studies were concerned with reaction mechanisms, catalyst deactivation may not have been a concern. Since part of this thesis is concerned with the kinetics of selective butadiene hydrogenation, changes in the activity and selectivity of a 0.5% Pd/AT-2 (palladium on a 90 m²/gm alumina, 1/8" pellet) catalyst as a result of aging were studied.

The aging experiments were conducted under CSTR conditions and lasted between two and three days. The results of two nearly identical experiments are shown in Figures 13 and 14. The nominal feed composition for both experiments was 106 to 112 torr 1-butene, 10.4 to 10.9 torr butadiene, 16 to 17 torr hydrogen, with the balance being nitrogen. The feed rate was 47 to 48 cc/min at ambient temperature. Since experiments by LeViness (35) on acetylene selective hydrogenation had shown that the greatest changes in catalytic behavior occur in the early stages of the reaction, our study concentrated on this region.
The experiments were continued until clear trends developed (pseudo steady-state behavior) and were then terminated. LeViness has also shown that complete deactivation may take up to several weeks after the pseudo steady-state period is established. Both aging experiments were terminated at approximately 50 percent butadiene conversion.

Figure 13. Aging Behavior During Selective Butadiene Hydrogenation (Experiment A)
Figure 14. Aging Behavior During Selective Butadiene Hydrogenation (Experiment B)
Discussion

In both aging experiments the trans/cis ratio was initially less than unity and increased as the catalyst aged, reaching an approximate value of two (2.25 (A), 2.00 (B)) by the time the reaction was terminated. LeViness (35) observed similar trends in the trans/cis ratio of 2-butene formed during the selective hydrogenation of acetylene. Both the 2-butene and the butane selectivity declined during catalyst aging.

Although the alumina support was not tested for isomerization activity, it is unlikely that the butene isomerization occurred to large extent on the alumina. Rather, the observed changes in trans/cis ratios, 2-butene selectivity, and butane selectivity are consistent with butene isomerization and hydrogenation on palladium. During the early stages of these experiments both the butadiene and hydrogen pressures were below four torr. At these butadiene pressures, one would expect butene to compete with butadiene for adsorption sites. In addition, with the low hydrogen pressures the isomerization of 1-butene is likely to yield low trans/cis ratios (49,50). As the catalyst deactivates, the butadiene pressure rises, causing a decrease in butene adsorption. The decrease in butene adsorption in turn produces a decrease in the 2-butene and butane selectivity. An increase in the trans/cis ratio also occurs because a greater percentage of the 2-butene is produced by butadiene hydrogenation.

Although this catalyst was not characterized, it appeared that the depth of metal impregnation was rather small. When a spent pellet was broken in half, the exterior of the pellet was black while the interior
of the pellet was off-white. The black exterior was assumed to result from hydrocarbon deposits on and around the metal. Given this observation and the fact that butane selectivity was relatively low, I do not believe that intraparticle diffusion was a significant factor in either of these two experiments.

Furukawa, et al. (9) have studied the aging behavior of a Pd/alumina catalyst used for the selective hydrogenation of butadiene in the presence of 1-butene in the liquid phase. They observed no change in activity or selectivity in a run lasting 480 hours. The authors further state that in a commercial plant the life of the catalyst (before regeneration) was between 1 and 2 years, depending on the butadiene concentration in the feed stream. Similar results were reported by other industrial researchers for liquid phase selective hydrogenation of butadiene (29,38). The fact that selective hydrogenation catalysts age at a much faster rate under vapor phase operation than they do under liquid phase operation makes it doubtful whether a comparison of aging phenomena between the two phases is really meaningful.
E. Labeled 1-Butene Studies

Results

The use of isotopic tracers has, for many years, proven to be a powerful method for gaining information in complex reactions. In this thesis, experiments using 1-butene-4-$\text{C}^{13}$ were conducted to answer two questions. Which butene(s) are the source of n-butane? Are isotopic tracer methods useful in detecting the effects of hydrogen spillover?

Batch experiments (near atmospheric pressure) were conducted using an approximate reactor charge of 50 torr 1,3-butadiene, 50 torr labeled 1-butene-4-$\text{C}^{13}$, and 100 torr hydrogen with the balance nitrogen. A 0.02% Pd/AT-2 catalyst with eggshell metal deposition was used in an experiment to determine the source or sources of n-butane. To test if tracer methods may be useful in detecting induced support activity caused by spillover hydrogen, a mixed catalyst (5% Pd/AP-21 and AP-21, 1:2) was used.

Figure 15 shows the hydrocarbon product distribution for the experiment on the 0.02% Pd/AT-2 catalyst. The n-butene distributions are shown in Figures 16 and 17. Figure 16 gives information on those butenes coming primarily from butadiene hydrogenation, whereas Figure 17 displays data on butenes mostly resulting from 1-butene-4-$\text{C}^{13}$ isomerization. The isotopic composition of the n-butane indicated that approximately 45 percent had come from unlabeled butenes, conclusively demonstrating that butane is formed from both 1- and 2-butene hydrogenation.
Figure 15. Hydrocarbon Distribution for Labeled 1-Butene Experiment Using 0.02% Pd/AT-2 Catalyst

Figure 16. Butene (56) Distribution for Labeled 1-Butene Experiment Using 0.02% Pd/AT-2 Catalyst
Figure 17. Butene (57) Distribution for Labeled 1-Butene Experiment Using 0.02% Pd/AT-2 Catalyst

The experiment to test tracer methods as technique for investigating the effects of hydrogen spillover was a failure. There was no evidence of hydrogen spillover. However, this experiment on a 5% Pd/AP-21 catalyst does support the findings of the previous labeled experiment. Figure 18 gives the hydrocarbon distributions as a function of time for this experiment. Figures 19 and 20 show the butene distributions of butene (56) and butene (57), respectively.
Figure 18. Hydrocarbon Distribution for Labeled 1-Butene Experiment Using 5% Pd/AP-21 Catalyst

Figure 19. Butene (56) Distribution for Labeled 1-Butene Experiment Using 5% Pd/AP-21 Catalyst
Figure 20. Butene (57) Distribution for Labeled 1-Butene Experiment Using 5% Pd/AP-21 Catalyst
Discussion

These two labeled experiments add significantly to the understanding of selective butadiene hydrogenation in the presence of a large excess of n-butenes (primarily 1-butene). They provide information on the source of n-butane formation, on the intrinsic selectivity of butadiene hydrogenation on palladium, and on the selectivity of 1-butene isomerization of two supported palladium catalysts of very different metal loadings.

The source of n-butane has been an unresolved question in selective butadiene hydrogenation. Pradier, et al. (17), from studies of butadiene hydrogenation on Pt(100), have claimed that n-butane comes from the hydrogenation of 1-butene. Boitiaux and co-workers (21) have cited c-2-butene as the source of n-butane formation on supported palladium catalysts. However, neither of these studies used labeled compounds but instead drew their conclusions on consecutive reaction schemes.

From the isotopic compositions of butane and each butene, it was clear that butane was formed from both 1-butene and 2-butene. In Figure 15 one observes that significant production of butane did not occur until almost all of the butadiene was consumed. Given that 45% of the butane was unlabeled, there is no way it could have come from either 1-butene or 2-butenes alone. At 250 hours, when the butane concentration became high enough that samples could be isotopically analyzed, the unlabeled fractions of the butenes were: 1-butene, 27%, t-2-butene, 85%, and c-2-butene, 64%. Thus it is clear that butane must come from both 1- and 2-butenes.
However, it should be pointed out that from the total product distribution (Figure 15) it appears that the butane comes from 1-butene. The percentage of 1-butene is decreasing as the percentages of butane, t-2-butene, and c-2-butene are all increasing. This simply means that the rate of 1-butene isomerization is faster than the rate of butene hydrogenation. Without labeled experiments one may be mislead into drawing an incorrect conclusion.

Throughout much of this thesis attention has been drawn to the fact that the observed trans/cis ratios were considerably lower than those found by other researchers in gas phase hydrogenation (4,6). Both of these labeled experiments shed light on this matter. Figures 16 and 19 show that the trans/cis ratios of 2-butenes formed by butadiene hydrogenation are much higher than the trans/cis ratio of all 2-butenes (Figures 15 and 18). While the maximum trans/cis ratio observed (about 5) was smaller than those reported by Bond, et al. (6), 9.7 and Meyer and Burwell (4), 11, they confirm that the hydrogenation of butadiene on these catalysts is significantly more trans selective than one would be led to believe just looking at the overall trans/cis ratios. The fact that the trans/cis ratios are lower than other reported values is likely the result of isomerization rather than any variation in the selectivity of butadiene hydrogenation on palladium.

Finally, our labeled experiments provide some information about the isomerization of 1-butene to 2-butene on these two supported palladium catalysts. In both labeled experiments, the trans/cis ratios of the 2-butenes coming predominately from 1-butene isomerization are near unity. From Figure 20 it is evident that the trans/cis ratio from
1-butene isomerization does not significant depart from unity until the butadiene is nearly consumed. As has been discussed in this thesis, a low trans/cis ratio might come from either isomerization on the alumina support or from isomerization on the palladium with short contact times. In a batch experiment such as this, short contact times would be analogous to low butene turnover frequency. As reported in a previous section, the AP-21 catalyst was tested for activity; none was observed. A sample of the AT-2 support was unavailable for testing. There is no way to exclude with a high degree of certainty either of these possibilities. Without complete catalyst characterization, one cannot exclude the possibility that some contaminant like Cl- might be present on the supported metal catalyst and not present on the support. However, if these trans/cis ratios near unity are the result of 1-butene isomerization on palladium (with the extent of isomerization rather low), this helps to explain why low trans/cis ratios were sometimes observed even on catalysts like Pd/silica (Table 14) and Pd/C (Table 10), whose supports are unlikely to isomerize butenes.
CHAPTER V

SUMMARY

In this thesis several questions concerning the selective hydrogenation of 1,3-butadiene in the presence of n-butenes over supported palladium catalysts have been investigated. These questions dealt with the kinetics of butadiene hydrogenation both in the presence and absence of CO; what roles hydrogen spillover and the support might play in the behavior of a selective hydrogenation catalyst; and the catalyst's aging behavior.

The vapor phase kinetics of butadiene hydrogenation were studied in a CSTR using a 0.02% Pd/alumina catalyst. Although the rate of butadiene hydrogenation was independent of butadiene pressure above a minimum butadiene pressure, it varied linearly with the hydrogen pressure. Using a power law model for the rate of butadiene hydrogenation, the observed activation energy was $13.3 \pm 0.8$ kcal/mole.

Using the same catalyst, the hydrogenation kinetics of butadiene in the presence of 40 ppm of CO were measured. Carbon monoxide did not affect the reaction order for either hydrogen or butadiene at this concentration. Its primary effect was to reduce the rate of butadiene hydrogenation. Applying the same power law model for the rate of butadiene hydrogenation as was used in the absence of CO, the activation energy was $15.5 \pm 0.5$ kcal/mole in the presence of 40 ppm CO, or about 2 kcal/mole higher than that observed in the absence of CO.
The manner in which CO altered the kinetic expression for butadiene hydrogenation was examined. From the onset it was clear that CO must compete with hydrogen for adsorption (competition with a zero order reactant like butadiene would be unlikely to decrease the rate). Over the range of 25 to 145 ppm CO, the rate of butadiene hydrogenation depends on the CO pressure to the minus one half power.

The catalytic properties of six supported palladium catalysts were investigated to determine if the catalytic behavior significantly depended on the support material. The six supports examined were activated carbon, alumina, barium carbonate, barium sulfate, silica gel, and titania. Experiments were conducted under CSTR conditions using catalysts with five weight percent palladium loading. There were only slight differences in the amount of isomerization and hydrogenation between experiments with and without a large excess of 1-butene. Of course those experiments without any 1-butene in the feed stream exhibited smaller degrees of butene isomerization and hydrogenation, as would be expected. The addition of CO had a large negative effect on the rate of hydrogenation of both butadiene and n-butenes, but had only a small effect on butene isomerization.

The hydrogen to butadiene ratio in the feed stream also had a strong effect. In almost all cases, experiments carried out under hydrogen deficient condition exhibited lower butane selectivities and higher trans/cis ratios. Lower than expected trans/cis ratios are believed to be caused by butene isomerization on palladium rather than on the supports. Three of the supports (alumina, silica, and titania) were tested for catalytic activity; all were negative. If the
isomerization is associated with the support, the hydrogen pressure should have little effect; however, increasing the hydrogen pressure was in many cases seen to increase significantly the amount of isomerization as well as the trans/cis ratio. But, since complete catalyst characterization was unavailable, one cannot rule out that some of the supported Pd catalysts may have had supports which were active for butene isomerization.

The alumina, silica, and titania supported palladium catalysts exhibited roughly the same catalytic behavior. All three were good selective hydrogenation catalysts. Lower metal loadings would have been more appropriate for this type of study. The barium carbonate and barium sulfate supported catalysts were definitely inferior to those supported on the refractory oxides. Support activity may be responsible for their poor performance.

The role that hydrogen spillover might play in decreasing the olefin selectivity of an acetylene/diolefin selective hydrogenation catalyst was largely left unanswered. In several experiments using a Pd/silica catalyst it appeared that spillover hydrogen activated both alumina and silica supports which were acting as diluents. Neither of these supports had any activity on their own. Results with Pd/alumina were not perfectly reproducible. Starting the experiment under flowing hydrogen improved the reproducibility of the results. However, the evidence of hydrogen spillover was weaker than for Pd/silica. Although these were hardly conclusive results of hydrogen spillover induced support activity, they do imply that under more controlled conditions such an effect might be observed.
The aging behavior of a 0.5% palladium/alumina catalyst was studied to determine how the activity and selectivity vary as the catalyst deactivates. The greatest changes in activity and selectivity were observed in the first ten hours of the reaction after which the changes were gradual. Butane and 2-butene selectivities decreased as the catalyst ages. This decrease is due to the catalyst deactivating, which produces higher butadiene pressures, thereby reducing butene adsorption. The trans/cis ratio increase as the catalyst aged. High trans/cis ratios are seen because a higher fraction of the 2-butenes are being produced from butadiene hydrogenation rather than by 1-butene isomerization.

It is unclear if further gas phase studies of catalyst aging during butadiene hydrogenation are warranted. The aging behavior differs to such a great extent from that seen in liquid phase hydrogenations that it may have little practical use.

Labeled $^{13}$C 1-butene studies have shown that n-butane is formed from both 1- and 2-butenes. They have demonstrated that all three reactions, butadiene hydrogenation, butene isomerization, and butene hydrogenation occur simultaneously over this catalyst and that the observed selectivities actually reflect the combination of several reactions. This indicates that in study of selective hydrogenation, isotopic labeling is an indispensable method in decoupling the effects of several competing reactions.
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Studying the gas phase kinetics of butadiene hydrogenation at low to moderate conversions is not particularly difficult, once one is able to account for deactivation. However, studying butadiene hydrogenation at high butadiene conversions is a difficult matter because first order kinetics no longer hold and butene isomerization and hydrogenation are significant. It may be possible to overcome these difficulties by using labeled reactants.

To this author's knowledge there have been no liquid phase hydrogenation studies of butadiene selective hydrogenation at the academic level. Although at ambient temperatures these hydrocarbons will liquefy at pressures slightly above two atmospheres, it would probably be desirable to conduct liquid phase hydrogenations using a non-volatile solvent like n-decane. The butadiene, butenes, and hydrogen could be bubbled though the solvent using a spinning basket reactor. Such an experiment would allow one to measure the kinetics under more realistic conditions. One also may obtain information about the rate of oligomerization from liquid phase operation. By analyzing the solvent phase, one could monitor the rate of oligomerization and possibly relate it to changes in the catalytic behavior.

Results obtained with catalysts containing 5% metal loadings to test for possible differences in catalytic behavior attributable to the support proved to be of limited value. The metal loading was too high
to discern any differences between alumina, silica, and titania supported palladium; perhaps if lower loadings had been available some differences may have appeared. Since these differences may be small, this type of experiment should not be attempted again unless full catalyst characterization can be accomplished. It is my belief that studying bi-metallic selective hydrogenation catalysts would be more productive.

Further investigation of hydrogen spillover phenomena in selective hydrogenation reactions should be carried out. Although the results in this thesis were not conclusive, they do suggest that if more controlled conditions were used, questions concerning any support activity for olefin hydrogenation or isomerization could be resolved. Support activity induced by spillover hydrogen would be undesirable in a selective hydrogenation catalyst but may be very useful in catalysts with considerable amounts of coking, e.g. reforming catalysts.

Further study of selective butadiene hydrogenation in the vapor phase might also include some optimization of the reaction conditions. The space velocity and butadiene/1-butene ratio in the feed are good starting points. Additionally, the method of initiating the reaction should be examined. The present equipment could have a vent added to the feed line so that the feed stream can be vented for several minutes prior to starting the reaction. Finally, the apparatus should be computer controlled. Computer control of the present equipment would be neither difficult nor costly and would improve reproducibility and productivity.
CHAPTER VII

LITERATURE CITED

2. Boitiaux, J. P., Cosyns, J., Derrien, M., and Leger, G.,
   (1963).
12. Boitiaux, J. P., Cosyns, J., and Vasudevan, S., Preparation of
    Catalysts III: Proceedings of the 3rd Int. Symp. on the
    Scientific Bases for the Preparation of Heterogeneous Catalysts,


CHAPTER VIII

APPENDICES

A. Calculation of Thiele Modulus for 0.5% Pd/AT-9 Catalyst

The nominal properties of the catalyst are:
- pellet density $= \text{den}_p = 1.411 \text{ gm/cc}$
- surface area $= S_A = 4 \text{ m}^2/\text{gm}$
- pellet radius $= r_{\text{pellet}} = 0.16 \text{ cm}$
- pore radius $= r_{\text{pore}} = 600 \text{ Å}$

The following assumptions were made:
- Effective diffusion $= D_{\text{eff}} = 0.3 \text{ cm}^2/\text{s}$
- Observed pseudohomogeneous rate constant $= k_{h, \text{obs}} = 4.9 \text{ s}^{-1}$
- Effectiveness factor $= \text{EF} = 1$

The value of $k_{h, \text{obs}}$ was the value measured on the 0.02% Pd/AT-2 catalyst. Although these catalysts are likely to have different dispersions, it is not an unreasonable estimate. Estimating the effectiveness factor to be unity is conservative, since such a value implies no diffusional limitations. The actual value lies between zero and one.

The rate constant based on the volume of the catalyst, $k_{\text{v, c}}$, is calculated from the following equation, taking the reactor volume to be 200 cc (giving a catalyst bed density, $\text{den}_b$, of 0.005 gm/cc).
\[ k_{vc} = \frac{(k_{h, obs}) \cdot (\text{den}_p)}{(E.F.) \cdot (\text{den}_b)} \]

One obtains a value for \( k_{vc} \) of 1390 s\(^{-1}\)

There is now sufficient information to calculate the Thiele Modulus, \( O_s \).

\[ O_s = \left[ \frac{r_{pellet}}{(k_{vc}) \cdot (D_{eff})} \right]^{0.5} \]

The value of the Thiele Modulus is calculated to be 10.8. A Thiele modulus greater than unity indicates diffusional limitations. This calculation is consistent with the experimental observation that this catalyst was diffusonally limiting under the reaction conditions used.
B. Sample Results from the Gas Chromatograph and Mass Spectrometer

Gas Chromatograph - Typical Hydrocarbon Results

<table>
<thead>
<tr>
<th>RT</th>
<th>AREA TYPE</th>
<th>CAL#</th>
<th>AMOUNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.55</td>
<td>44707</td>
<td>PB</td>
<td>24.086</td>
</tr>
<tr>
<td>7.25</td>
<td>51105</td>
<td>PE</td>
<td>0.293</td>
</tr>
<tr>
<td>8.91</td>
<td>4.0857E+07</td>
<td>SBB</td>
<td>236.130</td>
</tr>
<tr>
<td>10.36</td>
<td>627620</td>
<td>TBB</td>
<td>3.593</td>
</tr>
<tr>
<td>11.50</td>
<td>327288</td>
<td>BB</td>
<td>1.888</td>
</tr>
<tr>
<td>13.89</td>
<td>998230</td>
<td>PE</td>
<td>5.699</td>
</tr>
</tbody>
</table>

TOTAL AREA = 4.2986E+07
MUL FACTOR = 1.00000E+08
Gas Chromatograph - Typical Hydrogen Results

RUN # 173       JAN/20/89  13:44:02
ESTD
RT      AREA TYPE  CAL#     AMOUNT
3.25     354080  PB  1      19.254

TOTAL AREA= 354080
MUL FACTOR= 1.0000E+00
Mass Spectrometer - n-Butane
Mass Spectrometer - $^{13}$C labeled 1-Butene
Mass Spectrometer - t-2-Butene
Mass Spectrometer - c-2-Butene
Mass Spectrometer - 1,3-Butadiene