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Yeung Ho Park
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A study on the effects of additives on selective hydrogenation of trace acetylene over palladium catalysts

Park, Yeung Ho, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1991
A Study on the Effects of Additives on Selective Hydrogenation of Trace Acetylene over Palladium Catalysts

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in
The Department of Chemical Engineering

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Abstract

The effects of both carbon monoxide (as a gas phase additive) and potassium (as a catalyst additive) on the selective hydrogenation of acetylene over Pd/Al2O3 was studied by deuterium tracer experiments combined with Kemball's steady-state treatment and temperature programmed reaction (TPR). The TPR of acetylene and ethylene in hydrogen, which was attempted in this study for the first time, enabled the investigation of the behavior of the adsorbed species on Pd.

CO addition to the reaction mixture significantly increased the probability of ethylene desorption during ethylene deuteration while minor effects due to CO displacement of hydrogen were observed for acetylene deuteration. In the case of selective removal of trace acetylene from ethylene streams, results suggest that CO blockage of H₂ adsorption sites is less important than CO displacement of ethylene in improving the overall selectivity of the industrial process.

In acetylene TPR, preadsorbed CO induced changes in oligomer yields, delayed desorption of oligomers and suppressed self-hydrogenation during the adsorption of acetylene. These results indicate that CO blocks the adsorption sites which accommodate acetylene and the hydrogen product from acetylene dissociation to result in the suppression of initiation and propagation reactions for oligomers.

Potassium doped catalysts yielded an enhancement in acetylene hydrogenation selectivity to ethylene, an increase in the rate of the acetylene hydrogenation reaction, and an increase in the oligomer yield from the hydrogenation of acetylene. In the acetylene TPR spectra of K doped catalysts, shifts of oligomer peaks to lower temperatures were
observed, indicating that desorption of the adsorbed species was enhanced by K addition. A increase in the probability of ethylene desorption was also found via ethylene deuteration experiments. A decrease in the rate of ethylene deuteration with K addition was observed, which contrasts with the enhanced rate of acetylene hydrogenation. The observed increase in the acetylene hydrogenation selectivity to ethylene appears to be due to easier ethylene desorption and suppressed ethylene adsorption. All of these effects may be explained by K–induced reduction in hydrocarbon adsorption strength. The effect of K arises through metal–support interactions.
I. INTRODUCTION

In our society, polymers are widely used in everyday life, and polyethylene production of about 18.6 billion lb/yr represents a sizeable fraction of the polymeric materials (Greek, 1988). Polyethylene is manufactured from ethylene which largely comes from steam cracking of light napthas. The raw hydrocarbon stream from steam cracking is distilled into its major components, but the ethylene fraction contains acetylene in amounts as high as 1% which is difficult to remove via fractionation (Derrien, 1986). Furthermore, acetylene is particularly unwanted as it has adverse effects on the ethylene polymerization process (Winterbottom, 1981). Therefore, acetylene is generally removed by selective hydrogenation using an appropriate catalyst. Other processes such as selective adsorption are not used as frequently because selective hydrogenation has the advantages of simplicity of implementation, efficiency, and ease of operation (Derrien, 1986).

There are many alternative selective hydrogenation processes which can be used to treat various kinds of feed stocks. A popular process is hydrorefining of an ethylene-rich cut (typically 1% C2H2, 79% C2H4, 20% C2H6) (Derrien, 1986). In this process, high purity hydrogen is introduced stoichiometrically (with respect to acetylene) into the feed and the acetylene concentration is reduced to 2 ppm. Along with hydrogen, a trace of carbon monoxide (50–500 ppm) may also be added to increase the ethylene selectivity. Typical reaction operating conditions are about 25 bar and 333 to 343 K. The catalyst used in this process is palladium supported on alumina (palladium content about 0.04%). Oligomers, which are by-products of acetylene hydrogenation, cause operational problems
in the form of oligomer accumulation which results in catalyst deactivation with time. The reactor temperature, hydrogen pressure, and CO content are then adjusted accordingly to maintain conversion while sacrificing ethylene selectivity. Eventually the catalyst must be regenerated.

In the industrial process, selectivity to ethylene is a key objective. Selectivity to ethylene is usually defined as the ethylene yield divided by the sum of ethylene yield and ethane yield. Hence, operating conditions, catalyst and type of process are optimized so as to achieve maximum selectivity. Higher capital investment or higher operating costs can be recovered rapidly if the ethylene yield is improved even slightly (Derrien, 1986). A better understanding of the selectivity phenomena over Pd catalysts is very important if we are to discover more efficient operating conditions or design improved catalysts.

Additives are frequently used to modify the selectivity or reaction rate in catalytic processing. These additives can be introduced in the reaction mixture (such as CO) or placed directly on the catalyst (such as a metallic promoter). In the selective hydrogenation of acetylene, CO has been used as a feed stream additive to enhance the selectivity of catalyst. However, the role of CO in improving ethylene selectivity is not well understood, though it has been the subject of several research efforts. Several catalyst promoters have also been used to enhance the selectivity of this process. There are reports on the addition of Pb and Zn to Pd (Lindlar, 1966; Miller, 1966; Peterson, 1977; Palczw ska, 1984) and the alloying of Pd with Group 1B transition metals including Ag (Bond et al., 1958), Cu (Schay et al., 1983; Leviness, 1984; Weiss, 1984),
and Au (VLsSer et al., 1974). The enhancement in the selectivity and reaction rate with the addition of Group 1B transition metals was ascribed to the donation of electrons from these metals to Pd (Boitiaux et al., 1985a). Alkali metal cations, also potential electron donors, might yield similar effects but there are no reports on the use of these potential promoters for catalysts useful for the selective hydrogenation of acetylene. Alkali metals have been shown to favorably alter the activity and selectivity of the transition metal catalysts in the processes of CO hydrogenation and ammonia synthesis (Mross, 1983), and the effect of alkali metals on these reactions is known to be due to electronic factors. Therefore, it is worthwhile to test alkali metal promoters for possible enhancement of selective hydrogenation of acetylene and to investigate the reasons for any associated effects.

In this study, the effects of CO and a potassium promoter on the selective hydrogenation of acetylene over Pd/Al₂O₃ has been studied using deuterium tracer and TPR techniques. K doped Pd/Al₂O₃ catalysts were prepared and tested for the catalytic performance. The product distribution from the deuteration of acetylene or ethylene has been assessed using Kemball's method and the influence of additives on each reaction step has been examined. We have developed the methods for TPR experiments applied to acetylene and ethylene reaction and investigated the adsorbed species on Pd/Al₂O₃ from C₂H₂ or C₂H₄ using this technique. The effects of additives on the behavior of these adsorbed species have been studied via TPR.
II. LITERATURE REVIEW

This study includes the investigation of adsorption and reaction of acetylene and ethylene on Pd so that previous studies on this subjects are particularly relevant and will be reviewed before discussing the present understanding of the reaction pathways and selectivity phenomena in the selective hydrogenation of acetylene. Previous studies on the effect of CO on this process and a general discussion on the effect of alkali metal doping of transition metal catalysts are also presented.

2.1 Adsorption of Acetylene and Ethylene on Palladium Catalysts

The surface species which are known to be formed on metal from acetylene and ethylene adsorption are summarized in Figure 2.1. Acetylene, when adsorbed on supported Pd, undergoes self-hydrogenation with the production of ethane (Webb, 1978). Ethylene was also observed to undergo self-hydrogenation to ethane upon adsorption on palladium-silica catalysts (Webb, 1978). Self-hydrogenation results from the dissociative adsorption of ethylene or acetylene which yields a hydrogen deficient hydrocarbon species and adsorbed hydrogen. Hydrogen atoms thus liberated react with acetylene or ethylene to produce ethane. The extent of dissociation is known to depend upon the temperature and the catalytic metal (Webb, 1978).

Little et al. (1960) observed associatively adsorbed acetylene at 293 K as IR bands which could be assigned to olefinic species. In the case of ethylene adsorption, associatively adsorbed species were small compared to dissociatively adsorbed species at 293 K, but with preadsorbed
Figure 2-1. Surface species on metals from the adsorption of C$_2$H$_2$ and C$_2$H$_4$ (Webb, 1978; Zaera and Somorjai, 1984).
hydrogen (Webb, 1978), bands due to saturated species for associatively adsorbed olefins predominated. Therefore, under conditions used for catalytic hydrogenation where hydrogen is present, ethylene is probably adsorbed associatively.

Al-Ammar and colleagues (1978a) have observed two types of adsorption from \(^{14}\)C tracer studies. The adsorption of \(^{14}\)Cacetylene and \(^{14}\)Cethylene on supported Pd catalyst results in a non-linear primary region where the species are dissociatively adsorbed, followed by a linear secondary region. The secondary adsorbed species were thought to exist as an overlayer on the dissociatively adsorbed hydrocarbons and to be involved in hydrogenation.

Recently, a stable surface species formed from ethylene has been determined to be ethylidyne (CH\(_3\)-C≡). On Pd, surface ethylidyne was immediately and irreversibly formed at 300 K but it was not formed below 240 K (Beebe et al., 1985). Ethylidyne is also formed by acetylene adsorption on Pd and is thought to originate from the reaction of adsorbed acetylene and hydrogen which is derived from dissociatively adsorbed acetylene. Zaera and Somorjai (1984) proposed that the ethylidyne species on Pt is hydrogenated to ethylidene (CH\(_3\)-CH≡) which serves as a 'cocatalyst' in the hydrogenation of ethylene, whereby ethylidene transfers its newly acquired \(\alpha\)-hydrogen to an ethylene molecule which is adsorbed in the overlayer. However Beebe et al. (1986) found that over Pd/Al\(_2\)O\(_3\), the formation and hydrogenation of ethylidyne is 2-3 orders of magnitude slower than ethylene hydrogenation, so that it is simply a spectator species over Pd.
Acetylene adsorbed on many different metals including Pd (Webb, 1978) was found to be retained as surface polymer. The existence of C₄ and C₆ compounds on evaporated Pd film was observed by McCarrol et al. (1970). There are no reports on oligomer formation from ethylene adsorption on Pd, but ethylene dimerization on Ni was observed in a FEM study (Whalley et al., 1970) and IR study (Morrow and Sheppard, 1969).

The chemisorption behavior of acetylene on Pd single crystal surfaces was studied by Gentle and Mutterties (1983), where five competing reactions were recognized including decomposition to carbon, reversible desorption, reversible C-H scission, trimerization to benzene and hydrogenation to ethylene. The cyclotrimerization to benzene has been the subject of several studies (Tysoe et al., 1983,1986; Logan et al., 1986). Of these, Tysoe et al.'s TPD study (1983) is particularly related to this study. When acetylene was adsorbed on Pd[111] at 175 K, a flat-lying acetylenic species predominates leading to low-temperature trimerization. For adsorption at 300 K, olefinic species with its C-C axis perpendicular to the surface were mainly observed and may act as the intermediate to partial hydrogenation to ethylene.

2.2 Selective Hydrogenation of Acetylene

Many studies on the selectivity phenomena in the acetylene hydrogenation process have appeared in the open literature. After early studies by Sheridan et al. (1945), acetylene hydrogenation was extensively studied by Bond et al. over pumice and alumina supported metals and metal powders. The reaction of acetylene with deuterium over nickel and alumina supported Group VIII metals has also been investigated. All of these works have been reviewed by Bond (1962,1963)
and Webb (1978). Of all the Group VIII metals, supported palladium was found to be the most active and selective catalyst for acetylene hydrogenation.

The general course of the acetylene reaction over Pd/alumina (Bond et al., 1965a) can be characterized by three basic regions which consist of a) an initial slow, zero order region in which the major product is ethylene (ethylene selectivity 95%), b) an acceleration region, and c) a rapid rate region which is essentially non-selective to ethylene. As the initial H₂/C₂H₂ ratio increased, regions a) and b) progressively disappeared until, at ratios of 10/1 or higher, only region c) is evident. The high selectivity in region a) was thought to be due to the ability of acetylene to displace H₂ and adsorbed ethylene which is formed on the palladium surface via single hydrogenation of acetylene. Regions b) and c) become evident as hydrogen begins to compete successfully with depleting amounts of acetylene for surface sites.

The selectivity to ethylene during acetylene hydrogenation has been explained by the concepts of 'mechanistic' and 'thermodynamic' factors which can be summarized as follows. During acetylene hydrogenation, both ethylene and ethane are formed during one residence of acetylene.

\[ \text{C}_2\text{H}_4(g) \]
\[ \text{C}_2\text{H}_2(a) \]
\[ \text{C}_2\text{H}_4(a) \]
\[ \text{C}_2\text{H}_6(a) \]

The knowledge of the rate constants, k₂ and k₃, along with the reaction orders in ethylene and hydrogen for ethane formation defines the mechanistic factor, which depends on the specific properties of the...
catalyst. Once ethylene is produced, the system contains another potential adsorbate and then a thermodynamic factor governs whether adsorption and hydrogenation of ethylene takes place. The surface coverages of acetylene and ethylene depend on a difference in their free energies of adsorption.

\[ \frac{\theta_{\text{C}_2\text{H}_4}}{\theta_{\text{C}_2\text{H}_2}} = \frac{P_{\text{C}_2\text{H}_4}}{P_{\text{C}_2\text{H}_2}} \exp \left( -\frac{(\Delta G_{\text{C}_2\text{H}_4} - \Delta G_{\text{C}_2\text{H}_2})}{RT} \right) \]

where:

\( \theta \) = surface coverage

\( P \) = partial pressure

\( \Delta G \) = free energy of adsorption

A free energy difference of only a few kilocalories per mole will result in a very high surface coverage of the more strongly adsorbed molecule. Since \( \text{C}_2\text{H}_2 \) adsorbs more strongly than \( \text{C}_2\text{H}_4 \), readsoption of \( \text{C}_2\text{H}_4 \) becomes of minor importance. The desorption of ethylene may also be assisted by adsorption of acetylene (displacement of ethylene by acetylene). In the case of palladium, which shows the highest selectivity, the thermodynamic factor is considered to be so large that it outweighs this metal's high activity for ethylene hydrogenation.

The hydrogenation of acetylene in excess ethylene was studied by McGown et al. (1977, 1978) using \(^{13}\text{C}\)-labeled acetylene and deuterium tracer experiments. They found that the majority of the ethane produced by hydrogenation of the acetylene/ethylene mixture came predominantly
from the ethylene even when the acetylene pressure was high enough to exclude ethylene almost completely from the metal. This observation led to the postulate that two types of sites exist on the catalyst surface identified as X sites where the hydrogenation of acetylene and ethylene proceed together and Y sites which hydrogenate ethylene even in the presence of acetylene. In deuteration experiments, the presence of a Y site was also supported by the finding that D₂ ethane was the predominant product in the presence of acetylene while ethane formed from ethylene in the absence of acetylene was mainly D₆ and D₄. McGown et al. also suggested two different modes of ethylene adsorption including α,α adsorbed species as an alternative to X sites and Y sites.

Al-Ammar and colleagues (1978a, 1978b, 1979) also studied acetylene hydrogenation in the presence of ethylene over alumina and silica supported palladium using ¹⁴C-tracers. They found that acetylene and ethylene adsorb on the catalyst in a primary region and secondary region as discussed above (section 2.1). The coadsorption of ethylene and acetylene showed that, under hydrogenation conditions, ethylene and acetylene are adsorbed at separate sites and undergo hydrogenation independently of each other. Acetylene adsorbed in the primary region yielded only ethane during a hydrogenation reaction while acetylene adsorbed in the secondary region yields ethylene and ethane. This suggests that three types of sites are involved in the hydrogenation of acetylene and ethylene. Type I sites are those responsible for the acetylene adsorbed in the secondary region; Type II sites are those responsible for the primary adsorbed acetylene species and Type III sites are those which are active for ethylene hydrogenation, but inactive for
acetylene hydrogenation. Acetylene adsorbed in the secondary region, which is an overlayer to the primary adsorbed species, was thought to be hydrogenated through a hydrogen transfer mechanism, in which activation of molecular hydrogen occurs by reaction with a dissociatively adsorbed $C_2H_x$ ($x<2$) primary species, followed by a hydrogen transfer between the resulting "hydrogen-rich" primary species and secondary adsorbed acetylene.

Since more recent studies with isotopic tracers show that independent sites for acetylene and ethylene adsorption exist, Bond's interpretation of selectivity in terms of thermodynamic and mechanistic factors is now considered to be inadequate. In order to fully understand the factors which influence the selectivity, information on the relative amounts of acetylene and ethylene adsorbed on independent sites and the relative amounts of different forms of adsorbed intermediates which can only lead to the formation of the ethane are necessary (Webb, 1978).

Other studies have led to a different view of Pd activity for the hydrogenation of trace acetylene in ethylene. The intrinsic selectivity of Pd has been studied using $^{14}$C-labeled ethylene and deuterium in the hydrogenation of unlabeled acetylene over a Pd black catalyst (Guczi et al., 1979; Margitfalvi et al., 1980,1981) and no ethylene hydrogenation could be detected above a critical acetylene pressure, which suggests that there are no independent sites on the metal for ethylene hydrogenation. Three types of adsorbed acetylene species leading to different reaction products on Pd were suggested:
(1) an associative form, which is the precursor of ethylene;

\[
\text{HC} = \text{CH} + 2\text{H} \rightarrow \text{H}_2\text{C} = \text{CH}_2
\]

(2) a dissociative form, \( \text{C}_x\text{H}_x \) \( x<2 \), which forms polymeric species;

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_2\text{C} = \text{CH} \\
\downarrow & \quad \downarrow \\
\text{C} = \text{CH} & \quad \text{C} = \text{CHCH} = \text{CH}
\end{align*}
\]

(3) a reactive form that produces ethylidyne (≡\text{C}-\text{CH}_3) and is responsible for direct ethane formation.

\[
\begin{align*}
\text{CH}_3 \\
\downarrow \\
\text{C} + 3\text{H} \\
\downarrow & \quad \downarrow \\
\text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]

Experimental conditions influence the relative concentrations of these surface species and alter the routes of the surface reaction, leading to different products from acetylene.

When Pd is supported on \( \text{Al}_2\text{O}_3 \), a separate site on the support for ethylene hydrogenation has been suggested (Weiss et al., 1984; Sarkany et al., 1984; Levinness et al., 1984; Moses et al., 1984). This site may be only operative for aged catalysts which are covered with surface polymer. A parallelism between the extent of ethylene hydrogenation and the amount of surface polymer has been observed, which leads to the postulate that ethylene adsorbed on the support reacts with hydrogen transferred from the metal through the surface polymer.

Two parallel processes were considered to play important roles in the final selectivity of the process according to models which involve support sites:
(1) Pd sites, which are covered exclusively by acetylene under the conditions normally applied in industry, hydrogenate acetylene in 94–96% yields to ethylene and 4–6% to ethane.

(2) The support, which is covered with ethylene, hydrogenates ethylene to form ethane, thereby decreasing the overall selectivity of the Pd catalyst.

Globally, there appears to be agreement on the existence of independent sites for ethylene hydrogenation on Pd/Al₂O₃ but conclusions on the nature of these sites are quite different. Different faces of Pd crystallites, overlayers on the primary adsorbed species, and support sites on the aged catalyst have all been postulated as separate, active sites. Hydrocarbon overlayers on the primary adsorbed species are particularly controversial since it considers the metal structure to be of only secondary importance, which contradicts the traditional concept of metal-catalyzed hydrogenation. Zaera and Somorjai (1984) proposed a similar mechanism for ethylene hydrogenation where ethylene adsorbed in the second layer is hydrogenated with hydrogen transferred through ethyldiene species, but ethylidyne, which is the precursor to ethyldiene, was thought to be a spectator species in the hydrogenation of ethylene on Pd/Al₂O₃ (Beebe et al., 1986). Hattori et al. (1979) also studied ethylene hydrogenation over Pt catalysts with pulse experiments but found that ethylene adsorbed on Pt reacts sequentially with two H–Pt sites to desorb as the alkane. In Sarkani et al.'s theory (1984) concerning ethylene hydrogenation sites which exist on the support, neither a hydrogen pool on the surface polymer nor a support site has
been proven experimentally. These inconsistencies and uncertainties, suggest that a more thorough study of reaction pathways and selectivity phenomena is warranted.

2.3 Oligomerization of Acetylene

Another important factor which affects the selectivity of acetylene removal processes is catalyst aging, which is caused by accumulation of oligomers (C₄, C₅... aliphatic hydrocarbons) on the catalyst. Oligomers are believed to be produced primarily from the acetylene component of the raw ethylene stream (McGown et al., 1978). In laboratory investigations, Sarkany (1984) reported that the intrinsic selectivity of acetylene during the selective hydrogenation of trace acetylene in ethylene as:

\[
\begin{array}{c}
\text{H}_2 \\
\text{C}_2\text{H}_2 \\
\text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_6 \\
\text{oligomers}
\end{array}
\]

for a reaction mixture consisting of 0.3% C₂H₂, 0.44% H₂, and balance C₂H₄ over an industrial Pd/alumina catalyst. Accordingly, acetylene that could have been recovered as ethylene is consumed in the oligomerization. In addition, catalyst aging gradually decreases the selectivity to ethylene. Leviness et al. (1984) and Sarkany et al. (1984) suggested that support sites become operative for ethylene hydrogenation with aging so that extensive hydrogenation takes place and results in additional ethylene losses.

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Few studies have been directed at the mechanism of the oligomerization of acetylene. Sheridan (1946) studied oligomerization during acetylene hydrogenation over pumice supported metals and proposed a reaction mechanism. The reaction was thought to be initiated by formation of a vinyl radical through hydrogenation of associatively adsorbed acetylene. This vinyl radical is isomerized to a free radical which reacts further with associatively adsorbed acetylene in a chain reaction to form oligomers. The presence of hydrogen was thought to be essential since there was no appreciable polymerization in the absence of hydrogen. As Webb (1978) pointed out, an adsorbed species may not be able to exist as a free radical on a metal surface but the free radical may be envisaged as a transition state in the formation of adsorbed vinyl from acetylene.

\[
\begin{align*}
H + HC≡CH & \rightarrow \text{CH}≡\text{CH}_2 & \rightarrow & \cdot\text{CH}≡\text{CH}_2 \\
\cdot\text{CH}^-\text{CH}_2 + HC≡CH & \rightarrow \cdot\text{CH}^-\text{CHCH}^-\text{CH}_2
\end{align*}
\]

Bond et al. (1965) analyzed the C\textsubscript{4} fraction from acetylene hydrogenation, and found it to consist of 1-butene, 1,3-butadiene, trans-2-butene, cis-2-butene, and n-butane. They also showed that the isomeric distribution of the butenes obtained from the hydrogenation of 1,3-butadiene on Pd agreed favorably with the distribution from acetylene hydrogenation indicating that 1,3-butadiene is the intermediate during acetylene oligomerization. Based on the stereochemical distribution

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of the 2-butene products, they further suggested that the most favored steric arrangement for the acetylene molecule on Pd is a form of staggered packing.

Later studies by other workers were focused on oligomerization during the selective hydrogenation of trace acetylene in ethylene over Pd/f-alumina. McGown et al. (1977) reported that the rate of C₄ production was second order in acetylene pressure, which confirms that acetylene molecules adsorbed on two adjacent sites are required for C₄ production. They also found that more 1,3-butadiene was formed at higher pressures of acetylene, and 'green oil', liquid product which is obtained in small yields, was found to consist of saturated chains of up to 22 carbon atoms. Sarkany (1984) reported that the composition of the volatile fraction of oligomer product was 86% C₄, 12% C₅, and 2% C₆. Margitfalvi (1980) showed that ethylene, which exists in large a excess in the industrial process, decreased oligomer formation.

Margitfalvi et al. (1981) proposed that oligomers are formed from dissociatively adsorbed acetylene rather than the associatively adsorbed form. In an isotopic tracer study they found that the dissociatively adsorbed species, C₂Hₓ (x<2), are formed on the bare Pd surface during the initial stage of acetylene hydrogenation and they observed a high D content in C₄ products, which led to the postulate that the C₂Hₓ species is the precursor to oligomers.

Trimm (1980) suggested that oligomerization of acetylene takes place on both the support and Pd but the amount of oligomerization on the support appeared to be small compared to oligomerization on Pd. According to Sarkany's study (1984), oligomer formation on the support
does not significantly affect the overall selectivity but accumulation of surface polymer and subsequent aging of the catalyst depends on oligomerization on the support so that Pd/α-Al₂O₃ (low surface area) produced less polymer than Pd/γ-Al₂O₃ (high surface area). In case of Pd/zeolite catalysts (Kranich, 1985), the acidity of the support was found to significantly affect the selectivity. Over Pd/silicalite whose acidic sites generated during reduction was not neutralized by sodium hydroxide, the rate of oligomer production was more than 20 times the rate of acetylene reaction (at low hydrogen pressure), indicating that the chief reaction was ethylene dimerization in the feed gas on acidic sites.

2.4 Effect of Carbon Monoxide

A feed stream additive which increases catalyst selectivity for acetylene hydrogenation is carbon monoxide and the interaction of CO with the Pd catalyst has been the subject of many studies. First, the studies on the interaction of CO with acetylene and ethylene on the catalyst will be reviewed followed by the effect of CO on selectivity during hydrogenation.

Carbon monoxide strongly adsorbs on metal sites so that it may block access to or displace adsorbed molecules. Al-Ammar et al. (1978a) found in a ¹⁴C tracer study that CO adsorption on Pd/SiO₂ is weaker than acetylene adsorption. When CO was adsorbed in the presence of acetylene, CO could occupy only 7% of the total surface, which is about the surface area predicted to be geometrically available after random acetylene adsorption which requires dual, adjacent sites. On the other
hand, preadsorbed CO was displaced by acetylene to 37.5% coverage. Acetylene and ethylene were thought to adsorb in a primary layer and a secondary overlayer and CO was found to only affect primary adsorption.

The surface and gas-phase species resulting from the interaction of CO with acetylene or ethylene on Rh/silica was studied by Reid et al. (1973b, 1973d) using a thermal desorption technique with mass spectrometry detection. When acetylene was adsorbed on a CO precovered surface, acetylene was recovered as the desorption product, indicating that self-hydrogenation of acetylene to ethylene or ethane was prevented by CO. In the case of ethylene, CO also suppressed self-hydrogenation and cracking to methane. Reid et al. (1973b, 1973d) postulated that CO either poisons self-hydrogenation sites or blocks sites which accept hydrogen formed via dissociative adsorption of acetylene.

In a study on the hydrogenation of acetylene in excess ethylene by McGown et al. (1977, 1978), a strong retarding effect of CO on the rate of ethylene hydrogenation was observed which resulted in a global enhancement in the ethylene selectivity. The selectivity enhancement was attributed to the adsorption of carbon monoxide in preference to ethylene on Y sites of Pd or to a reduction in the amount of ethylene which tends to α,α-adsorb.

On the other hand, Al-Ammar et al. (1978a, 1979) found that CO prevents the dissociative (primary) adsorption of hydrocarbon, but does not affect the secondary adsorption which they consider to be relevant to hydrogenation. So blockage of the hydrogen adsorption from the gas phase was considered to be responsible for the selectivity increase.
Weiss et al. (1984) and Leviness et al. (1984) studied CO effects on ethylene selectivity from the reaction of industrial raw ethylene streams. They suggested that CO displaces hydrogen from single, geometrically isolated sites which are left unoccupied after random acetylene adsorption on adjacent sites. Hydrogen spillover from the metal to the support is reduced and ethylene hydrogenation on the support is thereby suppressed. A direct CO effect on the adsorption of ethylene was precluded since, according to their mechanism, the primary sites for ethylene hydrogenation were on the support where CO can not adsorb.

The effect of CO on oligomer formation was investigated by Weiss et al. (1984) and Leviness et al. (1984). In a steady-state reaction, oligomer production was found to go through a maximum as the CO concentration was increased. The increase in oligomer yield at low CO pressure was thought to be due to a decrease in surface hydrogen while at higher CO pressures the adsorption of acetylene on adjacent sites is hindered which results in a decrease in oligomer production (Sarkany et al., 1984). Leviness et al. (1984) also postulated that CO blocks dissociative adsorption of acetylene which results in a decrease oligomer formation.

From this discussion, we conclude that the mechanism of the effect of CO on acetylene hydrogenation is not well established. Disagreement primarily results from differences in opinions concerning active sites on Pd/Al₂O₃ catalyst.
2.5 Effect of Alkali Metal Promoters

The effect of alkali metal promoters on the activity and selectivity of Pd catalysts has not been studied with respect to the selective hydrogenation of acetylene. However, several reports concerning other reactions exist and results from these studies might be applied to acetylene hydrogenation.

Potassium, an alkali metal, has been used as a promotor to improve the activity of iron and ruthenium based catalysts for ammonia synthesis (Aika et al., 1972, 1973). Potassium is known to increase the selectivity toward high molecular weight hydrocarbons and olefinic compounds from the hydrogenation of carbon monoxide (Anderson, 1956). Effects of alkali metals upon metallic catalysts are frequently attributed to electronic factor (Mross, 1983).

Alkali metals act as strong bases and transfer electrons to the active metallic component. Additional electron density on the transition metal surface would thus increase the bond strength of electron acceptor adsorbates, such as CO or N₂, while decreasing the bond strength of electron donor adsorbates like NH₃ or H₂. This role of electron donating or withdrawing agents in modifying the chemisorption properties of transition metals is called a 'ligand effect'. Examples of this effect follows. As a result of alkali metal addition, the heat of adsorption of CO increase by as much as 100%, while the heat of adsorption of H₂ falls only slightly (Dry et al., 1969). Due to the stronger CO chemisorption, formation of the primary complex from CO adsorption increases during CO hydrogenation. Consequently, chain growth is accelerated so that the product shifts toward heavier hydrocarbons. With respect to ammonia
synthesis, doping the catalyst with potassium accelerates the dissociative adsorption of N₂ by 2–3 orders of magnitude (Nielsen, 1981) resulting in an increase in the activity of catalyst, while desorption of NH₃ is easier (Frankenburg, 1955) which also enhances the activity of the catalyst.

Similar studies on the hydrogenation of benzene over Ni/SiO₂ have been reported by Prallaud et al. (1980). With K addition, the rate of benzene hydrogenation decreased by a factor of 3.6 while the selectivity to cyclohexene, the partially hydrogenated product, increased. These changes in catalytic properties were ascribed to an electronic interaction between K and Ni atoms.

In addition to changes in the strength of adsorption, the mode of adsorption may also change with alkali addition. In Shigehara et al.'s study on ethylene hydrogenation over Ni (1973), both self-hydrogenation of ethylene and catalyst deactivation was prevented by K doping. Shigehara et al. postulated that Ni became richer in electron density via electron donation from K resulting in a loss in its ability to dissociate ethylene.

In a study on acetylene conversion to benzene over Pd single crystals (Rucker et al., 1986), electron donating additives including potassium were found to reduce the amount of surface carbon (either graphite or polymer) that accumulates during the reaction and to thereby enhance the rate of benzene formation.

Other effects of alkali addition includes removal of acid sites and generation of basic centers, which yields changes in the chemical properties of support. Figoli and L'argeniere (1989) studied the effect of sodium additive to Pd/Al₂O₃ for the selective hydrogenation of styrene.
and found changes in the selectivity to ethylbenzene and the resistance to sulfur poisoning. Sodium was found to remove the acid sites of alumina and to affect the metal-support interaction between acid sites and Pd, which was thought to yield suppressed polymerization of styrene on acid sites and an increased susceptibility to sulfur effects.

2.6 Theories of the Research Techniques

Two experimental methods used in this study, TPR and Kemball's method, are complex and warrant review so the reader may understand the applicability to our studies.

2.6.1. Deuteration Experiments with Kemball's Steady State Treatment

Deuterium has been used extensively as an isotopic tracer in the study of hydrocarbon catalysis. The deuteration of acetylene and ethylene have often been studied with Kemball's steady state treatment method (1956), which yields the probability of each elementary step in the hydrogenation reaction by analysis of the deuterium distribution in the product. Bond et al. (1964a, 1965b, 1966a, 1966b, and 1968) used this method to elucidate the catalytic properties of Group VIII metals with respect to acetylene and ethylene hydrogenation and to establish reaction mechanisms for each catalyst. Briggs et al. (1980) also used this method to examine support effects on Pt catalysts.

When gas phase hydrogen is replaced with deuterium in the reaction mixture, products of the reaction will obtain deuterium by two major routes. First, direct deuteration of an unsaturated hydrocarbon results in the product molecule containing deuterium. A parallel reaction, however, is H/D exchange which complicates the interpretation of deuterium
distribution results. Notice that H/D exchange yields surface H which may then hydrogenate (as opposed to deuterate) a surface hydrocarbon. However, by setting up a systematic procedure for accounting for both deuteration and exchange, information regarding the reaction pathways by which adsorbed hydrocarbons undergo may be deduced. One procedure, originally devised by Kemball, is a steady state treatment method based on the general mechanism for hydrogenation.

For acetylene hydrogenation (Bond, 1966b, 1968), the reaction scheme is as follows

\[
\begin{align*}
+X & \quad \text{C}_2\text{X}_2(a) \quad +X \\
\text{C}_2\text{X}_3(a) & \quad \text{C}_2\text{X}_4(a) \quad (X = \text{H or D}) \\
-\text{X} & \quad \text{C}_2\text{X}_3(a)
\end{align*}
\]

where a half-hydrogenated species \(\text{C}_2\text{X}_3(a)\), known to be stable on the surface, is assumed to be the reaction intermediate. If we now consider probabilities that H or D may be involved in the reaction, we can write a probabilistic model with the following arguments. Assuming acetylene, \(\text{C}_2\text{X}_2(a)\), does not desorb, its relative hydrogenation rate is set to 1. If \(q\) is the probability of adsorbed acetylene picking up a deuterium atom \((X=D)\) then \(1-q\) is the probability of adding a hydrogen atom \((X=H)\). The intermediate, \(\text{C}_2\text{X}_3(a)\), either reverses to \(\text{C}_2\text{X}_2(a)\), probability \(1-p\), or hydrogenates to \(\text{C}_2\text{X}_4(a)\), probability \(p\). If \(\text{C}_2\text{X}_3(a)\) is hydrogenated, \(s\) is the probability for adding deuterium and \(1-s\) the probability of adding hydrogen. Thus:

\[
\begin{align*}
+X & \quad \text{C}_2\text{X}_2(a) \rightarrow \text{C}_2\text{X}_3(a) & \quad 1 \\
\text{C}_2\text{X}_3(a) + \text{H} & \rightarrow \text{C}_2\text{X}_2\text{H}(a) & \quad 1-q \\
\text{C}_2\text{X}_3(a) + \text{D} & \rightarrow \text{C}_2\text{X}_2\text{D}(a) & \quad q \\
-\text{X} & \quad \text{C}_2\text{X}_2(a) \rightarrow \text{C}_2\text{X}_3(a) & \quad 1-p
\end{align*}
\]
Assuming these probabilities are independent of isotopic content, the three isotopic adsorbed acetylenes (C\textsubscript{2}X\textsubscript{3}(a)), denoted A\textsubscript{1} - A\textsubscript{3} and the six isotopic vinyl radicals (C\textsubscript{2}X\textsubscript{3}(a)), B\textsubscript{1} - B\textsubscript{6}, are related by a series of simultaneous equations which are essentially H/D balances for each adsorbed species (Refer to Appendix A for further details). Notice that the surface reaction theory distinguishes between the stereochemical isomers of each deuterated species, but mass spectrometry is only able to detect species which differ in AMU. Therefore, a condensation of equations is used to obtain "mass spectrally" independent species. The nine simultaneous equations thus obtained may be solved for values of p, q and s to obtain a satisfactory fit between the calculated and observed deuterioethylene distributions. The relative amounts of the various surface species are also obtained in this calculation.

In ethylene deuteration, similar relationships are established using four probability parameters p, q, r, and s (Kemball, 1966; Bond, 1964a).

\[
\begin{align*}
\text{C}_2\text{X}_3(a) & \xrightleftharpoons{+X} \text{C}_2\text{X}_4(a) \\
\text{C}_2\text{X}_3(a) + H & \xrightarrow{p} \text{C}_2\text{X}_3\text{H}(a) \\
\text{C}_2\text{X}_3(a) + D & \xrightarrow{s} \text{C}_2\text{X}_3\text{D}(a) \\
\text{C}_2\text{X}_4(a) & \xrightarrow{+X} \text{C}_2\text{X}_5(a) \\
\text{C}_2\text{X}_5(a) & \xrightleftharpoons{-X} \text{C}_2\text{X}_4(a)
\end{align*}
\]

A half-hydrogenated species (C\textsubscript{2}X\textsubscript{5}(a)) is assumed to be the reaction intermediate. C\textsubscript{2}X\textsubscript{4}(a), either desorbs, probability 1/(1+p), or hydrogenates to C\textsubscript{2}X\textsubscript{5}(a), probability p/(1+p). If q/(1+q) is the probability of adsorbed acetylene picking up a deuterium atom (X=D) then 1/(1+q) is the probability of adding a hydrogen atom (X=H). The intermediate, C\textsubscript{2}X\textsubscript{5}(a), either reverses to C\textsubscript{2}X\textsubscript{4}(a), probability r/(1+r), or hydrogenates to
C_2X_8(a), probability 1/(1+r). If C_2X_8(a) is hydrogenated, s/(1+s) is the probability for adding deuterium and 1/(1+s) the probability of adding hydrogen. Thus:

\[
\begin{align*}
\text{C}_2\text{X}_4(a) &\rightarrow \text{C}_2\text{X}_4 & 1/(1+p) = 1-p^* \\
+X \\
\text{C}_2\text{X}_4(a) &\rightarrow \text{C}_2\text{X}_5(a) & p/(1+p) = p^* \\
\text{C}_2\text{X}_4(a) + H &\rightarrow \text{C}_2\text{X}_4\text{H}(a) & 1/(1+q) = 1-q^* \\
\text{C}_2\text{X}_4(a) + D &\rightarrow \text{C}_2\text{X}_4\text{D}(a) & q/(1+q) = q^* \\
-X \\
\text{C}_2\text{X}_5(a) &\rightarrow \text{C}_2\text{X}_4(a) & r/(1+r) = r^* \\
+X \\
\text{C}_2\text{X}_5(a) &\rightarrow \text{C}_2\text{X}_6(a) & 1/(1+r) = 1-r^* \\
\text{C}_2\text{X}_5(a) + H &\rightarrow \text{C}_2\text{X}_5\text{H}(a) & 1/(1+s) = 1-s^* \\
\text{C}_2\text{X}_5(a) + D &\rightarrow \text{C}_2\text{X}_5\text{D}(a) & s/(1+s) = s^*
\end{align*}
\]

Here, the probability parameters p,q,r and s are redefined as p*,q*,r* and s* to facilitate the interpretation. The six isotopic adsorbed ethylenes (C_2X_4(a)), denoted A_1 - A_6 and the twelve isotopic ethyl radicals (C_2X_8(a)), B_1 - B_12, are related by a series of simultaneous equations (Refer to Appendix A for further details). Upon condensation for mass spectral analysis, the 18 simultaneous equations thus obtained may be solved for the parameters (p,q,r and s) and the relative amounts of the various surface species in the same procedure as that used in acetylene deuteration experiments.

A modified procedure which incorporates isotope effects in the rupture of C-H and C-D bonds (Kemball and Wells, 1968) has been suggested but the improvement in the agreement between calculated and observed distributions was negligible. Due to the extra complexity with marginal improvement in accuracy, this modified method was not adopted in this study.
The values of \( p \) and \( r \) obtained by this procedure give information regarding the relative rates of the surface processes involving hydrocarbon species such as hydrogenation, reversal, and desorption, while \( q \) and \( s \) give information on the nature of the hydrogen donors (hydrogen atoms released by hydrogen-rich radicals or deuterium atoms adsorbed from the gas phase). The probability of ethylene desorption \( (1/(1+p)) \) determined from the ethylene deuteration data could be used as an index for ethylene adsorption strength as in the Briggs' study (1980).

2.6.2. Temperature Programmed Reaction (TPR)

The technique of temperature programmed desorption (TPD) has been used widely for the investigation of binding states of adsorbed species and reaction sites on catalysts (Falconer, 1983), but it has not been successfully applied to hydrocarbon adsorption on supported metal catalysts because adsorbed hydrocarbons could not be completely recovered during thermal desorption due to heavy decomposition and retention on the catalyst (Rye and Hansen, 1969; Carter and Rye, 1972; Komers et al., 1969; Tsuchiya and Nakamura, 1977). Recently, TPD with a reactive carrier gas, termed temperature programmed reaction (TPR), has been developed. TPR has been successfully applied to carbon monoxide catalytic reactions where CO undergoes partial decomposition into C and O during TPD (Zagli et al., 1979). Surface species formed from CO adsorption were recovered as methane and water from the surface by use of a hydrogen carrier gas and studies on the behavior of these species brought about a deeper understanding of reaction mechanism of CO hydrogenation. TPR was also useful in studying the effect of alkali-metal
promoters on CO hydrogenation (Falconer et al., 1985; Miura and Gonzales, 1982). Surface species from hydrocarbon adsorption on supported metal catalysts might be studied similarly.

TPR, a modified form of temperature programmed desorption (TPD), is a transient technique which consists of observing the products leaving a catalyst surface as a function of temperature during a known heating schedule. In a typical TPD experiment, a small amount of catalyst is contained in a reactor that can be heated by a furnace. An inert gas, usually helium, flows over the catalyst. Following catalyst pretreatment procedures, a gas is adsorbed on the surface, usually by pulse injection of the adsorbate into the carrier gas upstream from the reactor. After non-adsorbed gas is flushed out, the catalyst is heated to create a linear rise in temperature with time. A thermocouple situated near the catalyst records the temperature and a detector downstream determines the composition of the effluent gas. The detector can be of any type such as a mass spectrometer or thermal conductivity cell. With a sufficiently high carrier gas flow rate, the detector response is proportional to the rate of desorption if diffusion and readsoption in the catalyst bed are not significant. As the temperature increases, the desorption rate increases then goes through a maximum and drops back to zero as the surface is depleted of adsorbate. Often, the desorption spectrum features more than one peak due to different strengths of adsorption on different catalytic sites. The shapes and positions of the peak maxima provide information on the nature of the desorption process and therefore infers the mode of adsorption.
When the inert carrier gas is replaced by a reactive gas or when two reactive gases are coadsorbed, the technique is called TPR. TPR has recently been reviewed by Falconer (1983). This experiment contains detailed information on the reaction mechanism in addition to yielding kinetic data. TPR has several advantages over steady state kinetic experiments. Some of them related to this study are as follows (adapted from Falconer, 1983):

1. Specific activities (rates of reaction) are measured directly for each product, independent of the surface area measurement. Since several sites with different activities can be present on a catalyst, both the specific activities of the sites and their number can change with a change in catalyst properties. TPR can detect these changes from the peak temperature and peak area while steady state experiments only measure the sum of the products of specific activities times the number of sites with that activity.

2. Binding states of adsorbed reactants that are involved in the reaction may be measured. More weakly bound species will desorb at a lower temperature than more strongly bound ones. Analogously, the relative reactivity of a surface species can be determined since more reactive species will react and desorb from the surface at a lower temperature than less reactive ones.

3. Surface coverage of reactants and the surface composition of adsorbed species at the time of formation are determined directly.

With these advantages, we can directly examine the adsorbed species which previously had been examined by inference from the data of
steady state reactions. Furthermore, it is possible to observe the changes in relative population of adsorbed species with changes in catalyst properties.

There are several experimental difficulties associated with TPR. First the TPR spectra can be affected by factors such as readsoption of product gases, diffusional limitations, concentration gradients inside the pellet and response lag time. If the desorbed product readsorbs on the catalyst before it is swept free of the bed by the carrier gas stream, the resultant spectra for that product will shift to higher temperatures. This would obscure the kinetic parameters calculated from TPR spectra. Another problem is that the experimental conditions for TPR may not correspond to the reaction conditions. In TPR of C2H2, the gas phase concentration of C2H2 is extremely low while there is excess H2 in the carrier gas, whereas the industrial selective hydrogenation processes use ratios of C2H2/H2 of about 1/1. Care must be taken in experimental design and interpretation of TPR spectra due to these problems.

Previous TPR studies of CO hydrogenation show that the advantages of TPR far outweigh the disadvantages (Falconer, 1983), which suggests that the application of TPR to the study of C2H2 hydrogenation may be fruitful. In this study, TPR conditions were optimized to minimize problems relating to the factors described above and the importance of these factor have been evaluated according to Gorte's criteria (1982). The calculation results are given in Appendix B and they are discussed in chapter 5.
2.7 Overview

As discussed thus far, several points of disagreement on the nature of catalytic sites for the selective hydrogenation of acetylene still exist and, as a result, the interaction of carbon monoxide with these sites is not clearly understood. Also, the effects of alkali promoters for this reaction over Pd/Al₂O₃ have not been studied before and positive effects of alkali metals for other reactions suggest that promoters for this reaction may be important. A better understanding of the effects of these additives on the reaction selectivity might be achieved by a fundamental approach.

This study is focused on the effect of CO addition to the feed stream and K addition to the catalyst for the selective hydrogenation of acetylene. The study has led us to investigate acetylene hydrogenation particularly via TPR and Kemball's method in an effort to detect changes in the reaction mechanism which result from CO and K addition. Interpretation of these experimental efforts have also been facilitated by studies of similar phenomena for ethylene hydrogenation.
3.1 Experimental

3.1.1 Apparatus

The primary apparatus for this study, though physically a single unit, can be arranged in two basic configurations (Figure 3-1). One configuration is a batch recirculation reactor for kinetic & deuteration experiments and the other for TPR. The batch reactor system (690 ml) is made of pyrex glass with a U-tube pyrex reactor (Figure 3-2) containing a catalyst bed. The reactor temperature is controlled by an electric and digital temperature controller. Reactants were circulated through the catalyst bed by means of a magnetically operated piston pump with check valve arrangement. The entire system could be evacuated by means of a rotary mechanical pump. System pressures were monitored with digital readout diaphragm type pressure gauges. A three-way stopcock arrangement allowed the reactor to be isolated from the remainder of the system during reactant mixing and reaction initiation.

Reactor sampling was accomplished by evacuating a sample loop (1.07cc) on a 6 port chromatographic sampling valve and expanding the reaction products into the sampling loop. Switching the sampling valve diverted the sample into the analytical section.

In TPR configuration, the U-tube reactor was replaced with coaxial quartz reactor with a 14 mm OD jacket and 9 mm OD inner tube (Figure 3-3). A quartz frit at the bottom of the inner tube supported the catalyst and a removable thermowell (coaxially placed within the inner...
Fig. 3-1 Experimental Apparatus for Steady Reaction and TPR
Figure 3–2. U tube Pyrex Reactor for steady state Experiments.
Figure 3-3. Coaxial Quartz Reactor for TPR Experiments
tube) allowed for catalyst charging. Reactants flow downward through the jacket then upward through the fritted disk, catalyst, and inner tube. A three-way stopcock arrangement allowed the reactor to be attached either to the recirculating batch reactor for catalyst pretreatment and reactant adsorption or to a continuous flow of H₂/He carrier gas for the TPR experiment. The effluent could be directed through the chromatographic column to the MS or it could bypass the column and go directly to the MS. H₂ and He carrier gases could be independently controlled and monitored with mass flow controllers (MKS Co.) and digital readout. Heating tape were wrapped on carrier gas lines and valves to prevent condensation of higher hydrocarbons on the tube wall or the valve.

Both heating and cooling were required for TPR experiments, so the electric furnace was replaced with a cylindrical copper block (Figure 3-4) which has rod type heaters imbedded in it for heating and a copper cooling coil surrounding it. Compressed air, cooled by liquified nitrogen, was used as the cooling medium. The block temperature was controlled by a digital temperature controller (Omega CN 2010). Linear heating rates of 1–30 K/min. were attainable.

A versatile mass spectrometry system was used in analysis of TPR products. The mass spectrometer was a UTI 100C quadrupole with 2–200 AMU mass range, electron impact ion source operating at 70 ev, electron multiplier detector, and turbo molecular pumped vacuum system. A jet separator roughed with an independent mechanical vacuum pump provided the interface to atmospheric pressure. A cross pattern leak valve
Figure 3-4. Heating—cooling Block
(Nupro SS-2SX) was used to split off carrier flow rates in excess of 30 cc/min. The jet separator removed the bulk of the H2 and He from the carrier gases.

The system could be also operated as a rough GC/MS system by switching a chromatographic column in series with the jet separator by means of a six port chromatographic sampling valve. The chromatographic column could be contained either in a temperature controlled oven or in a constant temperature bath. This GC/MS configuration was used in analysis of the deuteration products, identification of TPR products, and calibration of the TPR spectra with standard mixtures.

For measurement of reactor temperature during TPR experiments, a digital thermocouple module (Metrabyte M1311) with RS-232 communications was used to monitor the reactor temperature. A IBM PS/2 Model 60 personal computer was used to gather raw mass spectral intensities from the MS and temperature measurements from the thermocouple module. A detailed description of the data acquisition system is given in Appendix C.

After the MS, a thermal conductivity detector (Gow-Mac) was attached to the effluent stream and it was used for product detection in the case of chromatographic observations. The TCD was contained in an insulated box and connected to a Gow-Mac power supply and HP3396A digital integrator. The TCD bridge current was set at 200 mA.

For C2H2, C2H4, and C2H6 separation, a 2 m Poropak NS column thermostatted at room temperature with an He flow of 180 cc/min. was used. For the separation of the acetylene oligomerization products, a 3.5 m SE-30 column (11.5% on chromosorb) at 298K, temperature programmed
from 298 K - 458 K in 12 min. with He flow of 80 cc/min. was used. For simultaneous separation of C₂ and C₄ products from acetylene hydrogenation, 2.7m Durapak column with a He flow of 30cc/min. was used at two different temperatures: The GC column was initially immersed in ice-salt bath (258 K) for separation of C₂ products and then in water bath (298 K) for C₄ product analysis. A typical gas chromatogram is shown in Figure 3-5 and the calibration data is given in Table 3-1.

A static volumetric adsorption apparatus used for determination of CO chemisorption is shown in Figure 3-6. It consists of an oil diffusion pump (Varian), a Welch duo-seal mechanical pump and MKS Baratron pressure transducers with a range of 0 to 13.3 kPa. The system was made of Pyrex glass. Purified helium and carbon monoxide were stored in 1-liter flasks. The catalyst was placed in the U-tube pyrex reactor, which was connected to the adsorption apparatus through a 10/30 ground glass joint. The 4-way stopcock of the reactor allowed either a flow configuration for catalyst reduction in H₂ flow or an isolated configuration for catalyst evacuation and gas adsorption experiment.

3.1.2 Materials

The materials and reagents used in this work are listed in Table 3-2. Hydrogen and helium from the gas cylinder were passed through an Supelpure (Supelco) purifier to further remove trace oxygen. Acetylene (99.6%) was purified by bulb-to-bulb distillation using liquid nitrogen and stored in a flask connected to the batch reactor apparatus.
Figure 3-5. Typical gas chromatogram of products from acetylene hydrogenation.
Table 3-1. Calibration Data for GC Analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative Retention Time (Min.)</th>
<th>Relative Response Factor</th>
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<tr>
<td>Ethane</td>
<td>1.808</td>
<td>1.000</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.047</td>
<td>1.072</td>
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<tr>
<td>Acetylene</td>
<td>4.453</td>
<td>1.235</td>
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<tr>
<td>n-Butane</td>
<td>10.305</td>
<td>0.636</td>
</tr>
<tr>
<td>1-Butene</td>
<td>13.820</td>
<td>0.661</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>16.348</td>
<td>0.698</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>17.347</td>
<td>0.668</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>18.610</td>
<td>0.668</td>
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Figure 3-6. Apparatus for CO Chemisorption.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Supplier</th>
<th>Specification</th>
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</thead>
<tbody>
<tr>
<td>Pd(NH$_3$)$_4$(NO$_2$)$_2$</td>
<td>Alfa Products</td>
<td>35.34% Pd</td>
</tr>
<tr>
<td>$\gamma$ Al$_2$O$_3$</td>
<td>Union Carbide</td>
<td>Bulk Density 36 lbs/ft.$^3$</td>
</tr>
<tr>
<td></td>
<td>(Linde 60-50)</td>
<td>Hg Pore Volume 0.71 cc/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface Area 215 m$^2$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Fisher Scientific</td>
<td>Type 60A, Grade 633</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>Fisher Scientific</td>
<td>99.4%</td>
</tr>
<tr>
<td>NH$_4$HCO$_3$</td>
<td>Malinckrodt</td>
<td>100.0%</td>
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<tr>
<td>SE 30</td>
<td>Teklab</td>
<td></td>
</tr>
<tr>
<td>Chromosorb</td>
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<tr>
<td>Porapak NS</td>
<td>Teklab</td>
<td></td>
</tr>
<tr>
<td>Durapak</td>
<td>Teklab</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>Matheson</td>
<td>99.6%</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>Matheson</td>
<td>99.5%</td>
</tr>
<tr>
<td>D$_2$</td>
<td>Matheson</td>
<td>99.5% atom.</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Matheson</td>
<td>99.99%</td>
</tr>
<tr>
<td>CO</td>
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<td>99.5%</td>
</tr>
<tr>
<td>H$_2$</td>
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<td>99.999%</td>
</tr>
<tr>
<td>He</td>
<td>Liquid Air</td>
<td>99.999%</td>
</tr>
</tbody>
</table>
Ethylene, carbon monoxide, ammonia, and deuterium gases were used directly from the lecture bottle. Water, which was used in catalyst preparation was distilled and deionized.

3.1.3 Catalysts

3.1.3.1 Catalyst Preparation

Catalysts were prepared by two methods which differ only slightly in procedure: wet impregnation and incipient wetness. A 1% Pd loading was used in both cases and the Pd solution was prepared using palladium tetraamine nitrate ($\text{Pd(NH}_3)_4(\text{NO}_3)_2$).

One batch of the Pd/Al$_2$O$_3$ catalyst was prepared via the wet impregnation method, where the procedure used by Benesi and Curtis (1968) was followed. The alumina support was calcined at 673 K for 3 hours before use. The impregnating solution (0.2 M aqueous Pd solution) was added to the dried alumina with just enough water to make a slurry. Water was boiled off on a hot plate, then the catalyst was dried at 393 K for overnight. The catalyst is finally calcined at 573 K for 4 hr in a muffle furnace. Pd catalysts supported on SiO$_2$ were prepared in the same procedure. This catalyst was used in the study of CO effects.

Other batches of 1% Pd/Al$_2$O$_3$ catalyst were prepared by incipient wetness impregnation of $\text{Pd(NH}_3)_4(\text{NO}_3)_2$ on $\gamma$-alumina (Linde 503) for the study of K doping effect. The Pd salt was dissolved in deionized water in an amount equivalent to the the pore volume of alumina (0.71 cm$^3$/g) and was added slowly to the dried alumina while being stirred. The catalyst was dried at 393 K overnight.
K addition to Pd/Al₂O₃ catalysts was done in two ways. One series of K doped catalysts was prepared by adding 1 and 4 wt% K as potassium carbonate to Pd/Al₂O₃ catalyst, which had been prereduced in H₂ flow at 773K for 2 hours, by incipient wetness impregnation following the same procedure as for Pd loading. This series of catalysts was then dried at 393K and is designated "K-Pd/Al₂O₃". Another series was prepared by pretreating alumina with 1, 2, and 4 wt% K in a procedure similar to that used by Figoli and L'argeniere (1989). Dried alumina was impregnated with K₂CO₃ solution, dried and calcined at 873K for 7.5 hr. Pd was loaded on this treated support by incipient wetness impregnation and the catalyst was dried before storage. These materials are designated "Pd/K-Al₂O₃".

3.1.3.2 Dispersion Measurements

The dispersion of each catalyst was determined by chemisorption of carbon monoxide in a static adsorption apparatus. The adsorption isotherms were obtained at 298 K with pressures ranging from 13.3 Pa to 13.3 kPa. For the chemisorption experiment, 500 mg of catalyst packed in U-tube reactor was reduced in H₂ flow at 573 K for 2 hr, evacuated at 673 K for 2 hr, and cooled to the room temperature. A known amount of carbon monoxide was admitted to the adsorption cell. After the equilibrium pressure was reached (about 30–60 minutes), the amount of CO in the gas phase was subtracted from the amount admitted to give the amount adsorbed, then a second dose of CO was added. By repeating this process, the chemisorption isotherm was constructed.
Carbon monoxide adsorbs weakly on the support, so a double adsorption method (Sinfelt et al., 1973) was used to correct for this weakly bound fraction. After monolayer coverage of CO was obtained, the catalyst was evacuated for 10 min. to remove the weakly adsorbed CO. The adsorption process was then repeated resulting in the adsorption isotherm for the weakly bound fraction. The strongly bound chemisorption isotherm, which can be used in calculating the metal dispersion, was obtained by subtracting the weakly bound isotherm from the total chemisorption isotherm.

The dispersion (the accessible fraction of Pd metal) was calculated from the number of Pd atoms which chemisorbs CO divided by total number of Pd atoms. Several values of the Pd:CO ratio ranging from 1.0 to 1.5 have been reported (Vannice and Garten, 1979; Sholten and Montfoort, 1962; Stephens 1959b; Vannice and Wang, 1981; Boitiaux et al., 1983), but it was assumed in our calculation that one CO atom adsorbs on one surface Pd atom so that dispersions are used only for comparative purposes.

A typical CO adsorption isotherm including both the total and weak parts is shown in Figure 3-7. A detailed calculation is given in Appendix D and the results are summarized in the Table 3-3.

Several batches of Pd/Al₂O₃ were prepared by both wet impregnation and incipient wetness impregnation method and the dispersion was determined to be difficult to control. When K was added to prerduced base catalyst (dispersion = 36.2%), the dispersion decreased slightly with K content (32.5% for 1% K catalyst; 26.1% for 4% K catalyst) indicating Pd sites were blocked at higher content of K.
Figure 3-7. Isotherms for CO adsorption on Pd/alumina.
Table 3-3. Dispersion of catalysts

<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Catalyst</th>
<th>Dispersion (%)</th>
<th>Catalyst</th>
<th>Dispersion (%)</th>
</tr>
</thead>
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<tr>
<td>Wet Impregnation</td>
<td>Pd/Al₂O₃</td>
<td>45.6</td>
<td>Pd/SiO₂</td>
<td>22.4</td>
</tr>
<tr>
<td>Incipient Wetness</td>
<td>Pd/4%K- Al₂O₃</td>
<td>23.2</td>
<td>4%K-Pd/Al₂O₃</td>
<td>26.1</td>
</tr>
<tr>
<td></td>
<td>Pd/2%K- Al₂O₃</td>
<td>32.5</td>
<td>1%K-Pd/Al₂O₃</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Pd/1%K- Al₂O₃</td>
<td>17.2</td>
<td>Pd/Al₂O₃ (base catalyst)</td>
<td>36.2</td>
</tr>
</tbody>
</table>

* Based on CO/Pd=1/1
3.1.4 Experimental Procedures

3.1.4.1 Reaction Studies of Acetylene Hydrogenation

Kinetic experiments were done in the recirculation batch reactor. 100 mg of catalyst was loaded into the U-tube reactor and the catalyst was reduced in H₂ flow at 773 K for 2 hr. The flow was then switched to He and the temperature was maintained at 773 K for an additional 30 min. to purge adsorbed H₂.

After the catalyst was cooled to room temperature, the reactor was bypassed and the recirculation system was filled with 5.3 kPa C₂H₂, 5.3 kPa H₂, and 90.4 kPa He. The reaction was executed at 298 K. The reaction mixture was periodically sampled, injected into the chromatographic column (Durapak), and analyzed by TCD.

3.1.4.2 Deuteration Reactions

For deuteration experiments, 100 mg (acetylene reaction) or 10 mg (ethylene reaction) of Pd/Al₂O₃ (40–60 mesh particles) was packed in the reactor and reduced at 773K for 1 hour in the recirculation system filled with 53 kPa H₂ (or D₂) and 53 kPa He with a liquid nitrogen trap in the circulating loop. The catalyst was reduced for two hours if CO had been adsorbed in a previous experiment.

When observing the acetylene deuteration reaction, 1.3 kPa C₂H₂, 1.3 kpa kPa D₂, and 103 kPa He were premixed and the reaction was initiated and followed at 323K. Samples of reaction product were periodically expanded into a sampling loop and injected into the chromatographic column for separation followed by analysis on the MS.
When observing ethylene deuteration, 13 kPa C₂H₄, 13 kPa D₂ and 80 kPa He were premixed and the reaction was initiated and followed at 223K.

3.1.4.3 TPR Experiments.

For TPR experiments, 50 mg of 200-325 mesh catalyst particles was packed in the reactor and reduced at 773 K for 1hr in the recirculation system filled with 53.2 kPa of H₂ and 53.2 kPa of He with a liquid nitrogen trap in the circulating loop. After reduction, the catalyst was flushed with He gas at 773 K for 30 minutes to remove adsorbed H₂ and it was then cooled to the adsorption temperature (normally 223 K) under He flow. A mixture of 73.2 Pa acetylene in 106.4 kPa He was circulated over the catalyst at 223 K for 15 minutes. In preparing the adsorption mixture, C₂H₂ was prediluted in He so that very small C₂H₂ doses could be repeated precisely. After adsorption, the apparatus was switched to TPR mode and the catalyst was flushed with He for 30 minutes to remove weakly bound acetylene and self-hydrogenation products. MS could be used to monitor this process if desired. The catalyst was the further cooled to 173 K, a flow of 20 cm³/min. H₂ and 180 cm³/min. He was established, and a linear temperature program at 5 K/min. was initiated. Mass spectra were recorded every 20 seconds until the catalyst reached 673 K. Ethylene TPR was done under the same conditions except the adsorption temperature (203 K) and TPR starting temperature (153 K).
3.2 Data Reduction Techniques

Three types of calculations outside the scope of simple procedures were performed.

3.2.1 Calculation of Kemball's Parameter

The Kemball's probability parameters for acetylene and ethylene deuteration have been determined from experimental measurements via computer calculations. Eight equations and one overall H/D balance equation with three parameters p, q, and s have been derived for acetylene deuteration as shown in the Appendix A. Since this mathematical system has more variables than equations along with inequality constraints, we have set up a least squares objective function based upon the sum of squares of the difference between the observed deuterium distribution of ethylene and the computed distribution. The objective function was then minimized using a standard non-linear optimization package, GRG2 (Lasdon et al., 1980, See Appendix E). In the case of ethylene deuteration, 18 H/D balance equations for the isotopic species generated via ethylene deuteration have been derived with four parameters p, q, r, and s, which were determined in a similar procedure.

In the computer program to calculate the Kemball's parameter, the simultaneous equations for each isotopic species represent the equality constraints while the non-negativity constraints for the parameters (p, q, r, and s) and the variables were imposed in the GRG2 program. Other information including the initial guess for each variable and the optimization parameters were also provided. Several sets of optimization
parameters were tested to find the best conditions for optimization. To generate an initial guess for the program, an isotopic distribution for the case where all the probabilities of elementary steps are 50% was determined by solving the simultaneous H/D balance equations. The optimization parameters and initial values used in this calculation are given in Appendix E.

In order to check the possibility of settling at a local minimum during optimization, other starting points were also tested, but the optimal points obtained were very close in each case, showing that a global minimum were reached. We also performed a stability test which showed that the parameters, p,q,r, and s, are not highly sensitive to minor errors in measurement of the deuterium distributions. Our derived H/D balance equations and optimization scheme were tested against the sets of calculated deuteration data reported (Kemball, 1956; Bond et al., 1964a, 1965b, 1966a), where the parameters determined by our scheme agreed well with their calculated parameters. Our calculation was also checked for a hypothetical case of no deuterium exchange (only D₂ ethylene or ethane exists in the product), where the predicted results (p= q= s= 1 for acetylene deuteration; p*= q*= s*= 1 with r* =0 for ethylene deuteration) were obtained in the calculation.

In all previous studies reported in the open literature, these parameters have been determined from the simultaneous equations by trial and error. For acetylene deuteration, two equations and a chart were used in computing the parameters so that a computer could not easily be used in this calculation (Bond, 1966b, 1968). The nine equations derived from the H/D balance in this study allowed us to avoid
the use of chart. The optimization technique was simple and efficient. Also the deuterium distribution obtained by our technique more closely followed the experimental distribution in Bond's work than their calculated distribution.

3.2.2 Determination of Deuterium Distribution in Products from the Deuteration Reaction

The products of deuteration reactions were analyzed at a fragmentation voltage of 70 eV which yields high sensitivity but also causes excessive fragmentation. Therefore, the composition of the isotopically enriched product was calculated using experimentally-determined fragmentation patterns for each of the possible isotopic species taken from the literature (Refer to Table 3-4). For C₂H₂ there are 3 isotopic species (D₀, D₁, and D₂), while for C₂H₄ and C₂H₆ there are 5 and 7 species respectively. We have monitored 5 masses from 24–28 AMU for C₂H₂, 8 mass from 25–32 AMU for C₂H₄ and 12 masses from 25–36 AMU for C₂H₆. In calculating the composition of the deuteroethanes, the relative sensitivity of each species was taken into account since there is a significant variation in the overall sensitivity of each species.

Since there were more observations (mass intensities) than unknowns (fraction of each deuterated species), an optimization was used to determine the unknowns. We have set up a least squares objective function from the sum of squares of the difference between the
Table 3-4. Experimental Fragmentation Pattern of C₂X₃⁺, C₂X₄⁺, and C₂X₆⁺

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<tr>
<th>Mass</th>
<th>( \text{C}_2\text{H}_2 )</th>
<th>( \text{C}_2\text{HD} )</th>
<th>( \text{C}_2\text{D}_2 )</th>
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<td>-</td>
<td>100.0</td>
<td>-</td>
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<tr>
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<td>12.0</td>
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<td>20.5</td>
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<tr>
<td>24</td>
<td>5.67</td>
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<table>
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<tr>
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<th>( \text{C}_2\text{HD}_2 )</th>
<th>( \text{C}_2\text{H}_2\text{D}_2 )</th>
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<td>-</td>
<td>100.0</td>
</tr>
<tr>
<td>34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.0</td>
<td>18.7</td>
<td>73.6</td>
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<td>-</td>
<td>-</td>
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<td>36.5</td>
<td>55.2</td>
<td>-</td>
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<td>-</td>
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<td>49.6</td>
<td>91.0</td>
<td>197.2</td>
<td>468.2</td>
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<tr>
<td>31</td>
<td>-</td>
<td>100.0</td>
<td>64.2</td>
<td>122.2</td>
<td>260.9</td>
<td>220.0</td>
<td>-</td>
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<tr>
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<td>100.0</td>
<td>72.9</td>
<td>232.4</td>
<td>286.8</td>
<td>155.9</td>
<td>63.6</td>
<td>99.2</td>
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<tr>
<td>29</td>
<td>76.2</td>
<td>316.7</td>
<td>220.7</td>
<td>91.0</td>
<td>58.5</td>
<td>41.4</td>
<td>-</td>
</tr>
<tr>
<td>28</td>
<td>388.5</td>
<td>168.1</td>
<td>99.3</td>
<td>57.5</td>
<td>67.7</td>
<td>52.2</td>
<td>7.0</td>
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<tr>
<td>27</td>
<td>104.3</td>
<td>78.2</td>
<td>56.5</td>
<td>41.5</td>
<td>28.3</td>
<td>15.5</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>68.1</td>
<td>44.9</td>
<td>22.9</td>
<td>12.5</td>
<td>8.00</td>
<td>6.90</td>
<td>7.00</td>
</tr>
<tr>
<td>25</td>
<td>7.80</td>
<td>6.70</td>
<td>3.80</td>
<td>2.80</td>
<td>1.30</td>
<td>1.00</td>
<td>-</td>
</tr>
</tbody>
</table>

| Relative Sensitivity | 1.00 | 0.95 | 0.89 | 0.84 | 0.78 | 0.73 | 0.68 |

* Mohler and Dibeler (1947)
* Diebeler et al. (1954)
* Amenomiya and Pottle (1968)
* Amenomiya and Pottle (1968), Normalized to \( \text{C}_2\text{H}_6 \)

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observed and computed spectra and minimized the function with non-negativity constraints on the mole fraction of each deuterated species using the GRG2 program.

In any given mass spectrum, the magnitude of the individual ions may vary greatly and the largest ions were found to dominate the optimization so that masses with minor intensities were ignored. To compensate for this problem, a weight of $1/(SO(i)+1)^2$ was applied to the square of the difference between the observed intensity, $SO(i)$, and the calculated intensity. When the extent of deuterium exchange was small, ions representing highly deuterated molecules were non-existent and if too many zeros were included, the results were skewed. Therefore, when it was clear that heavily deuterated species were not part of the product, these species were eliminated from the optimization. The validity of the calculation was finally checked by comparing observed intensities with calculated intensities. Optimization parameters for the GRG2 program were the same as those used in the calculation of Kemball’s parameters.

3.2.3 Determination of Reaction Products from TPR Spectra via Mass Spectrometry

During TPR, many products desorb, some at different temperatures, but many overlap. Take as an example the resultant spectrum in Figure 3–8. This figure shows the intensity of masses 30, 41, 43 and 78 as a function of temperature. Masses 14, 15, 26, 28, 56, 57, 58, 71, 84, 85 and 86 were also observed but are not shown in the figure in the interest of simplicity. The overall mass spectra were converted into the
Figure 3-8. Raw TPR spectra (mass spectral form) of acetylene adsorbed on Pd/alumina at 223K.
Figure 3–9a. TPR spectra (molar form) of acetylene adsorbed on Pd/alumina (dispersion = 45.2 %) at 223K.
Figure 3–9b. TPR spectra (molar form) of acetylene adsorbed on Pd/alumina (dispersion = 45.2 %) at 223K.

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individual component spectra (Figures 3-9a,b) to allow quantitative analysis. The composition of TPR products eluting at each moment was determined by the following procedure.

We first determined which hydrocarbon species were globally present in a TPR experiment by collecting all products from a complete run in a liquid nitrogen trap placed at the exit of the reactor. This sample was then injected into the carrier gas stream by thawing the trap quickly and the components were separated on a gas chromatographic column (SE 30 on chromosorb column, 14 ft.). The separated products were identified by their MS fragmentation patterns. In the example case, the major products identified were ethane, n-butane, n-hexane, benzene, and cyclohexane along with higher paraffins including n-octane and n-decane and traces of pentane, 2-methylpentane, 3-methylpentane, methylcyclopentane, and heptane (See Table 3-5). The n-octane, n-decane and trace components were difficult to determine quantitatively and were therefore not used in the quantitation calculation. A standard mixture was then prepared from all the known components and this standard was injected in known quantities to generate a fragmentation pattern and sensitivity factor for each component (Table 3-6). Carefully selected ions which are characteristic of each component were monitored in this process. The fragmentation patterns were corrected to response per micromole and this procedure was periodically performed to correct for changes in the MS sensitivity with time.

This calibration procedure allowed us to construct a matrix such that the columns represented the fragmentation patterns of individual components and the rows represented particular mass numbers. An
Table 3-5. Identification of Major TPR Products by GC/MS

<table>
<thead>
<tr>
<th>Product</th>
<th>( t_r^a ) (min.)</th>
<th>Most Significant Masses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>28</td>
<td>27 30 26 29 25</td>
</tr>
<tr>
<td>TPR(^b)</td>
<td>51 100.0</td>
<td>34.8 19.8 26.1 21.5 3.8</td>
</tr>
<tr>
<td>Sample(^c)</td>
<td>146 100.0</td>
<td>30.5 19.1 20.7 21.2 2.8</td>
</tr>
<tr>
<td>n-Butane</td>
<td>43</td>
<td>29 27 28 41 39 42 58</td>
</tr>
<tr>
<td>TPR(^b)</td>
<td>174 100.0</td>
<td>65.7 53.9 53.1 43.5 16.4 17.4 6.4</td>
</tr>
<tr>
<td>Sample(^c)</td>
<td>261 100.0</td>
<td>44.7 34.6 34.6 33.5 11.5 14.5 4.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>41</td>
<td>43 57 29 27 56 42 86</td>
</tr>
<tr>
<td>TPR(^b)</td>
<td>1578 100.0</td>
<td>82.1 81.7 70.5 45.7 43.4 44.6 5.6</td>
</tr>
<tr>
<td>Sample(^c)</td>
<td>1500 100.0</td>
<td>85.2 61.6 74.7 48.8 35.3 48.8 3.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>78</td>
<td>51 39</td>
</tr>
<tr>
<td>TPR(^b)</td>
<td>2625 100.0</td>
<td>28.6 27.8</td>
</tr>
<tr>
<td>Sample(^c)</td>
<td>2445 100.0</td>
<td>27.3 30.7</td>
</tr>
<tr>
<td>Cyclo-hexane</td>
<td>56</td>
<td>41 55 42 84 69 43</td>
</tr>
<tr>
<td>TPR(^b)</td>
<td>2835 100.0</td>
<td>87.9 37.0 35.8 34.3 18.6 15.5</td>
</tr>
<tr>
<td>Sample(^c)</td>
<td>2590 100.0</td>
<td>109.3 41.2 46.7 35.8 11.6 20.9</td>
</tr>
</tbody>
</table>

\(^a\) Retention time
\(^b\) TPR Product collected in liquid nitrogen trap was injected by replacing the cold trap by hot water bath rapidly.
\(^c\) Standard mixture of these compounds was injected through sampling valve.
<table>
<thead>
<tr>
<th></th>
<th>Nitrogen</th>
<th>Methane</th>
<th>Acetylene</th>
<th>Ethylene</th>
<th>Ethane</th>
<th>Butane</th>
<th>Hexane</th>
<th>Benzene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>78.9</td>
<td>148.0</td>
<td>12.0</td>
<td>68.0</td>
<td>16.0</td>
<td>8.0</td>
<td>5.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>0.0</td>
<td>1000.0</td>
<td>35.0</td>
<td>17.0</td>
<td>39.0</td>
<td>39.0</td>
<td>40.0</td>
<td>4.0</td>
<td>46.0</td>
</tr>
<tr>
<td>26</td>
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<td>0.0</td>
<td>1000.0</td>
<td>676.0</td>
<td>238.0</td>
<td>59.0</td>
<td>51.0</td>
<td>43.0</td>
<td>37.0</td>
</tr>
<tr>
<td>28</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>1000.0</td>
<td>358.0</td>
<td>97.0</td>
<td>38.0</td>
<td>151.0</td>
</tr>
<tr>
<td>30</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>186.0</td>
<td>11.0</td>
<td>13.0</td>
<td>0.0</td>
<td>2.0</td>
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<tr>
<td>41</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>355.0</td>
<td>1000.0</td>
<td>0.0</td>
<td>860.0</td>
</tr>
<tr>
<td>43</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>777.0</td>
<td>4.0</td>
</tr>
<tr>
<td>56</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>11.0</td>
<td>411.0</td>
<td>0.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>57</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>17.0</td>
<td>750.0</td>
<td>0.0</td>
<td>38.0</td>
</tr>
<tr>
<td>58</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>59.0</td>
<td>27.0</td>
<td>2.0</td>
<td>9.0</td>
</tr>
<tr>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>23.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>78</td>
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<td>0.0</td>
<td>0.0</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>47.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Sensitivity\(^a\) = 130000 95005 64613 188901 357517 659816 643360 605864 660793

\(^a\) Sensitivity in (Integrated Peak Intensity) / (Micromoles) / 1000
experimentally determined mass spectrum at any instant is the product of the matrix and the vector representing the moles of each component eluting at that instant. In order to effectively solve for the mole vector, we set up a least squares minimization of the difference between the actual spectrum and the computed spectrum. Non-negativity constraints were imposed on all components of the mole vector. The calculation was performed with the GRG2 program as in the analysis of deuterated products. By repeating this calculation for the set of TPR mass spectra, individual spectra for each product was obtained. In the optimization procedure, a weight of $1/(SO(1)+1)^2$ was also used to prevent dominance of masses with large intensities using the same GRG2 optimization parameters that were used for the calculation of Kemball's parameters. The product composition calculated at any given instant was used as the starting point for the next optimization. Several starting points for the initial data point were tested but all these calculations gave the same result. Validity of the calculation was finally checked by examining the difference spectra which were obtained by subtracting the calculated spectra from the observed spectra.
IV. DEUTERIUM TRACER STUDIES ON THE EFFECT OF CARBON MONOXIDE ON ETHYLENE SELECTIVITY IN ACETYLENE REACTION OVER Pd

The effect of CO on the ethylene selectivity in selective hydrogenation of acetylene has been studied using isotopic tracer methods. The effect of CO on the product distribution in the deuteration of acetylene and ethylene has been assessed using Kemball's method (1956) and the interaction of CO with adsorbed ethylene was investigated by displacement experiments.

4.1 Procedures

4.1.1. Deuteration Reactions with CO

1. Deuteration Reactions

The base conditions for deuteration experiments are as given in the experimental section (section 3.1.4.2). CO was used to modify these base reaction conditions by either 1) adding additionally 0.13 kPa CO along with the initial C₂H₂/D₂/He mixture (comixed) or 2) preadsorbing CO by circulating 0.13 kPa CO in 1.3 kPa He over the catalyst at 323 K. In this preadsorption step, the CO pressure corresponds to 9.2 CO molecules/Pd atom in the catalyst so that only a small portion of the CO actually adsorbs on the catalyst. Following preadsorption of CO, the reactor section was bypassed, but the unadsorbed CO was not evacuated. Instead, 1.3 kPa C₂H₄, 1.3 kPa D₂, and an additional 102 kPa He were mixed with the remaining CO, then the catalyst was brought back into the circulating loop at 323 K to initiate the reaction. When observing ethylene deuteration, 13 kPa C₂H₄, 13 kPa D₂ and 80 kPa He
were mixed and the reaction was initiated and followed at 223 K. As in
the acetylene deuteration reaction, CO was either added to the base
reaction mixture (comixed) or preadsorbed on the catalyst. Procedures
were the same as described above except that the CO pressures were
0.13 Pa and 1.33 Pa in the CO/C$_2$H$_4$/D$_2$/He mixture and 1.33 Pa CO was
used in the preadsorption experiment. Note that these CO pressures are
2–3 orders of magnitude lower than used in the C$_2$H$_2$ reaction. 1.33 Pa
CO corresponds to 0.9 CO/Pd and 0.13 Pa CO corresponds to 0.1 CO/Pd.

4.1.2. Adsorption Study

In order to test whether CO can displace C$_2$H$_4$ by competitive
adsorption, a displacement experiment was performed. For this
experiment, 100 mg of 200–325 mesh catalyst particles were initially
reduced in the same way as the deuteration reactions with the system
in circulation mode. After reduction, the catalyst was flushed with He
gas at 773 K for 30 minutes to remove adsorbed H$_2$ and it was then
cooled to the adsorption temperature (173 K) under He flow. A mixture
of 79 Pa C$_2$H$_4$ in 105 kPa He was circulated over the catalyst at 173 K
for 6 minutes then the apparatus was switched to flow mode and the
catalyst was flushed with He for 6 minutes to remove weakly bound C$_2$H$_4$
CO was then injected onto the catalyst as successive pulses and the
effluent from the reactor was continuously monitored by the mass
spectrometer.

4.2 Results

4.2.1. Acetylene Deuteration
Experiments were performed without CO, with CO mixed with reactants (comixed), and with CO contacted with the catalyst prior to introduction of other components (preadsorbed). Conversion versus time for each of these cases is given in Figure 4-1 while the selectivity to ethylene for each case is given in Figure 4-2. We observed a strong effect in overall reaction rate when CO was added but there is little difference whether CO is comixed or preadsorbed on the catalyst. \( \text{C}_2\text{H}_4 \) selectivity is not a strong function of conversion as in Figure 4-2 but CO does appear to modify the selectivity and the order of CO addition (comixed or preadsorbed) has a minor but observable effect on the selectivity.

Samples depicted in Figures 4-1 and 4-2 have also been subjected to deuterium content analysis and the ethylene distributions are detailed in Table 4-1. We have found that the deuterium product distribution is virtually independent of conversion, so these values have been reported in the vicinity of 50% conversion. In all cases, a dominance of the \( \text{d}_2 \) ethane species was observed but broadening of the distribution at the expense of the \( \text{d}_2 \) intensity was notable when CO was comixed or preadsorbed.

4.2.2. Ethylene Deuteration

Similar experiments were performed for the ethylene deuteration reaction. The rate of the ethylene reaction is several orders of magnitude faster than the acetylene reaction so that reaction conditions (most notably the reaction temperature) had to be adjusted to allow the observation of reasonable rates. Figure 4-3 compares the three cases, no CO, 1.33 Pa CO comixed and 0.13 Pa CO preadsorbed. There is
Figure 4-1. CO effect on the rate of acetylene deuteration over 100 mg Pd/Al2O3 at 323 K. (PC2H2)0 = 1.3 kPa, (Pd2)0 = 1.3 kPa. Run 1, without CO; Run 2, with 0.13 kPa CO comixed; Run 3, with 0.13 kPa CO preadsorbed.

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Figure 4-2. Ethylene selectivity in acetylene deuteration over Pd/Al₂O₃. Experimental conditions and run types as in Fig. 4-1.
Table 4-1. Effect of CO on acetylene deuteration
(C$_2$H$_2$ 1.3kPa, D$_2$ 1.3kPa at 323 K, 100 mg catalyst)

<table>
<thead>
<tr>
<th>Ethylene D Distribution</th>
<th>Parameters$^b$</th>
<th>Conv(%)</th>
<th>S$_{C2H4}$$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d$_0$</td>
<td>d$_1$</td>
<td>d$_2$</td>
</tr>
<tr>
<td>Run 1 (Without CO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.$^d$</td>
<td>0.0</td>
<td>0.151</td>
<td>0.636</td>
</tr>
<tr>
<td>Calc.$^b$</td>
<td>0.0</td>
<td>0.152</td>
<td>0.636</td>
</tr>
<tr>
<td>Run 2 (With 0.13kPa CO, comixed, CO/Pd = 9.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.$^d$</td>
<td>0.0</td>
<td>0.202</td>
<td>0.569</td>
</tr>
<tr>
<td>Calc.$^b$</td>
<td>0.0</td>
<td>0.202</td>
<td>0.569</td>
</tr>
<tr>
<td>Run 3 (With 0.13kPa CO, preadsorbed, CO/Pd = 9.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp.$^d$</td>
<td>0.0</td>
<td>0.187</td>
<td>0.597</td>
</tr>
<tr>
<td>Calc.$^b$</td>
<td>0.0</td>
<td>0.188</td>
<td>0.598</td>
</tr>
</tbody>
</table>

Calculated Deuterium Distribution$^b$

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>Vinyl (Surface Species)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d$_0$</td>
<td>d$_1$</td>
</tr>
<tr>
<td>Run 1</td>
<td>.744</td>
<td>.218</td>
</tr>
<tr>
<td>Run 2</td>
<td>.699</td>
<td>.248</td>
</tr>
<tr>
<td>Run 3</td>
<td>.726</td>
<td>.230</td>
</tr>
</tbody>
</table>

$^a$ Average d atoms / molecule
$^b$ Calculated from Kemball's method
$^c$ S$_{C2H4}$ = Y$_{C2H4}$(Y$_{C2H4}$ + Y$_{C2H6}$)
$^d$ Experimental result

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Figure 4-3. CO effect on the rate of ethylene deuteration over 10 mg Pd/Al₂O₃ at 223K (P₇₅₅ₙ₆)₀ = 13 kPa, (P₉₆)₀ = 13 kPa. Run 1, without CO; Run 2, with 1.33 Pa CO comixed; Run 3, with 0.13 Pa CO preadsorbed.
virtually no observable effect on the conversion versus time curve for ethylene deuteration when CO is preadsorbed at 0.13 Pa. At 1.33 Pa comixed CO, however, we see a strong poisoning of the reaction at high conversions, but the initial rate is only slightly affected.

The deuterium distributions of the ethylene reactant and ethane product are given in Table 4–2. The most abundant product species was $d_1$-ethane, which agrees with Bond's result (1966a) at similar conditions. With added CO, the most abundant species changed to $d_2$-ethane and the distribution became narrower. Also note that 0.13 Pa of CO preadsorbed on the catalyst affected the ethane distribution (with respect to the broadness of the distribution) to a greater extent than 1.33 Pa of comixed CO without a significant change in the reaction rate (Figure 4–3).

4.2.3. Ethylene Displacement Study

Displacement experiments shows that CO adsorption can proceed on an ethylene-precovered surface (Figure 4–4). Ethylene and ethane products were observed when CO pulses were added repeatedly to the precovered surface.

4.3 Discussion

A quantitative analysis of the product distribution of deuterated species from the acetylene or ethylene reaction is possible by Kemball's method (1956). Table 4–1 contains a synopsis of these calculations for the acetylene deuteration reaction with and without CO. Calculated and experimental distributions show excellent agreement. The computed parameters p, q, and s did not show a trend with conversion for the
Table 4-2. Effect of CO on ethylene deuteration
(C2H4 13 kPa, D2 13 kPa at 223 K catalyst 10 mg)

<table>
<thead>
<tr>
<th>Ethylene</th>
<th>Ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>d1</td>
<td>d2</td>
</tr>
</tbody>
</table>

Run 1 (Without CO)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>0.160</th>
<th>0.009</th>
<th>0.0</th>
<th>0.0</th>
<th>0.091</th>
<th>0.266</th>
<th>0.264</th>
<th>0.116</th>
<th>0.067</th>
<th>0.028</th>
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<tbody>
<tr>
<td>Calc.</td>
<td>0.144</td>
<td>0.053</td>
<td>0.013</td>
<td>0.002</td>
<td>0.088</td>
<td>0.269</td>
<td>0.271</td>
<td>0.115</td>
<td>0.037</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Run 2 (With 1.33 Pa CO, comixed, CO/Pd = 0.9)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>0.157</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.082</th>
<th>0.191</th>
<th>0.337</th>
<th>0.127</th>
<th>0.079</th>
<th>0.027</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>0.143</td>
<td>0.052</td>
<td>0.013</td>
<td>0.002</td>
<td>0.039</td>
<td>0.213</td>
<td>0.337</td>
<td>0.142</td>
<td>0.047</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Run 3 (With 0.13 Pa CO, preadsorbed, CO/Pd = 0.1)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>0.202</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.097</th>
<th>0.132</th>
<th>0.408</th>
<th>0.110</th>
<th>0.051</th>
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</thead>
<tbody>
<tr>
<td>Calc.</td>
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<td>0.047</td>
<td>0.008</td>
<td>0.001</td>
<td>0.016</td>
<td>0.159</td>
<td>0.415</td>
<td>0.119</td>
<td>0.027</td>
<td>0.004</td>
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</tbody>
</table>

Kemball’s Parameters

<table>
<thead>
<tr>
<th>p*</th>
<th>q*</th>
<th>r*</th>
<th>s*</th>
<th>Overall</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>0.88</td>
<td>0.55</td>
<td>0.78</td>
<td>0.58</td>
<td>13.9</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.84</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
<td>13.1</td>
</tr>
<tr>
<td>Run 3</td>
<td>0.67</td>
<td>0.83</td>
<td>0.62</td>
<td>0.83</td>
<td>14.0</td>
</tr>
</tbody>
</table>

* Experimental result
b Calculated from Kemball's method

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Figure 4-4. Displacement of preadsorbed ethylene by CO pulses. Temperature for ethylene adsorption and CO displacement = 193 K. The response of CO has been divided by 1000.
three cases (no CO, comixed, and preadsorbed). Only minor effects are noted as a function of conversion and the presence of CO and the contacting method has only a slight effect.

Our primary consideration is how CO affects the distribution of surface species and the ultimate mode by which the rates of reaction and the selectivity to ethylene are affected by CO. Clearly, the overall deuterium content of acetylene goes up when CO is added (see values for M in Table 4-1) and there is a corresponding increase in the deuterium content of the adsorbed vinyl species (Table 4-1). However, there is simultaneously a drop in the deuterium content of the ethylene product when CO is added (Table 4-1). These observations may be explained as follows. According to Bond's mechanism (1963; and a review by Webb, 1978) for acetylene hydrogenation over Pd (see also Figure 4-5), hydrogen (deuterium) adsorption is irreversible and ethylene formation proceeds primarily by vinyl disproportionation (reaction 4, Figure 4-5) suggesting that the hydrogen which is formed during vinyl disproportionation is not desorbed. Notice that when D₂ is used as the gas phase reactant, this disproportionation provides a source of H atoms which is the reason that the ethylene product is not exclusively d₂-ethylene. Hydrogen atoms liberated by vinyl reversal must either combine with acetylene or vinyl. When CO is added (either before or during the reaction), we have obtained a decline in the p value so vinyl reversal (reaction 4a in Fig. 4-5, probability 1-p) is enhanced over vinyl hydrogenation (reaction 4b in Fig. 4-5, probability p). This may be accomplished if adsorbed hydrogen produced by vinyl disproportionation is displaced by CO. However, the fact that the reversal reaction
Figure 4.5. Reaction mechanism for acetylene hydrogenation over Pd/Al2O3 suggested by Bond (1968).
is favored ensures a higher population of H (which comes from the hydrogen-rich radicals) than D and we expect a decline in the overall deuterium content of the ethylene as observed. This postulate is also consistent with the observation that $s$, which is the probability of incorporating deuterium in vinyl hydrogenation, decreases which has also been observed (Table 4-1).

One problem we have encountered is that we would like to be able to distinguish whether the primary effect of CO addition on the selectivity to ethylene during acetylene hydrogenation is to reduce the amount of adsorbed hydrogen or the reactivity or amount of adsorbed ethylene. Though these results show that CO reduces surface hydrogen, the acetylene hydrogenation mechanism (Bond 1963; and a review by Webb, 1978), on which Kemball's method is based does not allow us to make a direct observation regarding possible effects due to ethylene displacement or the blockage of ethylene reactivity because one of the fundamental assumptions in the mechanism is that desorption of adsorbed ethylene is certain (probability = 1.0) and that further reactions of ethylene are impossible. This requires the selectivity to ethylene to be 100% which of course is not quite true. Therefore, the relative effects on adsorbed hydrogen and ethylene cannot be deduced using this mechanism. We have considered extending Bond's theory to allow a small probability of ethylene hydrogenation, but the equations become very complex and we have been unable to accurately measure the ethane deuterium distribution because it arises in such low concentrations (the selectivity to ethylene is indeed high). Therefore, we have turned to
measuring the effect of CO on the hydrogenation of ethylene directly and hope to be able to use this data in further discussions regarding the selective hydrogenation of the acetylene.

The calculation results for ethylene deuteriation are given in Table 4-2. Unlike the case for acetylene deuteriation, Kemball's parameters (extracted from both the ethane and ethylene deuterium distributions) are strongly dependent upon degree of conversion as in Figure 4-6. Deuterium distributions are difficult to obtain in the low conversion region because the amount of ethane is not large enough to be analyzed accurately. High conversions of ethylene tend to give randomly scrambled products so that all reactions extrapolate toward the same parameters. Therefore, we have chosen to compare parameters near 14% conversion which is the lowest practical conversion for which reliable data could be extracted. In ethylene deuteriation, the calculated product distribution also shows reasonable agreement with the experimental distributions. The values of Kemball's parameters showed large changes with CO, reflecting the corresponding changes in the product distribution. We also observe that preadsorbed CO has the greatest effect on Kemball's parameters even at the lowest partial pressure of CO.

Table 4-2 shows that the values of p* and r* dropped with addition of CO while those of q* and s* increased. These results are equivalent to an increase in the probability of desorption of ethylene 1-p*, a decrease in the probability of reversal of ethyl r*, and increases in the probabilities of deuterium incorporation, q* and s*. In other words, when CO is added, ethylene desorption is favored, ethyl reversal is suppressed, and hydrogenation depends less on surface hydrogen which comes from the hydrogen-rich adsorbed hydrocarbon
Figure 4–6. Kemball's parameters in ethylene deuteration over Pd/Al₂O₃. Experimental conditions as in Fig. 4–3.
species. With a decrease in adsorbed ethylene, further deuterium exchange between ethylene and ethyl would decrease. With the decrease of ethyl reversal, the amount of surface hydrogen would decrease and the deuteration reaction would depend more on deuterium from the gas phase. Therefore, the product from the deuteration of ethylene, \( \text{d}_2 \)-ethane, is expected to be predominant and the deuterium distribution in ethane should become a narrower, which agrees with the observed changes in the experimental deuterium distribution.

The observation that the probability of ethylene desorption is enhanced in the presence of CO can be explained by two possible alternatives. The first possibility is direct displacement of adsorbed ethylene by CO during the reaction, and the second possibility is a decrease in the availability of surface hydrogen for the conversion of adsorbed ethylene in which case it would be more likely that ethylene desorbs rather than reacts. If this latter case is the main reason that CO enhances ethylene desorption, we should observe a parallel decrease in the probability of ethyl hydrogenation, \( 1 - r \), since the source of hydrogen in the two additional steps are the same. (The parameters \( q \) and \( s \), which represent the source of hydrogen, were similar in each case as seen in Table 4-2). But the observed result is the opposite; an increase in the probability of ethyl hydrogenation was observed.

Furthermore, the observed overall ethylene deuterium distribution cannot be explained by the hydrogen displacement theory. The ethylene deuterium distribution depends on the relative rates of the deuterium exchange reaction and the direct hydrogenation (deuteration) reaction. If the surface concentration of hydrogen is reduced, the adsorbed hydrocarbon intermediate \( \text{C}_2\text{X}_2(a) \) would tend to undergo the reverse
reaction rather than the forward hydrogenation reaction so that the
degree of deuterium exchange would increase. This is similar to the
observations already made for acetylene deuteration. However, for
ethylene deuteration, CO caused a decrease in the deuterium exchange,
evidenced by a sharper distribution around d₂ ethane. Therefore, it is
concluded that direct displacement of ethylene by CO is the main
reason for the reduction in surface ethylene. The ethylene displacement
experiment showed directly that CO can displace ethylene preadsorbed on
Pd (Figure 4-4), and therefore the alternative that CO directly displaces
adsorbed ethylene is feasible.

Our results also show that preadsorbed CO is more effective in
altering the ethane deuterium distribution than comixed CO even though
a smaller amount of preadsorbed CO was used. The relatively small
amount of preadsorbed CO (0.1 CO/Pd), however did not significantly
alter the hydrogenation rate. These observations are easily explained.
Preadsorbed CO (0.1 CO/Pd) simply dilutes the surface concentration of
ethylene. Since the hydrogenation reaction involves one surface
hydrocarbon species and surface hydrogen, we expect a reduction in
surface hydrocarbons to linearly affect the rate of the hydrogenation
reaction. Exchange occurs primarily via disproportionation of two surface
hydrocarbons, so we expect a greater effect on the exchange reaction as
observed. In the preadsorption case, CO does not have to compete with
ethylene while in the comixed case, it must displace ethylene. In Figure
4-3, we see that the initial rate of the ethylene reaction is similar in
all cases. However, the rate of the reaction falls rapidly in the comixed
case as CO coverage increases via successful competition with ethylene
for surface sites.
With these results in hand, we turn our attention to the application of these theories to the selective removal of acetylene from raw ethylene streams and the effect of CO under conditions nearer to the actual conditions used industrially. First, our studies have been performed at subambient temperatures while real processes operate at about 333–353 K. However, Bond (1966b) has shown that the effect of temperature on both the acetylene and ethylene hydrogenation reactions are similar. Higher temperatures generally promote conversion of acetylene to vinyl or ethylene to ethyl rather than causing a complete shift in reaction mechanism. Therefore, we cautiously suggest that the results we have obtained are roughly applicable to industrial temperatures. Also, we must consider that we have studied the acetylene reaction at high partial pressures of acetylene compared to industrial conditions where the actual process stream might be of the order 0.35% acetylene, 0.40% H₂, and the balance ethylene with the reaction proceeding nominally at atmospheric pressure. Under these conditions nearer the actual conditions, ethylene may successfully compete with acetylene for Pd sites (Guczi, 1979) while our conditions virtually exclude this possibility.

Now consider the overall conversion processes which probably occur under real conditions:

\[
\begin{align*}
2H & \rightarrow C_2H_4(a) \\
C_2H_2(a) & \rightarrow C_2H_4(a) \\
4H & \rightarrow C_2H_6(a) \\
C_2H_4(a) & \rightarrow C_2H_6(a) \\
2H & \rightarrow C_2H_6(a)
\end{align*}
\]

(from adsorption of excess C₂H₄ in the feed)
To form \( \text{C}_2\text{H}_6 \) from \( \text{C}_2\text{H}_2 \), the ethylene intermediate which is produced via single hydrogenation of acetylene undergoes a second hydrogenation, or acetylene is hydrogenated after a single adsorption to \( \text{C}_2\text{H}_6 \). Another source of \( \text{C}_2\text{H}_6 \) is via hydrogenation of ethylene which competes for Pd sites. McGown et al. (1977, 1978) suggested that \( \text{C}_2\text{H}_6 \) comes mainly from gas phase \( \text{C}_2\text{H}_4 \) when studying the ethylene-rich mixture, \( \text{C}_2\text{H}_2 \) 14\%, \( \text{C}_2\text{H}_4 \) 57\%, \( \text{H}_2 \) 29\%. However, others such as Guczi et al. (1979) and Al-Ammar et al. (1979) argue that the main route to \( \text{C}_2\text{H}_6 \) is direct hydrogenation of \( \text{C}_2\text{H}_2 \) but their experiments were done with acetylene-rich mixtures. Another proposed route to \( \text{C}_2\text{H}_6 \) formulation was given by Sarkany et al. (1984) as \( \text{C}_2\text{H}_4 \) hydrogenation on support sites of aged catalysts. Our results suggest that CO displaces ethylene or blocks adsorption of ethylene, which favors the theory that the primary effect of CO is to slow the formation of \( \text{C}_2\text{H}_6 \) by reducing adsorbed ethylene, not by halting direct hydrogenation of acetylene to ethane through the ethylidyne species.

Conversely, Al-Ammar et al. (1978a, 1978b, 1979) suggested the primary effect of CO on ethylene hydrogenation is to block hydrogen adsorption sites. They postulated that ethylene adsorbs dissociatively on metal sites and molecularly on other sites, possibly carbonaceous overlayers, as a secondary adsorption. This secondary adsorption was thought to be involved in hydrogenation and was found to be independent of CO preadsorption. However, our \( \text{C}_2\text{H}_4 \) displacement experiments show that adsorbed ethylene can be displaced as ethylene by CO. This observation indicates that ethylene adsorbs on the metal surface associatively to some extent, if we assume that CO adsorbs only
on metal sites. Our deuterium tracer experiments also showed that carbon monoxide displaces ethylene that is directly involved in the hydrogenation, and these observations cannot be explained with the secondary adsorption theory.

An effect on hydrogen adsorption sites was also suggested in the study by Leviness et al. (1984) and Weiss et al. (1984), who argued that CO effectively competes with hydrogen atoms for ethylene hydrogenation, while reducing the rate of acetylene hydrogenation. The possibility that CO blocks ethylene adsorption was excluded since the primary sites for ethylene adsorption during the selective hydrogenation of acetylene was thought to be support sites which are activated by the accumulation of surface polymer. We cannot make a direct comparison of our results with this study since we have studied fresh catalysts.

4.4 Conclusions

1. Addition of CO to the reaction mixture increased the probability of ethylene desorption during the ethylene deuteration experiment, which is ascribed to CO displacement of ethylene.

2. CO addition decreased the probability of hydrogenating adsorbed vinyl in acetylene deuteration, which is caused by displacement of surface hydrogen by CO.

3. In the industrial process of selective hydrogenation, where independent hydrogenation of ethylene is significant, the selectivity improvement with CO addition is largely due to displacement of ethylene rather than that of hydrogen.
V. TPR STUDIES OF ACETYLENE AND ETHYLENE ADSORPTION ON Pd

In this chapter, the development of the TPR experiment and its application to the adsorption of acetylene and ethylene on Pd/Al₂O₃ and Pd/SiO₂ to investigate the behavior of the surface species is reported.

5.1 Adjustment of TPR Conditions and Interpretation of Spectra

The standard conditions for the acetylene TPR experiment which are described in the section 3.1.4.3. (experimental section) has been determined after several exploratory TPR experiments at various conditions to get meaningful TPR spectra.

A subambient temperature was used for the adsorption of acetylene to minimize decomposition but very low temperature resulted in excessive physisorption of acetylene, which interfered the TPR spectra. In order to investigate effects associated with physically adsorbed acetylene, a series of experiments on Pd/Al₂O₃, Pd/SiO₂, Al₂O₃ and SiO₂ were performed. Results given in Table 5–1 show the effect of physisorbed acetylene, and we immediately note physisorbed acetylene in large quantities remaining on the alumina support even after extended flushing (> 30 min.) with He. The SiO₂ support shows considerably less physisorbed C₂H₂ than Al₂O₃ and this apparently translates to much smaller quantities of C₂ products which are obtained from Pd/SiO₂ under TPR conditions than from Pd/Al₂O₃. Notice that C₄–C₆ products from Pd/SiO₂ compare closely to Pd/Al₂O₃. Also, compare the yield of C₂ species from Al₂O₃ (36.80 μmoles/g as acetylene) to Pd/Al₂O₃ (38.42 μmoles/g as ethylene and ethane) and compare C₂ species from SiO₂ (1.85 μmoles/g) to Pd/SiO₂ (4.48 μmoles/g). In the case of Pd/Al₂O₃, the vast majority of the C₂ products therefore
<table>
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<tr>
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<th>Pd/Al₂O₃</th>
<th>Pd/SiO₂</th>
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<th>SiO₂</th>
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<tr>
<td></td>
<td>μmole/g T(K)</td>
<td>μmole/g T(K)</td>
<td>μmole/g T(K)</td>
<td>μmole/g T(K)</td>
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<td>28.41 222</td>
<td>4.48 248</td>
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<td>4.21 254</td>
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<td>-</td>
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<td>n-hexane</td>
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<td>1.41 307</td>
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<td>-</td>
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<tr>
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<td>1.42 321</td>
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</tr>
<tr>
<td></td>
<td>0.12* 573</td>
<td>0.49* 523</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>cyclo-hexane</td>
<td>5.67 350</td>
<td>2.25 344</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* broad peak, not complete by 573 K

Table 5-1. Effect of Physisorbed Acetylene on Acetylene TPR (146.3 Pa C₂H₂ partial pressure, 15 min. exposure, 223 K, 100 mg catalysts)

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may be attributed to material originally adsorbed on the support. However, we find that ethane and ethylene elute from Pd/Al₂O₃ during TPR at much lower temperatures (column 1) than acetylene from Al₂O₃ (column 3). Our interpretation of these phenomena are that, as physisorbed acetylene elutes slowly from the support during TPR (in the case of Pd/Al₂O₃), it readsorbs on vacant Pd sites which have been created by hydrogenation of acetylene and is hydrogenated to ethane and ethylene. As we will discuss in chapter 6, there are single, isolated Pd sites which can accommodate hydrogen adsorption and supply hydrogen for this reaction. Since physisorbed ethylene and ethane on Al₂O₃ at 223K determined by TPR in separate experiments were small compared to acetylene physisorbed on Al₂O₃, ethane and ethylene products from TPR over Pd/Al₂O₃ would elute much faster than acetylene since they are not adsorbed on Al₂O₃ as strongly as acetylene (acetylene probably undergoes many adsorption/desorption cycles before eluting) and therefore appear as products at temperatures lower than acetylene from Al₂O₃.

The conditions for TPR experiments have been adjusted so that the effect of undesired physisorption was minimized as much as possible. The catalyst amount was decreased to 50mg and the catalyst particle size to 200/325 mesh to facilitate acetylene flushing. The adsorption pressure of acetylene was lowered to 73.2 Pa but much lower acetylene pressure could not be used. When 20.0 Pa acetylene was adsorbed, a larger amount of higher oligomers were produced at the expense of C₄ and C₆ products (Table 5-2). These higher oligomers were difficult to calibrate with our system due to their low vapor pressure.
Table 5-2. Effect of Adsorbate Pressure on TPR of Acetylene (15 min. exposure, 223 K, 50 mg Pd/Al₂O₃)

<table>
<thead>
<tr>
<th></th>
<th>P&lt;sub&gt;C₂H₂&lt;/sub&gt; = 73.2 Pa (Pd:C₂H₂ = 1:9.5)</th>
<th></th>
<th>P&lt;sub&gt;C₂H₂&lt;/sub&gt; = 20.0 Pa (Pd:C₂H₂ = 1:2.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmole/g</td>
<td>T(K)</td>
<td>µmole/g</td>
</tr>
<tr>
<td>acetylene</td>
<td>1.16</td>
<td>205</td>
<td>-</td>
</tr>
<tr>
<td>ethylene</td>
<td>7.78</td>
<td>213</td>
<td>1.42</td>
</tr>
<tr>
<td>ethane</td>
<td>34.82</td>
<td>215</td>
<td>17.90</td>
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<td>n-butane</td>
<td>8.34</td>
<td>237</td>
<td>5.04</td>
</tr>
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<td>n-hexane</td>
<td>2.99</td>
<td>288</td>
<td>1.34</td>
</tr>
<tr>
<td>benzene</td>
<td>0.70</td>
<td>325</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>0.88&lt;sup&gt;a&lt;/sup&gt;</td>
<td>640</td>
<td>0.88&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>7.56</td>
<td>340</td>
<td>1.77</td>
</tr>
<tr>
<td>C₆&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.3 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>497</td>
<td>1.3 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> broad peak, not complete by 673 K
<sup>b</sup> integrated intensity of mass 43 characteristic of C₆ and heavier paraffins.
The adsorption temperature could not be raised above 223K. When adsorption was done at 243K (Table 5-3), significant portions of higher hydrocarbon products were found to be removed during flushing. With 203K adsorption, the physisorption of acetylene was much heavier so that it increased the yields of ethane significantly and even affected that of C₄ product.

Though the C₂ products in acetylene TPR appear to arise primarily from physisorbed acetylene, the C₄ and C₆ oligomers are rather insensitive to the presence of physically adsorbed acetylene under the adsorption conditions which have been employed and these oligomers were not observed during the postadsorption flushing process. Therefore, the oligomers appear to represent the products which can be obtained from the species which were originally adsorbed on Pd.

The reproducibility of TPR spectra was tested in three identical runs. (Table 5-4). In the second run, the same catalyst was tested after reduction and He purge while new catalyst from the same batch was used in the third run. The resultant spectra are similar each other to allow a reliable comparison of TPR spectra obtained at different conditions (except benzene whose peaks were very broad and incomplete by the end of TPR run so that accurate integration could not be obtained).

The acetylene TPR spectra showed significant changes in the yield of cyclic products when the same experiment was done after some time period (as the TPR spectra in Table 5-2 and Table 5-4). This problem is not associated with run to run variability but is due to a change in the prediluted acetylene/helium mixture. Similar changes in cyclic oligomer yields were also observed in the preliminary experiments.
<table>
<thead>
<tr>
<th></th>
<th>$T_{ads} = 203$ K</th>
<th>$T_{ads} = 223$ K</th>
<th>$T_{ads} = 243$ K</th>
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</thead>
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<td>$\mu$ mole/g T(K)</td>
<td>$\mu$ mole/g T(K)</td>
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<tr>
<td>acetylene</td>
<td>55.52 219</td>
<td>1.16 205</td>
<td>-</td>
</tr>
<tr>
<td>ethylene</td>
<td>34.76 220</td>
<td>7.78 213</td>
<td>-</td>
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<tr>
<td>ethane</td>
<td>53.80 226</td>
<td>34.82 215</td>
<td>7.14 203</td>
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<tr>
<td>n-butane</td>
<td>11.36 234</td>
<td>8.34 237</td>
<td>5.38 239</td>
</tr>
<tr>
<td>n-hexane</td>
<td>3.07 290</td>
<td>2.99 288</td>
<td>3.03 286</td>
</tr>
<tr>
<td>benzene</td>
<td>0.66 327</td>
<td>0.70 325</td>
<td>1.69 328</td>
</tr>
<tr>
<td></td>
<td>0.92a 601</td>
<td>0.88a 640</td>
<td>0.25 623</td>
</tr>
<tr>
<td>cyclo-hexane</td>
<td>7.28 343</td>
<td>7.56 340</td>
<td>7.51 343</td>
</tr>
</tbody>
</table>

*a broad peak, not complete by 673 K*
Table 5-4. Reproducibility of the TPR Spectra of Acetylene
(73.2 Pa C₂H₂ partial pressure, 15 min. exposure, 223K, 50 mg Pd/Al₂O₃)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1st. Run</th>
<th>2nd. Run</th>
<th>3rd. Run</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pmole/g</td>
<td>T(K)</td>
<td>pmole/g</td>
</tr>
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<td>acetylene</td>
<td>4.60</td>
<td>213</td>
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<tr>
<td>ethylene</td>
<td>10.95</td>
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<td>13.20</td>
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<tr>
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<td>37.19</td>
<td>221</td>
<td>39.67</td>
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<tr>
<td>n-butane</td>
<td>7.57</td>
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<td>8.49</td>
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<tr>
<td>n-hexane</td>
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<tr>
<td>benzene</td>
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<td>328</td>
<td>2.36</td>
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<td></td>
<td>0.96c</td>
<td>629</td>
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<td>341</td>
<td>10.78</td>
</tr>
</tbody>
</table>

* Same catalyst was reduced before 2nd. run.
* Fresh catalyst of the same batch with first run.
* Broad peak, not complete by 673 K
coupled with small changes in the acetylene adsorbate pressure. As long as the same dilution mixture was used, run to run reproducibility was observed and therefore, in each table presented in this report where we make column to column comparisons, the same dilution mixture was used.

It was not attempted to calculate kinetic parameters for desorbed products (such as activation energies of desorption) due to virtually unavoidable experimental difficulties due to heavy physisorption of acetylene during the TPR experiment as discussed above. Our standard TPR conditions were checked for transport effects according to Gorte's criteria (1982) (See Appendix B) and there is a possibility of concentration gradients in the catalyst pellet even though other problems such as lag time in the catalyst bed, gas diffusion within the catalyst pore, and readsorption of TPR products (other than benzene possibly) were not probable. TPR experiments were therefore focused on obtaining qualitative information on the adsorption of acetylene and ethylene on Pd.

5.2 Results of TPR experiments

The results of acetylene TPR and TPD experiments executed at the standard condition are given in Table 5-5 (See also Figure 3-9a,b for acetylene spectra). It is shown in the TPR spectra that ethane, acetylene, ethylene, n-butane, n-hexane, benzene, and cyclohexane are formed from acetylene adsorption at 223K. In contrast, only acetylene, benzene and small amount of C4 products were observed in TPD, which show a partial recovery of adsorbed species from acetylene. Almost 50%
Table 5-5. Comparison of Acetylene TPR and TPD
(73.2 Pa C₂H₂ partial pressure, 15 min. exposure, 223K, 50 mg Pd/Al₂O₃)

<table>
<thead>
<tr>
<th></th>
<th>TPR</th>
<th>TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmole/g</td>
<td>T(K)</td>
</tr>
<tr>
<td>acetylene</td>
<td>1.16</td>
<td>205</td>
</tr>
<tr>
<td>ethylene</td>
<td>7.78</td>
<td>213</td>
</tr>
<tr>
<td>ethane</td>
<td>34.82</td>
<td>215</td>
</tr>
<tr>
<td>n-butane</td>
<td>8.34</td>
<td>237</td>
</tr>
<tr>
<td>n-hexane</td>
<td>2.99</td>
<td>288</td>
</tr>
<tr>
<td>benzene</td>
<td>0.70</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td>0.88b</td>
<td>640</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>7.56</td>
<td>340</td>
</tr>
<tr>
<td>total carbonc</td>
<td>194.</td>
<td>132.</td>
</tr>
</tbody>
</table>

- a sum of all C₄ products; primarily butenes.
- b broad peak, not complete by 673 K
- c total carbon recovered, μmole/g
more total carbon in the form of various hydrocarbons and almost twice as much carbon as oligomers (C₄⁺) were recovered in the TPR experiment versus the TPD experiment.

TPR spectra of ethylene adsorbed at 203 and 298K are given in Table 5-6. When ethylene was adsorbed at 203K, a small amount of ethane was produced along with production of benzene and high oligomers at higher temperatures. Adsorption at room temperature produced methane, butane and hexane in addition to reduced amounts of ethane and high oligomers.

5.3 Discussion

When acetylene is adsorbed on Pd at the base conditions of 223K, the surface species were recovered primarily as aliphatic oligomers (n-butane, n-hexane) and cyclic oligomers (benzene, cyclohexane) upon TPR as in Table 5-5. C₂ products are believed to be the result of acetylene physisorbed on Al₂O₃ as discussed previously. Aliphatic oligomers are in addition to benzene which have been observed by other researchers using TPD (Tysoe et al., 1983,1986; Logan et al., 1986). Cyclohexane observed in our TPR is believed to be the hydrogenated form of the benzene product. Our results are similar to a previous thermal desorption study (Reid et al., 1973c) on the existence of C₄ and C₆ products from Rh/silica. Aliphatic oligomers are also similar to products observed from the direct hydrogenation of acetylene (Bond and Wells, 1965a).
### Table 5-6. Effect of Adsorption Temperature on Ethylene TPR
(73.2 Pa C_{2}H_{4} partial pressure, 15 min. exposure, 223K, 50 mg Pd/Al_{2}O_{3})

<table>
<thead>
<tr>
<th></th>
<th>T_{ads.} = 203 K</th>
<th></th>
<th>T_{ads.} = 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmole/g T(K)</td>
<td>µmole/g T(K)</td>
<td></td>
</tr>
<tr>
<td>methane</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
</tr>
<tr>
<td>ethylene</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ethane</td>
<td>24.0</td>
<td>173</td>
<td>8.0</td>
</tr>
<tr>
<td>n-butane</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>n-hexane</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>benzene</td>
<td>0.5^{b}</td>
<td>548</td>
<td>-</td>
</tr>
<tr>
<td>C_{6}^{+}</td>
<td>4.2 \times 10^{7} \text{ c}</td>
<td>481</td>
<td>3.4 \times 10^{6} \text{ c}</td>
</tr>
<tr>
<td></td>
<td>8.2 \times 10^{5} \text{ c}</td>
<td>556</td>
<td>1.3 \times 10^{5} \text{ c}</td>
</tr>
</tbody>
</table>

^{a} 20.0 \text{ Pa of CO preadsorbed}

^{b} \text{ Not completed by 673 K}

^{c} \text{ Integrated intensity of mass 43 characteristic of C}_{6} \text{ and heavier paraffins.}
Surface oligomerization is probably completed during adsorption of acetylene rather than during the TPR experiment since acetylene interactions with Pd would be limited by the surface oligomers which had already formed during adsorption and because acetylene which could undergo further oligomerization was only available in the initial stages of TPR during desorption of the physisorbed acetylene. The products from the interaction of this acetylene with Pd were C₂ species, not oligomers as we have already discussed. Other researchers have also observed oligomer formation on Pd at low temperatures. In a TPD study by Tysoe et al. (1983), benzene was formed from acetylene on Pd [111] when adsorbed at 195K and benzene elution began at 195K and reached a maximum at 230K (which is comparable to our adsorption temperature of 223K) in the resultant TPD spectrum. Our results also demonstrated that oligomers can be formed directly on Pd during adsorption at 223K because masses 43 and 78 were observed initially while monitoring the effluent during the postadsorption flush and these are the result of benzene and C₄ paraffins and olefins.

Acetylene TPR spectra were found to depend upon the adsorption conditions, of which the partial pressure of acetylene during adsorption was the most significant variable affecting the product distribution among the oligomers. When the acetylene pressure was low (20.0 Pa), higher oligomers were produced in preference to C₄ and C₅ oligomers (Table 5-2). Monolayer coverage on Pd might not be obtained in the case of 20.0 Pa acetylene pressure even though the acetylene pressure corresponded to C₂H₂/Pd=2.6 because a significant fraction of the acetylene was physisorbed on the support. When the surface coverage is less than a full monolayer, surface oligomers can form without steric...
hindrance from neighboring acetylene molecules which contrasts with the case of the fully covered surface where the surface is sterically hindered. Sheridan (1945) and McGown et al. (1978) have discussed the packing arrangements of acetylene at high and low surface coverages. According to their theories, high surface coverages favor smaller oligomers in a greater overall abundance than low surface coverages and these theories compare favorably with our observations. Therefore, the partial pressure effect on oligomer formation can be traced to steric effects on the surface.

Oligomerization of acetylene to aliphatics apparently is initiated by a free radical which is formed either from partial hydrogenation of acetylene (Sheridan, 1945) or from dissociation of acetylene (Margitfalvi et al., 1981; Leviness et al., 1984). This free radical reacts in series with associatively adsorbed acetylene to form oligomers. We have observed some acetylene decomposition upon adsorption at 223K as evidenced by the formation of a small amount of ethylene which was observed in the effluent during the postadsorption catalyst flush. This ethylene must be produced via self-hydrogenation of acetylene during adsorption. Thus, a source of radicals from both dissociated acetylene and vinyl radicals is readily apparent.

TPR bands for benzene and cyclohexane (which are thought to come from the same common intermediate) were much broader and had larger areas than n-hexane (which has same number of carbons) even though the formation of the cyclic oligomers is more difficult due to a restricted configuration of molecules. This suggests that sites for the production of C₆ cyclic oligomers are distinct from sites for aliphatic oligomers. In fact, if we compare the changes in yields of cyclohexane and hexane for
different adsorption pressures (see Table 5-2) we note that the cyclohexane yield goes up by a factor of 4.3 while the hexane yield goes up by a factor of 2.3 when the acetylene adsorption pressure is increased from 20 to 73 Pa. This observation is further evidence that cyclic oligomers form on distinct sites and that these sites are more difficult to fill completely than aliphatic oligomer sites. Some possibilities concerning the exact identification of these sites may be extracted from the open literature. In acetylene hydrogenation over on Ni/pumice catalyst, Sheridan (1945) suggested that the sites for aliphatic oligomers were Ni[110], where polymerization of adsorbed acetylene is allowed without the rupture of C–Ni bonds due to wider spacings of the metallic sites. Pd[111] was found to be the most active among low Miller-index planes in benzene formation in several studies (Tysoe et al., 1983, 1986; Logan et al., 1986). Inoue et al. (1976) suggested the stepped surfaces around Pd[111] terraces as the active sites for benzene formation. We have no direct evidence to discriminate among these possibilities.

A desorption behavior different from aliphatic oligomers has also been observed for cyclic compounds. The yield of cyclic oligomers was similar for both TPR and TPD while aliphatic oligomers were not observed in TPD (Table 5-5). Cyclohexane was the primary cyclic product in acetylene TPR while benzene was the main product in TPD. These observations are consistent with a mechanism suggested by Tysoe et al. (1983) which involves an initial formation of a 1,3,5-hexatriene species followed by closure to cyclohexadiene. Formation of 1,3,5-hexatriene occurs by a series of bimolecular reactions. Cyclohexadiene can be desorbed as benzene (after Pd-induced dehydrogenation) during TPD or

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as cyclohexane via hydrogenation during TPR. There is no net consumption of hydrogen in the formation of benzene so its formation is allowed even in the absence of hydrogen (TPD).

The TPR spectrum of ethylene and acetylene are very different particularly in that the degree of ethylene oligomerization is very small compared to acetylene oligomerization (see Tables 5–5 and 5–6). When we monitored the reactor effluent during the postadsorption reactor flush following ethylene adsorption, the catalyst flushed quickly indicating that very little weakly bound material was present and therefore physisorption of ethylene was minor. However, a significant amount of ethane was detected during flushing and it follows that ethylene undergoes self-hydrogenation extensively.

When ethylene was adsorbed at 203K, ethane, benzene and high oligomers were detected upon subsequent TPR but the TPR spectrum following 298K adsorption was drastically different where methane, butane, and hexane were observed, the ethane and high oligomer yields were strongly attenuated, and benzene was not detected (Table 5–6). Butane and hexane probably originate from dissociatively adsorbed ethylene which is favored at the higher adsorption temperature.

Oligomerization of ethylene contrasts to the case of acetylene, where C₄ and C₅ oligomers are formed extensively from adsorption at 223K and the mechanism of ethylene oligomerization is clearly different from that of acetylene. The relative difficulty of ethylene oligomerization seems to come partly from its double bond as was suggested by Sheridan (1945). When ethylene is adsorbed associatively, each carbon atom shares one electron with the metal atom so the molecule has no unshared electron pair which can interact with another adsorbed molecule, unlike
acetylene which remains unsaturated upon adsorption on a metal and is reactive toward other hydrocarbons on the surface so that polymerization can propagate. Our results are consistent with the report of Stephens (1958) which requires residues of ethylene self-hydrogenation on Ni for the formation of C₄ oligomers. Webb (1978) also suggested that C₄ species arise from random polymerization of dissociatively adsorbed ethylene residues.

The methane product from TPR following ethylene adsorption at 298K appears to be related to a distinct surface species. Ethylene is known to form a stable ethyldyne species (C=CH) when it is adsorbed at room temperature on Pd (Beebe et al., 1985; Beebe and Yates 1986) and was observed to decompose at 450K. Other researchers (Komers et al., 1969; Tsuchiya and Nakamura, 1977) have observed methane from TPD of ethylene over Pt at 493K and Salmeron and Somorjai (1982) observed decomposition of ethyldyne into C and CH surface species at 493K. The formation and hydrogenation of ethyldyne is known to be a very slow process below 353K (Beebe et al., 1985). The source of methane from the TPR of ethylene adsorbed at 298K is likely this species which undergoes decomposition instead of hydrogenation due to its low reactivity. Ethyldyne apparently can not be formed at 203K so that no methane was observed in the resultant TPR.

5.4 Conclusions

1. Temperature programmed reaction in H₂ flow was applied successfully to acetylene and ethylene adsorbed on Pd/Al₂O₃ and various
desorption products were recovered from the surface including ethane, ethylene, acetylene, butane, hexane, benzene, cyclohexane etc. in the case of acetylene.

2. Of the products from acetylene TPR, C₄, C₆ oligomers were obtained without interference from physisorbed acetylene at the optimum experimental conditions so that products could be analyzed quantitatively and traced to the surface species which were originally formed on Pd during adsorption.

3. The observations that yields of oligomers from ethylene TPR were much smaller than those of acetylene TPR along with different desorption characteristics show that the mechanism of ethylene oligomerization is different from that of acetylene oligomerization.

4. The unique behavior of cyclic products from acetylene TPR indicates that distinct Pd sites which are specific for forming cyclic oligomers from acetylene are operable.
VI. TPR STUDIES ON THE EFFECT OF CO ON ACETYLENE AND ETHYLENE ADSORPTION ON Pd

TPR was applied to the adsorption of acetylene and ethylene on Pd/Al₂O₃ in the presence of coadsorbed carbon monoxide to examine the CO effect on the adsorption and surface reaction of acetylene and ethylene on Pd. Effects of carbon deposits on Pd on the oligomerization were also examined by acetylene TPR for comparison with the CO effect.

6.1 Experimental Procedures

In TPR experiments designed to study CO effects, CO was adsorbed in the batch recirculation system, either before or after adsorption of the hydrocarbon. In the case of preadsorption, the catalyst was exposed to CO for 15 minutes at the same temperature as hydrocarbon adsorption and flushed briefly with He. Then, the hydrocarbon was adsorbed and the standard TPR procedures followed. For postadsorption studies, the order of adsorption was reversed.

In an investigation on the effect of carbon deposits on the catalyst, surface carbon was deposited on Pd/Al₂O₃ by exposing the reduced catalyst to 73.2 Pa acetylene at 673K for 15 minutes. After flushing the catalyst for 10 min. with He, a standard TPR of acetylene followed.

6.2 Results

For reference purposes, the TPR of CO (under the same conditions as acetylene TPR) are presented in Figure 6-1. A broad CO band extending from 225 to 375K and methane band at 501K are the primary features of this spectrum.

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Figure 6-1. TPR spectra of carbon monoxide adsorbed on Pd/alumina at 223K.
The results of acetylene TPR with both preadsorbed and postadsorbed CO are summarized in Table 6-1. When 20.0 Pa of CO was preadsorbed (column 2), the yield of each oligomer was reduced by 27 - 65 % and all peaks were shifted to higher temperatures (except for the broad, high temperature benzene peak). However, when the same amount of CO was adsorbed following acetylene (postadsorbed, column 3), aliphatic oligomer yields showed slight increases while large increases for benzene and cyclohexane were evident. Peak temperatures were again higher than the base case without CO. When the pressure of postadsorbed CO was increased to 73.2 Pa (column 4), the oligomer yields were reduced slightly and the peaks shifted to even higher temperatures.

Large effects on C₂ products are also noted. For all the cases with CO, acetylene was the primary C₂ product, while ethane was the major product without CO. Peak temperatures for C₂ products were observed at 35 - 45K higher when compared to the case without CO. The C₂ and C₄ peak shapes are interesting in the case of preadsorbed CO and are therefore included in Figure 6-2. Notice that ethane and butane bands begin abruptly on the acetylene tail. This contrasts to the case without CO (Figure 3-9 and Table 6-1) where ethane and butane peaks are more symmetrical and appear at nearly the same temperature as acetylene.

Table 6-2 also includes the effect of CO on ethylene TPR. With preadsorbed CO, ethane and unreacted ethylene were produced at much higher temperatures along with a reduction in higher oligomer yields.

Similar experiments over a Pd/Al₂O₃ catalyst which was poisoned by surface carbon were also performed and the results are given in Table 6-3 where a significant effect on the TPR spectrum of acetylene is noted. The oligomer yields decreased by roughly 1/2 to 1/3 and the
Table 6-1. The Effect of CO on Acetylene TPR
(73.2 Pa C$_2$H$_2$ partial pressure, 15 min.
exposure, 223K, 50 mg Pd/alumina)

<table>
<thead>
<tr>
<th></th>
<th>No CO</th>
<th>Pre-ad. CO</th>
<th>Post-ad. C</th>
<th>Post-ad. CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmole/g</td>
<td>T(K)</td>
<td>µmole/g</td>
<td>T(K)</td>
</tr>
<tr>
<td>methane</td>
<td>-</td>
<td>-</td>
<td>5.60</td>
<td>532</td>
</tr>
<tr>
<td>acetylene</td>
<td>1.16</td>
<td>205</td>
<td>34.94</td>
<td>253</td>
</tr>
<tr>
<td>ethylene</td>
<td>7.78</td>
<td>213</td>
<td>0.84</td>
<td>251</td>
</tr>
<tr>
<td>ethane</td>
<td>34.82</td>
<td>215</td>
<td>11.62</td>
<td>258</td>
</tr>
<tr>
<td>n-butane</td>
<td>8.34</td>
<td>237</td>
<td>5.24</td>
<td>265</td>
</tr>
<tr>
<td>n-hexane</td>
<td>2.99</td>
<td>288</td>
<td>2.10</td>
<td>291</td>
</tr>
<tr>
<td>benzene</td>
<td>0.70</td>
<td>325</td>
<td>0.16</td>
<td>330</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.88$^a$</td>
<td>640</td>
<td>0.71$^a$</td>
<td>639</td>
</tr>
</tbody>
</table>

$^a$ broad peak, not complete by 673K

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Figure 6-2. TPR spectra of acetylene with preadsorbed CO on Pd/alumina at 223K. CO adsorption pressure 20.0 Pa.
Table 6-2. Effect of CO on Ethylene TPR
(73.2 Pa C₂H₄ partial pressure, 15 min.
exposure, 203K, 50 mg Pd/alumina)

<table>
<thead>
<tr>
<th></th>
<th>No CO</th>
<th></th>
<th>With CO⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmole/g</td>
<td>T(K)</td>
<td>μmole/g</td>
</tr>
<tr>
<td>methane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ethylene</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
</tr>
<tr>
<td>ethane</td>
<td>24.0</td>
<td>173</td>
<td>5.0</td>
</tr>
<tr>
<td>n-butane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-hexane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>benzene</td>
<td>0.5ᵇ</td>
<td>648</td>
<td>-</td>
</tr>
<tr>
<td>C⁶⁺</td>
<td>4.2x10⁷ᶜ</td>
<td>481</td>
<td>4.1x10⁶ᶜ</td>
</tr>
<tr>
<td></td>
<td>8.2x10⁴ᶜ</td>
<td>556</td>
<td>9.8x10⁸ᶜ</td>
</tr>
</tbody>
</table>

ᵃ 20.0 Pa of CO preadsorbed
ᵇ not complete by 673K
ᶜ integrated intensity of mass 43 characteristic of C⁶ and heavier paraffins.
Table 6-3. Effect of Carbon Deposits on Acetylene TPR
(73.2 Pa C₂H₂ partial pressure, 15 min. exposure, 223K, 50 mg Pd/alumina)

<table>
<thead>
<tr>
<th></th>
<th>Fresh Pd/Al₂O₃</th>
<th>C-deposited Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmole/g T(K)</td>
<td>μmole/g T(K)</td>
</tr>
<tr>
<td>acetylene</td>
<td>4.60 213</td>
<td>-</td>
</tr>
<tr>
<td>ethylene</td>
<td>10.95 216</td>
<td>7.34 214</td>
</tr>
<tr>
<td>ethane</td>
<td>37.19 221</td>
<td>44.78 219</td>
</tr>
<tr>
<td>n-butane</td>
<td>7.57 237</td>
<td>3.68 252</td>
</tr>
<tr>
<td>n-hexane</td>
<td>2.99 287</td>
<td>0.83 312</td>
</tr>
<tr>
<td>benzene</td>
<td>3.16 328</td>
<td>1.78 347</td>
</tr>
<tr>
<td></td>
<td>0.96* 629</td>
<td>-</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>10.59 341</td>
<td>2.77 361</td>
</tr>
</tbody>
</table>

*a* broad peak, not complete by 673K
peak temperatures shifted to higher values by 15–24K with carbon deposition on the catalyst. Decreases in the yields were larger for the higher oligomers, while little change was observed for C₂ products.

6.3 Discussion

The TPR spectrum of CO (Figure 6–1) yields both CO and CH₄ indicating that CO adsorbs on Pd in two states composed of weakly adsorbed CO which desorbs molecularly at low temperatures and strongly adsorbed CO which reacts with H₂ and desorbs as methane at higher temperatures. In the TPR spectrum of acetylene with CO (Table 6–1), the existence of strongly adsorbed carbon monoxide on the catalyst surface is observed as a methane peak around 532K, a slightly higher temperature than in the TPR spectrum of pure CO. This methane peak was always observed in acetylene/CO experiments regardless of whether CO was preadsorbed or postadsorbed, which indicates that there are particular sites where only CO can adsorb. These sites may be single isolated sites which cannot accommodate acetylene.

A global effect of CO on the adsorption of acetylene and ethylene which has been observed in the TPR experiments is the suppression of self-hydrogenation. When CO was adsorbed before acetylene, no ethane or ethylene was observed in the effluent during the postadsorption flush. This effect has also been observed on Rh/SiO₂ (Reid et al., 1973a, 1973c). The reduction in self-hydrogenation is probably caused by CO blockage of single sites which accommodate the hydrogen product of dissociative chemisorption of hydrocarbons and therefore, no hydrogen is available for self-hydrogenation.
The product distribution of C₂ products from TPR of acetylene with adsorbed CO (Table 6-1) indicates how CO affects the hydrogenation of acetylene. During the initial stages of TPR, physisorbed acetylene desorbs from the support and, when no CO is present, readsorbs on available metal sites for hydrogenation to ethane (as discussed in the above) which is observed as the primary product. When CO was adsorbed, unconverted acetylene was the predominant product in the early stages of TPR. Acetylene eluting from the support could not be converted to ethane because single metal sites, which normally are available to supply hydrogen for the reaction, have been blocked by CO.

The effect of CO on oligomerization is shown in the TPR spectra of acetylene which are summarized in Table 6-1. The amount and the order of CO adsorption strongly influenced the results. When 20.0 Pa of CO was preadsorbed, a decrease in the yield of all oligomers was observed. However, postadsorption of the same amount of CO resulted in an increase in the oligomer yield particularly with respect to C₆ cyclic products. When the CO pressure was increased to 73.2 Pa (the same as the acetylene pressure), postadsorbed CO caused a slight decrease in the oligomer yield.

The effect of preadsorbed CO on oligomerization is caused by CO blockage of acetylene adsorption and suppression of acetylene dissociation. Acetylene probably cannot displace preadsorbed CO completely. In the case of Rh/SiO₂ only 40% of the preadsorbed CO could be displaced by acetylene (Reid et al., 1973b). CO left on the surface would be especially effective in suppressing oligomerization because oligomerization requires nearby adsorbed acetylene molecules to proceed. A reduced dissociation of acetylene could also prevent formation of free
radicals which would destroy initiation and result in suppression of oligomerization. The relative importance of each effect in suppressing oligomerization probably depends on the pressure of CO and acetylene. Suppression of acetylene dissociation would be the main effect when the CO pressure is much lower than acetylene, since CO may not be able to compete for acetylene sites effectively, but CO could still occupy single sites which cannot accommodate acetylene and block these sites which normally would accept the hydrogen product of acetylene dissociation.

All resultant spectra of acetylene TPR modified with CO yielded shifts of products to higher temperatures (Table 6-1). This effect is probably due to a limited hydrogen supply during TPR caused by hydrogen site blockage by CO. Unsaturated products are difficult to desorb so a delay in hydrogenation results in the observed shifts. The shift was also observed for the low temperature benzene peak which does not require hydrogen for its desorption. The mechanism for benzene formation discussed above may explain this trend. CO blocks the vacant sites necessary to accommodate hydrogen which comes from the benzene precursor during the dehydrogenation step so that the desorption of benzene is delayed.

The observed temperature shift was more severe for ethane and butane products than higher oligomers. Hydrogenation of surface oligomers apparently is most affected in the early stages of TPR when the hydrogen supply is more strongly suppressed by CO. As the temperature is increased, weakly bound CO desorbs creating sites for the hydrogen supply. Hydrogenation and subsequent desorption of surface species results. The existence of weakly bound CO has been demonstrated by TPR experiments of CO without acetylene and is still
possible in the presence of acetylene. Blyholder (1964) suggested that CO adsorbs on corner and edge sites strongly and weakly on plane sites. Single plane sites may exist as geometrically isolated sites surrounded by multiply adsorbed acetylene molecules.

Results on the effects of CO are comparable, in some ways, to the effects of carbon deposits where decreases in oligomer yields and shifts in peak temperatures were observed (Table 6-3). Since the source of carbon deposited on Pd was acetylene, hydrocarbon sites active for acetylene adsorption should be blocked effectively. The results reflect this expectation and a geometric effect on oligomerization is clearly shown in the product distribution. The butane yield decreased by half while the yields of n-hexane and C₆ cyclic compounds were cut to one third. Higher oligomers were suppressed to a greater extent because oligomerization requires adjacent adsorbed species for propagation.

However, carbon deposition had little effect on C₂ products and acetylene was not the major C₂ product as was observed for CO poisoning. Peak temperatures for C₂ products showed virtually no shift while significant shifts were noted for oligomers. Since carbon deposits are probably located on sites normally associated with acetylene adsorption which are multiple sites, single sites would be left unaffected and these sites can promote hydrogenation particularly of C₂ species. Also, hydrogenation of oligomer precursors requires more hydrogen than C₂ species so geometric effects of carbon should be more evident as observed. Thus, carbon deposition has little effect on C₂ formation in contrast to CO which can block single sites for hydrogen adsorption.
One of the physical differences in the poisoning effects associated with surface carbon versus carbon monoxide is due to the fact that CO adsorption can be reversed by raising the temperature while carbon blockage of sites is virtually irreversible and can not be removed during TPR. Carbon deposits are therefore still effective at high temperatures during TPR and this results in upscale temperature shifts for high oligomers which are even larger than shifts caused by CO.

When the effects of CO on acetylene adsorption are compared to the effects of carbon deposits as discussed above, the existence of single, isolated Pd sites for H₂ adsorption which can be blocked by CO becomes even more apparent. The deuterium tracer studies (chapter 4) showed that the effect of CO on acetylene hydrogenation is due to the blockage of hydrogen adsorption by CO. The results in this chapter further amplify these findings and have helped to identify the affected hydrogen adsorption sites as single, isolated sites.

The effect of CO on ethylene adsorption is similar to the effect on acetylene particularly in the suppression of hydrogenation. When CO was preadsorbed on Pd prior to TPR of ethylene adsorbed at 203K, unconverted ethylene was observed in the effluent which was not observed in the case of pure ethylene. Ethylene could not undergo hydrogenation to ethane due to CO blocking the hydrogen supply as in the case of acetylene TPR. The decrease in the yield of high oligomers with preadsorbed CO is probably due to CO suppressing decomposition of ethylene, which precedes oligomerization of ethylene.

6.4 Conclusions

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In acetylene TPR with CO, many effects on the formation and reaction of adsorbed species from acetylene were observed including suppression of self-hydrogenation, oligomerization, and hydrogenation of surface oligomers. From these observations the following conclusions were obtained.

1. The primary effects of CO on the hydrogenation of acetylene are the abilities of CO to block hydrogen adsorption particularly at isolated Pd sites and to slow dissociative adsorption of hydrocarbons by blocking sites which would normally accommodate the hydrogen product from the dissociative adsorption.

2. Geometric effects of CO and coke deposits are also apparent in attenuating the production of high oligomers.

3. Distinct, isolated Pd sites where H₂ or CO can adsorb are operable.
VII TPR AND DEUTERIUM TRACER STUDIES ON THE EFFECT OF K ON Pd/Al₂O₃ CATALYSTS FOR ACETYLENE HYDROGENATION

In this chapter, we report on experiments aimed at testing the performance of K doped Pd/Al₂O₃ catalysts and understanding associated effects of K promoters on the catalytic behavior of Pd/Al₂O₃. Potassium was added to Pd/Al₂O₃ both before and after Pd loading, to determine if there is a difference between direct modification of the catalyst and support modification. The activity and selectivities of these catalysts were tested for acetylene hydrogenation. The techniques used to study K effects were acetylene TPR and ethylene deuterium tracer experiments.

7.1 Procedures

The procedures for preparation and characterization of K doped catalysts, steady state reaction of acetylene hydrogenation, acetylene TPR, and ethylene deuteration reaction have been described in the chapter 3.

Ammonia TPD of the catalyst support was also used as a characterization tool. In this experiment, 50mg of support was treated in He flow at 773K for 1 hr and cooled to the adsorption temperature, 298K. The sample was exposed for 15 min. to a mixture of 0.67 kPa ammonia and 106.4 kPa He circulating in the batch system and flushed in He flow for 1 hr for removal of weakly adsorbed ammonia. Then the sample was heated at the rate of 10K/min. and desorbing ammonia was monitored by MS. TPD of acetylene was observed in the same procedure, except that
1.33 kPa acetylene was adsorbed to obtain an acetylene capacity of the support materials. The BET areas of these supports were also measured by Omnisorp 360C (OMICRON) adsorption apparatus.

7.2 Results

Physical properties of the catalysts are given in Table 7–1 and TPD of ammonia and acetylene are given in Figures 7–1 and 7–2, respectively. The BET surface area of the alumina decreased only slightly with K addition. Pd dispersion was difficult to control as can be seen in two separate preparations shown in Table 7–1. These two preparations will be referred to separately by their degree of dispersion. The acidity of the support, measured by ammonia adsorption, decreased as expected with K addition so that 72% of the total acid sites were removed at 4% K content, but as can be seen in Figure 7–1, the high temperature NH₃ shoulder (indicating stronger acid sites) is especially strongly attenuated. K had little effect on acetylene adsorption except at the 4% level where an increase in capacity of about 4 times was observed. The acetylene peak temperature did not shift significantly as K was added to Al₂O₃ (Figure 7–2).

The results for the acetylene hydrogenation reaction over K doped catalysts are given in Table 7–2. Reaction curves were consistent with curves reported by others (Bond and Wells, 1966) which begin with a slow zero order region that extends until almost all the acetylene has been depleted. Product selectivities are virtually constant with conversion in this region, so we have elected to report product compositions at 70% acetylene conversion (which is still within the zero
Table 7-1. Physical Properties of the K Doped Catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Dispersion(^b) (%)</th>
<th>Surface Area (m(^2)/g)</th>
<th>NH(_3) Capacity(^a) (µmole/g)</th>
<th>C(_2)H(_2) Capacity(^a) (µmole/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al(_2)O(_3)(^c)</td>
<td>36.2</td>
<td>215.6</td>
<td>292.9</td>
<td>22.9</td>
</tr>
<tr>
<td>Pd/Al(_2)O(_3)(^d)</td>
<td>16.7</td>
<td>215.6</td>
<td>292.9</td>
<td>22.9</td>
</tr>
<tr>
<td>1% K-Pd/Al(_2)O(_3)</td>
<td>33.5</td>
<td>215.6</td>
<td>292.9</td>
<td>22.9</td>
</tr>
<tr>
<td>4% K-Pd/Al(_2)O(_3)</td>
<td>26.1</td>
<td>215.6</td>
<td>292.9</td>
<td>22.9</td>
</tr>
<tr>
<td>Pd/1% K-Al(_2)O(_3)</td>
<td>17.2</td>
<td>189.8</td>
<td>257.9</td>
<td>18.8</td>
</tr>
<tr>
<td>Pd/2% K-Al(_2)O(_3)</td>
<td>32.5</td>
<td>186.5</td>
<td>233.7</td>
<td>17.5</td>
</tr>
<tr>
<td>Pd/4% K-Al(_2)O(_3)</td>
<td>23.2</td>
<td>182.7</td>
<td>80.8</td>
<td>81.2</td>
</tr>
</tbody>
</table>

\(^a\)properties before Pd Impregnation
\(^b\)based upon CO/Pd = 1/1
\(^c\)first batch
\(^d\)second batch
Figure 7-1. TPD spectra of ammonia adsorbed on K doped aluminas at 298K.
Figure 7-2. TPD spectra of acetylene adsorbed on K doped aluminas at 298K.
Table 7-2. Effect of K on Acetylene Hydrogenation Product Distribution and Reaction Rate

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd/Al₂O₃</th>
<th>Pd/Al₂O₃</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>1% K-Al₂O₃</th>
<th>2% K-Al₂O₃</th>
<th>4% K-Al₂O₃</th>
<th>1% K-Pd/Al₂O₃</th>
<th>4% K-Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion (%)</td>
<td>36.2</td>
<td>16.7</td>
<td>17.2</td>
<td>32.5</td>
<td>23.2</td>
<td>33.5</td>
<td>26.1</td>
<td>23.2</td>
<td>33.5</td>
<td>26.1</td>
<td>26.1</td>
</tr>
<tr>
<td>Rate</td>
<td>5.87</td>
<td>4.68</td>
<td>5.94</td>
<td>7.75</td>
<td>9.86</td>
<td>5.87</td>
<td>7.93</td>
<td>5.87</td>
<td>7.93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Product Distribution (mole% at 70% conversion)**

<table>
<thead>
<tr>
<th></th>
<th>Pd/Al₂O₃</th>
<th>Pd/Al₂O₃</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>1% K-Al₂O₃</th>
<th>2% K-Al₂O₃</th>
<th>4% K-Al₂O₃</th>
<th>1% K-Pd/Al₂O₃</th>
<th>4% K-Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>7.2</td>
<td>10.7</td>
<td>6.0</td>
<td>5.6</td>
<td>6.6</td>
<td>5.8</td>
<td>3.6</td>
<td>82.1</td>
<td>78.4</td>
<td>81.3</td>
<td>81.2</td>
</tr>
<tr>
<td>ethylene</td>
<td>81.1</td>
<td>78.4</td>
<td>82.1</td>
<td>81.3</td>
<td>78.2</td>
<td>81.2</td>
<td>82.7</td>
<td>78.4</td>
<td>82.1</td>
<td>81.3</td>
<td>81.2</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.3</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.0</td>
<td>4.0</td>
<td>3.7</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>1-butene</td>
<td>4.0</td>
<td>3.7</td>
<td>3.4</td>
<td>3.6</td>
<td>4.2</td>
<td>3.5</td>
<td>3.7</td>
<td>1.8</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>t-2-butene</td>
<td>1.8</td>
<td>1.7</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
<td>1.9</td>
<td>1.5</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>c-2-butene</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
<td>1.7</td>
<td>1.4</td>
<td>1.4</td>
<td>1.3</td>
<td>4.5</td>
<td>3.7</td>
<td>4.7</td>
<td>5.4</td>
</tr>
<tr>
<td>butadiene</td>
<td>4.5</td>
<td>3.7</td>
<td>4.7</td>
<td>5.4</td>
<td>7.2</td>
<td>5.7</td>
<td>7.3</td>
<td>81.1</td>
<td>81.2</td>
<td>81.3</td>
<td>81.4</td>
</tr>
</tbody>
</table>

**Selectivities**

<table>
<thead>
<tr>
<th></th>
<th>Pd/Al₂O₃</th>
<th>Pd/Al₂O₃</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>Pd/</th>
<th>1% K-Al₂O₃</th>
<th>2% K-Al₂O₃</th>
<th>4% K-Al₂O₃</th>
<th>1% K-Pd/Al₂O₃</th>
<th>4% K-Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄/C₄</td>
<td>91.8</td>
<td>88.0</td>
<td>93.2</td>
<td>93.6</td>
<td>92.2</td>
<td>93.3</td>
<td>95.8</td>
<td>92.6</td>
<td>70.7</td>
<td>73.4</td>
<td>71.9</td>
</tr>
<tr>
<td>C₄H₂ (global)</td>
<td>92.5</td>
<td>70.7</td>
<td>73.4</td>
<td>72.0</td>
<td>68.0</td>
<td>71.9</td>
<td>72.6</td>
<td>20.9</td>
<td>19.7</td>
<td>21.3</td>
<td>23.0</td>
</tr>
</tbody>
</table>

*base catalyst for K-Pd/Al₂O₃ series catalysts

1rate of reaction in μmole/min for the zero order initial region

1defined as 100* Y₂/([Y₂] + [Y₃]), where Y is yield

1defined as 100* Y₂/([Y₂] + 2[Y₃]), where C₂ = I all two carbon products, C₄ = I all four carbon product

1defined as 100* 2Y₃/([Y₃] + 2Y₄)
order region in all cases) and we have computed a global rate from the slope of the zero order line which is also reported in Table 7-2. From the table we immediately see that reversing the order of K doping has very little effect on the catalytic properties. However global effects of K are apparent. First, K improves the rate of acetylene conversion and second, the ratio of ethylene to ethane was generally improved for all levels of K content. Yields of C₄ products also increased with K addition but this increase was largely due to an increase in the yield of 1,3-butadiene. Because the increase in C₄ yield offsets the improved selectivity of acetylene to ethylene, the overall ethylene selectivity is relatively constant. Differences in the Pd dispersion among the catalysts has only a slight effect compared to the effect of K.

The TPR spectra of acetylene over Pd/Al₂O₃ and K doped catalysts are summarized in Table 7-3 and a typical spectrum for a K doped catalyst (4% K-Pd/Al₂O₃) is given in Figure 7-3. Large changes in the peak area and temperature were observed for catalysts which contain K compared to Pd/Al₂O₃. Changes in the peak temperatures for oligomers are especially evident. Hexane shifted 8-14K lower over K doped catalysts compared to Pd/Al₂O₃ while peak areas remained similar on all catalysts. Butane displayed a similar trend except for catalysts with 4% K where the yield was roughly twice as large. The peak temperatures for benzene from K containing catalysts shifted to lower temperatures while the peak area increased significantly, but the cyclohexane yield was attenuated. Over Pd/Al₂O₃, most of the C₆ cyclic component appears as cyclohexane while benzene is favored over K doped materials but it appears at lower temperatures.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Pd/Al₂O₃</th>
<th>Pd/Al₂O₃</th>
<th>Pd/1%K-Al₂O₃</th>
<th>Pd/2%K-Al₂O₃</th>
<th>Pd/4%K-Al₂O₃</th>
<th>1%K-Pd/Al₂O₃</th>
<th>4%K-Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmole</td>
<td>T(K)</td>
<td>μmole</td>
<td>T(K)</td>
<td>μmole</td>
<td>T(K)</td>
<td>μmole</td>
</tr>
<tr>
<td>acetylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35.49</td>
<td>238</td>
</tr>
<tr>
<td>ethylene</td>
<td>3.77</td>
<td>208</td>
<td>0.34</td>
<td>211</td>
<td>-</td>
<td>2.04</td>
<td>206</td>
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<tr>
<td>ethane</td>
<td>32.66</td>
<td>209</td>
<td>37.86</td>
<td>221</td>
<td>8.61</td>
<td>204</td>
<td>13.27</td>
</tr>
<tr>
<td>n-butane</td>
<td>6.06</td>
<td>235</td>
<td>7.24</td>
<td>234</td>
<td>5.90</td>
<td>226</td>
<td>4.99</td>
</tr>
<tr>
<td>n-hexane</td>
<td>2.24</td>
<td>286</td>
<td>2.75</td>
<td>285</td>
<td>2.20</td>
<td>275</td>
<td>1.81</td>
</tr>
<tr>
<td>benzene</td>
<td>2.35</td>
<td>326</td>
<td>1.83</td>
<td>327</td>
<td>7.79</td>
<td>309</td>
<td>9.00</td>
</tr>
<tr>
<td></td>
<td>1.04⁴</td>
<td>628</td>
<td>1.05⁴</td>
<td>631</td>
<td>1.03⁴</td>
<td>647</td>
<td>-</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>8.76</td>
<td>342</td>
<td>8.76</td>
<td>341</td>
<td>4.79</td>
<td>354</td>
<td>2.51</td>
</tr>
<tr>
<td>Dispersion</td>
<td>36.2%</td>
<td>16.7%</td>
<td>17.2</td>
<td>32.5</td>
<td>23.2%</td>
<td>33.5%</td>
<td>26.1%</td>
</tr>
</tbody>
</table>

¹Yields based on 1 gr catalyst
²Base catalyst for K-Pd/Al₂O₃ series catalysts
³Broad peak not finished by 673K
Figure 7–3a. TPR spectra of acetylene adsorbed on 4% K–Pd/alumina at 223K.
Figure 7-3b. TPR spectra of acetylene adsorbed on 4% K-Pd/alumina at 223K.
Changes in the TPR spectra in the C\textsubscript{2} region were also significant but are less meaningful than the oligomerization results since C\textsubscript{2} products originate from the physisorbed acetylene as discussed above. Yields of C\textsubscript{2} products follow the trends we expect from the acetylene capacity measurements on the support (Table 7-1), where we observed a large capacity increase for the 4% K support.

Ethylene deuterium results are given in Table 7-4. Over Pd/Al\textsubscript{2}O\textsubscript{3} catalysts at 223K, d\textsubscript{1} ethane was dominant, which agrees with the results by Bond et al. (1966). Conversely, d\textsubscript{2} ethane was dominant over K doped catalysts showing that H/D exchange which occurs along with deuterium has slowed relative to the rate of deuteration. Deuterium experiments were repeated at 263K for K doped catalysts to check for deuterium distribution changes at higher overall reaction rates, but the dominance of d\textsubscript{2} ethane was unchanged. These qualitative features are reflected quantitatively in the values of Kemball's parameters (Kemball, 1956; Kemball and Wells, 1968) given in Table 7-5, which shows increases in the probability of ethylene desorption and that of ethyl hydrogenation to ethane with K doping. We have also observed a much lower rate of ethylene deuteration for K doped catalysts than for the undoped catalysts at 223K (Table 7-4).

7.3 Discussion

The major changes in the acetylene hydrogenation reaction which we have observed upon addition of K to Pd/Al\textsubscript{2}O\textsubscript{3} were the enhancement of the partial hydrogenation of acetylene to ethylene, an increase in the rate of acetylene conversion, and an increase in the C\textsubscript{4} product selectivity. We have also observed that K addition caused a shift in the
Table 7-4 Product Distribution and Reaction Rate in Ethylene Deuteration

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temperature</th>
<th>Conversion/Reaction Time</th>
<th>Products (%)&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;D&lt;/sub&gt;</td>
</tr>
<tr>
<td>Pd/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>223K</td>
<td>16%/ 4min.</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>26.7</td>
</tr>
<tr>
<td>Pd/4%K-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>223K</td>
<td>13%/87min.</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>263K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30.5</td>
</tr>
<tr>
<td>Pd/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>223K</td>
<td>15%/10min.</td>
<td>31.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30.7</td>
</tr>
<tr>
<td>4%K-Pd/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>223K</td>
<td>15%/75min.</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>29.5</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>263K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31.0</td>
</tr>
</tbody>
</table>

<sup>1</sup> P<sub>Total</sub> 2.66 kPa, P<sub>H</sub> 2.66 kPa

<sup>2</sup> The first row of the data for each experiment represents the experimental distribution and the next row represents the calculated distribution.
Table 7-5. Kemball's Parameters from Ethylene Deuteration for K doped Catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T(K)</th>
<th>(100 -p*)%&lt;sup&gt;a&lt;/sup&gt;</th>
<th>(100 - r*)%&lt;sup&gt;b&lt;/sup&gt;</th>
<th>q&lt;sup&gt;c&lt;/sup&gt;, s&lt;sup&gt;c&lt;/sup&gt; %&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>223</td>
<td>11</td>
<td>8</td>
<td>32, 37</td>
</tr>
<tr>
<td>(D=16.7%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/4%K-Al₂O₃</td>
<td>223</td>
<td>38</td>
<td>25</td>
<td>55, 56</td>
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<tr>
<td></td>
<td>263</td>
<td>35</td>
<td>24</td>
<td>62, 62</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>223</td>
<td>13</td>
<td>8</td>
<td>26, 32</td>
</tr>
<tr>
<td>(D=36.2%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4%K-Pd/Al₂O₃</td>
<td>223</td>
<td>40</td>
<td>27</td>
<td>62, 62</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>41</td>
<td>27</td>
<td>64, 64</td>
</tr>
</tbody>
</table>

<sup>a</sup>equivalent to the probability of ethylene desorption

<sup>b</sup>equivalent to the probability of ethyl hydrogenation to ethane

<sup>c</sup>equivalent to the probability of D incorporation upon hydrogenation
oligomerization products from acetylene TPR to lower temperatures and noted an increase in the probability of ethylene desorption upon K addition during the deuteration of ethylene. The rate of ethylene deuteration (hydrogenation) was also reduced upon K addition.

Several possible explanations for these effects exist, but the results of the ethylene deuterium exchange reaction, which show that ethylene desorption is favored upon the addition of K, suggest that the strength of hydrocarbon adsorption decreases with K content. Oligomer bands from acetylene TPR appear at lower temperatures for K promoted materials compared to Pd/Al₂O₃ which is also consistent with this postulate.

The enhancement in the probability of ethylene desorption with the addition of K to Pd/Al₂O₃ could also be explained by a reduction in the availability of surface hydrogen. If hydrogen availability is limited by K, the probability of the hydrogenation of adsorbed ethyl radicals to ethane would be suppressed resulting in a greater probability that ethylene desorbs rather than reacts. However, our results show that the probability of ethyl hydrogenation also increases with K content and therefore, this postulate is unlikely. We might also attribute greater benzene/cyclohexane ratios from acetylene TPR for K containing catalysts to a limited hydrogen supply, but this would be inconsistent with the ethylene deuteration results. Also, Rieck and Bell (1986) have reported that alkali metal promotion of Pd/SiO₂ does not significantly alter the amount of hydrogen adsorption. The higher benzene/cyclohexane ratios fall into the more likely postulate that the strength of hydrocarbon adsorption is reduced with K content. Benzene desorption would therefore be favored over hydrogenation to cyclohexane.
The strong similarities of K-Pd/Al₂O₃ and Pd/K-Al₂O₃ suggest that the order of K addition has no effect on the catalytic properties and it appears that the effect is related to K-induced changes in the properties of the support which indirectly affects the Pd, probably through metal-support interactions. Though the surface area of Al₂O₃ was reduced 10-15% by the addition of K, transport property effects cannot completely explain our TPR results. If oligomers were eluted from K-containing materials at lower temperatures because of transport effects, all oligomers should shift to lower temperatures and this was not generally the case for cyclohexane.

The improved rate of acetylene hydrogenation and the contrasting decrease in the rate of ethylene hydrogenation caused by the addition of K may also be explained by a reduced strength of hydrocarbon adsorption. Acetylene dominates the Pd surface at the expense of hydrogen so that acetylene hydrogenation is slowed by the lack of hydrogen. If K reduces the strength of acetylene adsorption, hydrogen could compete more effectively for sites and a net increase in rate is expected. For the ethylene hydrogenation reaction, however, ethylene does not completely dominate the Pd surface so that a reduction in ethylene surface coverage should reduce the hydrogenation rate as we have observed.

The reduced strength of adsorption of hydrocarbons may be caused by an increased electron density on Pd particles. Pd would then have less propensity to share electrons with adsorbate hydrocarbons. The addition of piperidine (an electron donor) to the reaction mixture during the hydrogenation of 1-butyne over Pd/Al₂O₃ resulted in an increase in
both selectivity to 1-butene and overall hydrogenation activity (Boitiaux et al., 1985b), which is similar to our observations on the effect of K on acetylene hydrogenation.

Electronic effects on Pd can take place either through direct K-Pd interaction, or through a modification of the support properties which induces a change in metal-support interactions. Our acetylene and NH₃ TPD spectra of Al₂O₃ and K-Al₂O₃ shows that support properties change from acidic to basic upon K addition as expected. Acetylene is known to be slightly acidic (Yates and Lucchesi, 1961; Harrison and Boyd, 1983) so that the dramatically higher capacity of 4% K-Al₂O₃ for acetylene adsorption indicates a strong shift toward a basic support.

Electron transfer between metals and acidic supports has been suggested by several researchers. Figoli and L'argeniere (1989) studied selective hydrogenation of styrene over Pd/Al₂O₃ catalysts and found changes in the electronic state of Pd via XPS when sodium was added to the support. Free electrons on Pd were transferred to lower electron density sites on acidic Al₂O₃ and electron transfer was attenuated with added sodium. Figueras et al. (1973) studied benzene hydrogenation over Pd supported on several different acidic oxides and found that the support influences the electronic properties of Pd. Similar theories have been reported by Gallezot et al. (1977) and Anderson (1975). In our case, we suggest by analogy that the more basic nature of K-doped Al₂O₃ results in an electron transfer to Pd, resulting in a higher Pd electron density, and ultimately, a reduced strength of hydrocarbon adsorption. This leads to an increase in C₂H₄ selectivity from acetylene because
ethylene desorbs more readily before it can be further hydrogenated to ethane and because the ethylene product is less likely to readSORb and become hydrogenated.

One last point concerning the production of C₄ oligomers deserves discussion under this theory. Other researchers have suggested that acidic support sites contribute to oligomerization reactions (Trim, 1980; Chauda and Gosch, 1969; Kranich et al., 1985) but we have observed an increase in C₄ oligomers when the support is made more basic via the addition of K, which we attribute to a lower strength of hydrocarbon adsorption on Pd/Al₂O₃ modified by K. These theories are not necessarily mutually exclusive. If oligomers are formed at acidic support sites and the addition of K reduces the number of these sites, the reduced strength of hydrocarbon adsorption could possibly overcompensate for this effect resulting in a net increase in oligomers.

The observation that the activity and selectivity of Pd/Al₂O₃ for acetylene hydrogenation are improved via the addition of K suggests that these materials should be further tested as candidates for trace acetylene removal from ethylene streams. Activity, selectivity and aging characteristics need further examination under more realistic industrial conditions. If our observations can be extrapolated to industrial conditions, the improved ethylene selectivity from acetylene related to K addition would need to offset the simultaneous K-induced increase in oligomerization products for these materials to be a significant improvement in current technology, and it is likely that this requirement can be realized. It is known that ethylene hydrogenation proceeds independent of acetylene hydrogenation in the industrial situation where trace acetylene in an ethylene feedstock is hydrogenated (Moses, 1984).
K-modified Pd/Al₂O₃ should reduce the rate of direct ethylene hydrogenation and improve the rate of acetylene removal while the expected increase in oligomers, which comes from the trace acetylene component in the feedstock, should be trivial. We can also postulate that K-modified Pd/Al₂O₃ will be less susceptible to aging since desorption of low molecular weight oligomers may result in an attenuated accumulation of high molecular weight oligomers that foul the catalysts.

7.4 Conclusions

1. K addition to Pd/Al₂O₃ promoted partial hydrogenation of acetylene to ethylene, increased the rate of acetylene conversion, and increased C₄ oligomer yields.

2. The major effect of K doping of Pd/Al₂O₃ for acetylene hydrogenation is the reduced strength of hydrocarbon adsorption on Pd as suggested by the increase in the ethylene desorption probability (deuteration study) and the decreased binding energies of adsorbed species (TPR study). Potassium appears to modify the support, which indirectly increases the electron density of Pd through metal-support interactions.

3. The increase in the selectivity of acetylene to ethylene is due to easier desorption of ethylene on the Pd surface and suppressed readsoption of ethylene from the gas phase.

4. Testing of K doped catalysts under industrial conditions is desirable considering their ability to suppress ethylene hydrogenation while enhancing acetylene hydrogenation.
VIII. OVERALL CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The effects of carbon monoxide addition to the reactants and potassium to the catalyst, for the selective hydrogenation of acetylene over Pd/Al₂O₃ was studied by deuterium tracer experiments and temperature programmed reaction (TPR). Acetylene and ethylene deuteration experiments combined with Kemball’s steady-state analysis provided information concerning the relative rates of surface processes for hydrogenation. TPR of acetylene and ethylene in hydrogen, which was performed for the first time in this study, enabled an investigation of the behavior of adsorbed species on Pd from acetylene.

CO addition to the reaction mixture for ethylene deuteration increases the probability of ethylene desorption via CO displacement of ethylene. During acetylene TPR experiments, CO also suppressed the hydrogenation of adsorbed species by blocking hydrogen adsorption. Extrapolating these results to industrial conditions suggests that the main effect of CO on the ethylene selectivity in the selective removal of trace acetylene from raw ethylene streams is due to displacement of ethylene.

K doped catalysts yield an enhancement in the selectivity to ethylene, an increase in the rate of the acetylene reaction, and an increase in the oligomer yield for the hydrogenation of acetylene. K doping increases the probability of ethylene desorption during ethylene deuteration and lowers the desorption temperatures of surface species during acetylene TPR, which indicates a reduced strength of adsorption.
for all hydrocarbon species. The increase in the selectivity to ethylene is caused by easier desorption from the K doped catalysts and hindered adsorption of ethylene.

A comparison of the effects of CO and K reveals some common aspects of these additives even though the methods of modifying catalyst are totally different. For the hydrogenation of acetylene, both additives enhance the ethylene selectivity of Pd/Al₂O₃ and do so in the same way by suppressing the adsorption/reaction of ethylene. But the effects on the rate of acetylene conversion are opposite where CO blocks hydrogen adsorption sites resulting in a reduced reaction rate while K provides hydrogen sites by reducing the dominance of acetylene adsorption on Pd so that a higher rate is achieved.

The results obtained from acetylene TPR experiments are similar to the results of the hydro-oligomerization reaction, but TPR shows several advantages over the batch reaction experiments. More oligomeric species could be examined with TPR because yields of higher oligomers were too small to be detected in the batch reaction. The product of adsorbed poisons could also be examined via TPR more easily. Each reaction step is at least partially separated via TPR so that more detailed information on each step can be obtained. Peak temperatures and areas provided information about surface species and poisons could be adsorbed before or after reactants so that the corresponding effects could be compared. Acetylene TPR experiments clearly demonstrate the site blocking effect of CO and the electronic effect of K promoter. The results of this study shows that TPR can be a very useful technique for studying the fundamental aspects of hydrocarbon hydrogenation.
8.2 Recommendations

1. In this study, K doped catalysts were tested for the acetylene hydrogenation reaction in a batch reactor under conditions of relatively high acetylene partial pressures. Since our results seem promising from the standpoint of improved ethylene selectivity, it is recommended that K doped catalysts be tested under conditions normally employed in industry. In addition to testing the catalyst activity and selectivity, catalyst aging effects should be also be tested because K doping might decrease the formation of high oligomers through enhanced desorption of low molecular weight oligomers thereby halting propagation to high polymers which may be responsible for catalyst fouling.

2. Global effects of K doping on oligomer formation from acetylene could be found by an overall analysis of oligomer products including high molecular weight polymers that reside on the catalyst. Microbalance analysis of the catalyst while performing reaction experiments is suggested.

3. This study showed that preadsorbed CO was more effective than coadsorbed CO in enhancing the selectivity to ethylene during acetylene hydrogenation. Thus, industrial reactors may benefit from a CO treatment prior to introduction of the raw ethylene stream.

4. TPR experiments using acetylene and ethylene were severely hindered by heavy decomposition and physisorption of the adsorbates, so that the full potential of this technique was not realized. Application of more stable compounds such as benzene could yield more information on the hydrogenation mechanism.
5. The parameter optimization method developed in this study for the calculation of Kemball's parameters from hydrocarbon deuteration experiments was more efficient and accurate than the previous trial and error method. With this procedure, the parameters for the deuteration of higher olefins can probably be determined easily but these studies have been avoided in previous reports due to the complexity of the calculations in spite of the possible mechanistic value. We have already performed this calculation for propylene deuteration without any calculation problems. Further studies of hydrocarbon deuteration should perhaps be derived along these lines since such studies would be novel.
REFERENCES


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Appendix A. Derivation of H/D Balance Equations in Kemball's Method

H/D Balance Equations for Acetylene Deuteration

(adapted from Bond (1966b, 1968))

The general mechanism for acetylene deuteration is assumed as follows.

\[ \begin{align*}
\text{X} & \quad \text{C}_2\text{X}_2(\text{a}) \quad \text{X} \quad \text{C}_2\text{X}_3(\text{a}) \\
\text{C}_2\text{X}_2(\text{a}) & \quad \text{C}_2\text{X}_3(\text{a}) \quad 1 \\
\text{C}_2\text{X}_2(\text{a}) + \text{H} & \quad \text{C}_2\text{X}_2\text{H}(\text{a}) \quad 1-q \\
\text{C}_2\text{X}_2(\text{a}) + \text{D} & \quad \text{C}_2\text{X}_2\text{D}(\text{a}) \quad q \\
\text{C}_2\text{X}_3(\text{a}) & \quad \text{C}_2\text{X}_2(\text{a}) \quad 1-p \\
\text{C}_2\text{X}_3(\text{a}) & \quad \text{C}_2\text{X}_4(\text{a}) \quad p \\
\text{C}_2\text{X}_3(\text{a}) + \text{H} & \quad \text{C}_2\text{X}_3\text{H}(\text{a}) \quad 1-s \\
\text{C}_2\text{X}_3(\text{a}) + \text{D} & \quad \text{C}_2\text{X}_3\text{D}(\text{a}) \quad s
\end{align*} \]

All possible deuterium containing species may be present on the catalyst surface. In order to model the interconversion processes, we adopt the following nomenclature where lower case letters represent the fractions of corresponding uppercase species:

Acetylenes:

CHCH (A1), CHCD (A2), CDCD (A3)

Vinyls:

CHCH2 (B1), CHCHD (B2), CDCH2 (B3), CHCD2 (B4), CDCDH (B5), CDCD2 (B6)

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Ethylenes:
CH₂CH₂ (E₁), CH₂CHD (E₂), CHDCHD (E₃), CH₂CD₂ (E₄), CHDCD₂ (E₅), CD₂CD₂ (E₆)

A steady state deuterium/hydrogen balance equation among acetylene and vinyl species can be written for each of these species (except A₁) as follows.

\[ \text{[Rate of consumption]} = \text{[Rate of generation]} \]

Here, for consumption of a species only conversion to other species need to be considered since desorption of acetylene or vinyl radicals is not probable.

Ex) A₃ :
Rate of A₃ being converted to vinyl species:
\[
(\text{Probability of } x) \times (\text{fraction of } A₃) \\
\text{acetylene} \\
\text{hydrogenation}) \\
\frac{1}{a₃}
\]

Rate of A₃ being generated from vinyl species:
\[
(\text{Probability of } x) \times (\text{Fraction of } x) \times (\text{Probability of } H/D) \\
\text{vinyl reversal}) \times (\text{Fraction of } \text{vinyl}) \times (\text{Probability of } \text{H/D rupture from vinyl to generate } A₃) \\
(1-p) \times b₃ \times 1/2 \times (\text{from } B₃) \\
(1-p) \times b₄ \times 1 \times (\text{from } B₄)
\]
The balance is
\[ a_3 = (1-p)b_a/2 + (1-p)b_b \]

Eight simultaneous equations for isomers at steady state are as follows.
\[ a_2 = (1-p)b_a/2 + (1-p)b_b + (1-p)b_a/2 \]
\[ a_3 = (1-p)b_a/2 + (1-p)b_b \]
\[ b_1 = (1-q)a_1 \]
\[ b_2 = qa_1 + (1-q)a_2/2 \]
\[ b_3 = (1-q)a_2/2 \]
\[ b_4 = qa_2/2 \]
\[ b_5 = qa_2/2 + (1-q)a_3 \]
\[ b_6 = qa_3 \]

An equation for the total balance is added:
\[ 1. = a_1 + a_2 + a_3 + b_1 + b_2 + b_3 + b_4 + b_5 + b_6 \]

These equations are used as equality constraints in the optimization procedure described in Appendix E.

The ethylene fractions are related to the vinyl fractions and the parameters as follows:
\[ e_1 = p(1-s)b_1 \]
\[ e_2 = psb_1 + p(1-s)b_2 + p(1-s)b_2 \]
\[ e_3 = psb_2 + p(1-s)b_3 \]
\[ e_4 = psb_3 + p(1-s)b_4 \]
\[ e_5 = psb_4 + psb_5 + p(1-s)b_5 \]
\[ e_6 = psb_6 \]

These equations represent the the computed fractions of the deuterated ethylene species and are used in the least squares objective function.
H/D Balance Equations for Ethylene Deuteration

(adapted from Kemball (1956) and Bond (1964a))

The general mechanism for acetylene deuteration is assumed as follows.

\[
\begin{align*}
&\text{C}_2\text{X}_4 \quad \xrightarrow{X} \quad \text{C}_2\text{X}_4(a) \quad \xrightarrow{X} \quad \text{C}_2\text{X}_6 \\
&\text{C}_2\text{X}_4(a) \quad \xrightarrow{X} \quad \text{C}_2\text{X}_6(a) \quad \xrightarrow{X} \quad \text{C}_2\text{X}_6 \quad (X = \text{H or D})
\end{align*}
\]

where

\[
\begin{align*}
p &= \frac{\text{chance of } \text{C}_2\text{X}_4(a) \xrightarrow{X} \text{C}_2\text{X}_6(a)}{\text{chance of } \text{C}_2\text{X}_4(a) \xrightarrow{X} \text{C}_2\text{X}_4}
\end{align*}
\]

\[
\begin{align*}
r &= \frac{\text{chance of } \text{C}_2\text{X}_6(a) \xrightarrow{X} \text{C}_2\text{X}_4(a)}{\text{chance of } \text{C}_2\text{X}_6(a) \xrightarrow{X} \text{C}_2\text{X}_6}
\end{align*}
\]

\[
\begin{align*}
q &= \frac{\text{chance of } \text{C}_2\text{X}_4(a) + D \xrightarrow{X} \text{C}_2\text{X}_4D(a)}{\text{chance of } \text{C}_2\text{X}_4(a) + H \xrightarrow{X} \text{C}_2\text{X}_4H(a)}
\end{align*}
\]

\[
\begin{align*}
s &= \frac{\text{chance of } \text{C}_2\text{X}_6(a) + D \xrightarrow{X} \text{C}_2\text{X}_6D(a)}{\text{chance of } \text{C}_2\text{X}_6(a) + H \xrightarrow{X} \text{C}_2\text{X}_6H(a)}
\end{align*}
\]
All possible deuterium containing species may be present on the catalyst surface. In order to model the interconversion processes, we adopt the following nomenclature where lower case letters represent the fractions of corresponding uppercase species:

**Ethlenes:**
- CH$_2$CH$_2$ (E$_1$)
- CH$_2$CHD (E$_2$)
- CHDCHD (E$_3$)
- CH$_2$CD$_2$ (E$_4$)
- CD$_3$CD$_2$ (E$_5$)

**Ethyls:**
- CH$_2$CH$_3$ (F$_1$)
- CH$_2$CH$_2$D (F$_2$)
- CHDCH$_3$ (F$_3$)
- CHDCH$_2$D (F$_4$)
- CH$_2$CHD$_2$ (F$_5$)
- CD$_2$CH$_3$ (F$_6$)
- CH$_2$CD$_3$ (F$_7$)
- CD$_2$CH$_2$D (F$_8$)
- CHDCH$_2$D (F$_9$)
- CHDCH$_3$ (F$_10$)
- CD$_2$CH$_2$D (F$_{11}$)
- CD$_2$CD$_3$ (F$_{12}$)

**Ethaness:**
- CH$_3$CH$_3$ (G$_1$)
- CH$_3$CH$_2$D (G$_2$)
- CH$_3$CHD$_2$ (G$_3$)
- CH$_2$DCH$_2$D (G$_4$)
- CH$_2$DCHD$_2$ (G$_5$)
- CH$_3$CD$_3$ (G$_6$)
- CH$_3$CD$_3$ (G$_7$)
- CHD$_2$CH$_2$D (G$_8$)
- CHD$_2$CHD$_2$ (G$_9$)
- CD$_3$CD$_3$ (G$_{10}$)

The steady state deuterium/hydrogen balance equation among ethylene and ethyl species are generated for each of these species:

\[
\text{[Rate of consumption]} = \text{[Rate of generation]}
\]

or

\[
Q_m \left( 1 + \sum \mu_{m,n} \right) = \alpha_m (0) + \sum \mu_{i,m} Q_i
\]
where

\[ Q_m : \text{fraction of each entity} \]
\[ \mu_{mn} : \text{the ratio of the chance of an entity of the type } m \]
\[ \text{becoming an entity of type } n \text{ to the chance of } m \text{'s leaving} \]
\[ \text{the surface} \]
\[ a_m(0) : \text{the fraction of the entity present initially} \]
\[ (a_m(0)=1 \text{ for } E_1, \text{ and } a_m(0)=0 \text{ for all other entities}) \]

\[ \text{Ex) } E_1 : \]

Rate of \( E_1 \) disappearing either by desorbing from the surface
\[ Q_m \left(1 + \sum_{n} \mu_{mn} \right) \]

(Chance of \( x \) (fraction of a process) the species)
\[ 1 \quad e_1 \quad (\text{for desorption}) \]
\[ p \quad e_1 \quad (\text{for hydrogenation}) \]

Amount of \( E_1 \) initially present, \( e_1(0) = 1.0 \)

Rate of \( E_1 \) being generated from ethyl species,
\[ \sum_{i} \mu_{im} Q_i \]

(Chance of \( x \) (Fraction of ethyl reversal) of ethyl) (Probability of H/D rupture from ethyl to give \( E_1 \))
\[ r \quad f_1 \quad 1 \quad (\text{from } F_1) \]
\[ r \quad f_2 \quad 1/3 \quad (\text{from } F_2) \]

The balance is
\[ e_i(1+p) = 1 + rf_i + rf_2/3 \]

18 simultaneous equations for isomers at steady state including an equation for the total balance are as follows:

\[ e_1(1+p) = 1 + rf_1 + rf_2/3 \]
\[ e_2(1+p) = 2rf_2/3 + rf_3 + rf_4/3 + 2rf_5/3 \]
\[ e_3(1+p) = 2rf_4/3 + 2rf_5/3 \]
\[ e_4(1+p) = rf_5/3 + rf_6 + rf_7 + rf_8/3 \]
\[ e_5(1+p) = 2rf_8/3 + rf_9/3 + rf_{10} + 2rf_{11}/3 \]
\[ e_6(1+p) = rf_{12} + rf_{11}/3 \]
\[ f_1(1+r) = pe_1/(1+q) \]
\[ f_2(1+r) = pe_2/2(1+q) + pqe_1/(1+q) \]
\[ f_3(1+r) = pe_2/2(1+q) \]
\[ f_4(1+r) = pqe_2/2(1+q) + pe_3/(1+q) \]
\[ f_5(1+r) = pqe_2/2(1+q) + pe_4/2(1+q) \]
\[ f_6(1+r) = pe_4/2(1+q) \]
\[ f_7(1+r) = pqe_4/2(1+q) \]
\[ f_8(1+r) = pqe_4/2(1+q) + pe_5/2(1+q) \]
\[ f_9(1+r) = pqe_5/(1+q) + pe_5/2(1+q) \]
\[ f_{10}(1+r) = pqe_5/2(1+q) \]
\[ f_{11}(1+r) = pqe_5/2(1+q) + pe_6/(1+q) \]
\[ f_{12}(1+r) = pqe_6/(1+q) \]

These equations are used as equality constraints in the optimization procedure described in Appendix E.

Ethane fractions are related to the ethyl fractions and the parameter \( s \).
$g_1 = \frac{f_1}{1+s}$

$g_2 = \frac{sf_1}{1+s} + \frac{f_2}{1+s} + \frac{f_3}{1+s}$

$g_3 = \frac{sf_3}{1+s} + \frac{f_4}{1+s} + \frac{f_5}{1+s}$

$g_4 = \frac{sf_2}{1+s} + \frac{f_6}{1+s}$

$g_5 = \frac{sf_4}{1+s} + \frac{sf_5}{1+s} + \frac{f_7}{1+s} + \frac{f_8}{1+s}$

$g_6 = \frac{sf_6}{1+s} + \frac{f_9}{1+s}$

$g_7 = \frac{sf_7}{1+s} + \frac{sf_8}{1+s} + \frac{f_{10}}{1+s}$

$g_8 = \frac{sf_9}{1+s} + \frac{f_{11}}{1+s}$

$g_9 = \frac{sf_{10}}{1+s} + \frac{sf_{11}}{1+s} + \frac{f_{12}}{1+s}$

$g_{10} = \frac{sf_{12}}{1+s}$

These equations represent the computed fractions of the deuterated ethane species and are used in the least squares objective function described in Appendix E.
Appendix B. Mass Transfer Calculation for TPR Experiments

Gorte's criteria (1982) for transport effects in TPD/TPR includes four parameters representing the lag time for sample measurement, the lag time for gas diffusion within the catalyst pore, the importance of concentration gradients in the catalyst pellet the importance of readsorption. In order to test whether the experimental conditions for TPR satisfy these criteria, a calculation was performed for the hexane product from C$_2$H$_2$ TPR. N-hexane is a probable species for these effects due to its high molecular weight and low desorption temperature. In this calculation, the following data were used.

- Catalyst Weight, W: 0.05 g
- solid density, d$_s$: 0.98 g/cm$^3$
- Void Volume, V$_0$: 0.71 cc/g
- Surface Area, S$_0$: 215 m$^2$/g
- Catalyst Particle Size, dp: 7.4 x 10$^{-3}$ cm (200 - 325 mesh)
- Temperature (Desorption temperature for hexane during TPR), T: 273 K

For the experiment to yield the actual rate of desorption, the average residence time of the desorbing gas in the catalyst bed must be small. The lag time of a gas in the bed may be caused by a partial pressure buildup in the reactor. A large lag time will result in a broadening of the desorption peaks and an upscale shift in the desorption temperature. Via Gorte's criteria (1982), for the lag time to be negligible

\[
\frac{V B}{Q(T_f - T_0)} < 0.01
\]

where V is the volume of the catalyst bed, B is the heating rate, Q is
the carrier gas flow rate, and \((T_f - T_0)\) is the difference of the final and initial temperatures of the TPR experiment.

For \(\text{C}_2\text{H}_2\) TPR,

\[
V = 0.05 \text{ cm}^3, \quad Q = 200 \text{ cm}^3/\text{min.} \\
B = 5 \text{ K/min.}, \quad (T_f - T_0) = 500 \text{ K}
\]

therefore

\[
\frac{VB}{Q(T_f - T_0)} = 2.5 \times 10^{-6} \ll 0.01
\]

This shows that the lag time in the catalyst bed is negligible.

The second criteria is the lag time for a gas to diffuse out of a catalyst pore, which can cause an accumulation of desorbing gas inside the catalyst pore. This effect is negligible when:

\[
\frac{Br^2e}{(T_f - T_0)D_e} < 0.01
\]

where \(r\) is the radius of a spherical catalyst particle, \(e\) is the porosity, and \(D_e\) is the effective diffusivity of the desorbing gas through the carrier gas.

Here,

\[
r = \frac{dp}{2} = 3.7 \times 10^{-3} \text{ cm} \\
e = \frac{V_0d_0}{(V_0d_0 + 1)} = 0.41
\]

In the calculation of the effective diffusivity, the bulk diffusivity, \(D_{a,b}\), was first approximated by the Chapman-Enskog equation,

\[
D_{a,b} = 0.001858(T^9(1/M_a + 1/M_b))^{0.5} / (p\sigma_{a,b}\Omega)
\]

where \(M_a\) and \(M_b\) are molecular weights, \(p\) is pressure, \(\sigma_{a,b}\) is collision
In the integral and $Q_d$ is a dimensionless function of $T$ and Lennard-Jones parameters $\sigma_{AB}$ and $\epsilon_{AB}$.

In using this equation, the physical properties of B were taken to correspond to He since 90% of the carrier gas was He and the rest was H₂.

\[ T = 273 \text{ K} \quad p = 1 \text{ atm} \]
\[ M_A = 4 \quad M_B = 86 \]
\[ \sigma_{AB} = 4.243 \quad Q_d = 0.8735 \]

So

\[ D_{A,B} = 0.273 \text{ cm}^2/\text{sec} \]

The Knudsen diffusivity, $D_K$, was calculated by the equation,

\[ D_K = 9700a(T/M_B)^{0.5} \]

in which $a$ is the average pore radius

\[ a = 2V_b/S_b = 6.6 \times 10^{-7} \text{ cm} \]

Then

\[ D_K = 0.0114 \text{ cm}^2/\text{sec} \]

The effective diffusivity, $D_\varepsilon$, was then estimated from

\[ D_\varepsilon = (1/D_{A,B} + 1/D_K)^{-1}(\varepsilon/\tau) \]

where $\tau$ is tortuosity factor which is assumed to be 3, so
\[ D_e = 1.49 \times 10^{-2} \text{ cm}^2/\text{sec} \]

Using these values, we find

\[ \frac{Br^2e}{(T_f - T_0)D_e} = 6.2 \times 10^{-7} \ll 0.01 \]

This shows that the lag time within the catalyst pore is also negligible.

Concentration gradients within the catalyst pellet controlled by the ratio of the carrier gas flow rate to the diffusivity. In order to assume negligible concentration gradients

\[ \frac{Qr}{D_eA} < 0.1 \]

where A is the total external surface area of the catalyst sample. Since

\[ A = \frac{6W}{(d_0d_a)} = 41.4 \text{ cm}^2 \]

We find

\[ \frac{Qr}{D_eA} = 0.2 > 0.1 \]

This shows that there is a possibility of concentration gradients in the catalyst pellet, which would make it difficult to calculate kinetic parameters by the methods based on the assumption of uniform concentration of a product within the catalyst pellet.

Finally, the effects of readsorption of a desorbing gas may be neglected if

\[ \frac{\Gamma d_0Pr^2s}{T^4D_e} < 1 \]
where \( \Gamma \) is the active surface area, \( d_p \) is the density of the catalyst, \( F \) is flux of gas to the surface \( (=(RT/2\pi M_b)^{0.5}) \), and \( s \) is the sticking coefficient.

The active surface area, \( \Gamma \), of 1% Pd/Al\(_2\)O\(_3\) (dispersion 45.6%) was calculated to be 2.03 m\(^2\)/g from the knowledge of number of metal atoms per unit area of Pd surface, 1.27 \( \times \) 10\(^{19} \) m\(^{-2}\) (Anderson, 1975b). Then,

\[
\frac{d_p F \pi^2 s}{\Gamma^2 D_e} = 1.28 \times 10^8 s < 1
\]

No data for the sticking coefficient, \( s \), for hexane or other TPR products on Pd could be found in the open literature. But a qualitative reasoning on the effect of readsorption is possible. Except benzene, the TPR products are saturated hydrocarbons. Saturated hydrocarbons are known to adsorb weakly on metal atoms upon the loss of a hydrogen atom but this dissociative adsorption is prevented in the presence of hydrogen (Szabo et al, 1976). Since hydrogen can adsorb on Pd sites freely during TPR, readsorption of TPR products on the metal (except possibly for benzene) is probably negligible which is equivalent to a small value of the sticking probability.
Appendix C. Data Acquisition and Control System

In our experiments, the mass intensity data, temperature and time are monitored by an IBM-PC microcomputer controlled system (Refer to Figure C-1). This system consists of UTI 100C mass analyzer, Spectralink interface module (UTI), thermocouple signal conditioning module (MetraByte M1311), IBM-PC and a computer program, "TPR.C". Spectralink is the computer interface device for the UTI 100C mass analyzer which contains firmware to implement control and data communication programs. Therefore external control of the mass spectrometer and ion monitoring can be easily done by sending letter codes which invoke the firmware programs via RS-232 protocol. The signal conditioning module accepts signals from the thermocouple, performs analog/digital conversions, converts the data into temperature units and transmits this data via RS-232 protocol to the host computer.

The program, "TPR.C", controls the whole procedure of data acquisition and processing. It is written in C language and makes use of Greenleaf C library functions to perform various tasks including interrupts, sending and receiving data via RS-232 protocol, time recording, etc. With this program, temperature, time, and desired mass intensities can be assembled simultaneously at designated time intervals for disk storage and further processing.

The operating conditions for the mass spectrometer such as amplifier control, detector type, amplifier reading interval, etc. can be set from TPR.C through string commands sent to Spectralink. The program also allows calibration of exact mass locations through the invocation of Spectralink firmware which detects the existence of a known calibration
IBM PC

Program 'TPR.C'

Data file

Temperature

Signal conditioning module
(A/D Converter, Amplifier)

Thermocouple

String command

Mass intensities

UTI Spectralink
(Computer interface device)

UTI 100C

Mass analyzer

String command

Figure C-1. Data Acquisition and Control System.
compound and corrects the measured mass location to the true, known location. Our procedure used biphenyl as a calibration compound which was leaked into the mass spectrometer by passing a He stream over a short bed of biphenyl granules. The mass spectrometer was then tuned to the mass numbers of 18, 28, 39, 44, 51, 63, 76, 89, 102, 115, 128, 139, and 154, which are known to exist in the biphenyl mass spectrum or in the mass spectrometer background. This calibration procedure was found to be very important for the accurate determination of TPR products.

For a typical TPR experiment, the run conditions including mass numbers to be monitored, sampling intervals, and run duration are accepted by the TPR.C program along with the name of a file for data storage. When the TPR experiment is ready, the analysis procedure is implemented by TPR.C.
Appendix D. Sample Calculation for Dispersion Measurement

The amount of CO chemisorbed on Pd, \( n_{ad} \), was determined from the difference between the initial pressure of CO, \( P_i \), in the adsorption volume (\( V \)), and its equilibrium pressure, \( P_e \), as follows

\[
n_{ad} = (P_i - P_e)V/RTW
\]

where \( T \) = temperature of adsorption volume

\( W \) = catalyst weight

In a chemisorption experiment with Pd/Al₂O₃ prepared by wet impregnation,

\( V = 23.77 \text{ cm}^3 \)
\( T = 294.2 \text{ K} \)

and the adsorption data were as follows.

<table>
<thead>
<tr>
<th>( P_i ) (torr)</th>
<th>( P_e ) (torr)</th>
<th>( n_{ad} ) (µmoles/g)</th>
</tr>
</thead>
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<tr>
<td>(Total Adsorption)</td>
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<tr>
<td>46.02</td>
<td>24.10</td>
<td>56.80</td>
</tr>
<tr>
<td>67.15</td>
<td>43.59</td>
<td>61.06</td>
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<td>89.72</td>
<td>64.82</td>
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<td>114.50</td>
<td>88.38</td>
<td>67.68</td>
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<tr>
<td>(Weak Adsorption)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46.75</td>
<td>39.53</td>
<td>18.70</td>
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<td>71.25</td>
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<td>22.58</td>
</tr>
<tr>
<td>96.33</td>
<td>86.35</td>
<td>25.60</td>
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</table>
The adsorption isotherm is given in Figure 3–7 and the amount of the strongly adsorbed CO, which is equal to the difference between the total adsorption and the weak adsorption, was calculated to be 41.46 μmoles/g. The metal dispersion, D is given by

\[
D = \frac{n_{ad,s}X}{n_{pd}}
\]

where
- \(n_{ad,s}\): the number of moles of CO strongly adsorbed on Pd
- \(X\): stoichiometric number of CO adsorption on Pd
- \(n_{pd}\): the number of atoms of Pd in 1 g Pd/Al₂O₃ (1% Pd content)

\(n_{pd}\) is calculated to be \(9.398 \times 10^{-8}\) moles/g catalyst and \(X\) is assumed to be 1, then

\[
D = 0.441 (44.1%)
\]

Upon repeating the experiment, D was 47.0 % so the dispersion of Pd/Al₂O₃ catalyst prepared by wet impregnation was taken as 45.6 %, the average of the two measured values.
Appendix E. Optimization using the GRG2 Program for the Determination of Kemball’s Parameters

Formulation for optimization

- Objective Function:

The sum of the differences between the observed deuterium distribution and the calculated distribution.

\[ g = \sum (x_i^o - x_i^c)^2 \]

where,

\[ x_i^o = \text{observed fraction of isotopic species in gas phase} \]

(Ethylene for acetylene deuteration; ethylenes and ethanes for ethylene deuteration. Surface species are not included since they cannot be analyzed by MS)

\[ x_i^c = \text{calculated fraction of isotopic species} \]

\[ i = \text{number of deuterium atoms} \]

- Equality Constraints:

H/D balance equations for isotopic species derived in Appendix A

- Inequality Constraints:

\[ 0 \leq x_i \leq 1 \]

\[ 0 \leq p, q, s \leq 1 \]

(for acetylene deuteration)

\[ 0 \leq p, q, r, s \]

(for ethylene deuteration)

Optimization Parameters and Initial Values

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- GRG2 Optimization parameters used:

- EPN 0.1E-6, EPT 0.1E-6, EPI 0.1E-3, EPP 0.1E-3
- PH1 0.1E-4

- Initial Guess:

(1) Acetylene Deuteration

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<th>a₃</th>
<th>b₁</th>
<th>b₂</th>
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<td>.0208</td>
<td>.0208</td>
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(2) Ethylene Deuteration

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<th>e₅</th>
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<table>
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<th>f₅</th>
<th>f₆</th>
<th>f₇</th>
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<th>f₉</th>
<th>f₁₀</th>
<th>f₁₁</th>
<th>f₁₀</th>
</tr>
</thead>
<tbody>
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<td>.0082</td>
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<td>.0001</td>
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<td>.0008</td>
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<td>.0000</td>
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Appendix F. Raw TPR/TPD Data

In order to avoid making chapters too cumbersome, many of the TPD and TPR spectra were not included but only summarized in tables in the appropriate chapters. Actual spectra which were not included in previous chapters are contained in this Appendix.
Figure F-1a. TPR spectra of acetylene adsorbed on 100 mg Pd/alumina at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-1b. TPR spectra of acetylene adsorbed on 100 mg Pd/alumina at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-2a. TPR spectra of acetylene adsorbed on 100 mg Pd/silica at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-2b. TPR spectra of acetylene adsorbed on 100 mg Pd/silica at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-3. TPR spectra of acetylene adsorbed on 100 mg alumina at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-4. TPR spectra of acetylene adsorbed on 100 mg silica at 223K (acetylene 146.3 Pa, Table 5-1).
Figure F-5a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (acetylene 20.0 Pa, Table 5-2).
Figure F-5b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (acetylene 20.0 Pa, Table 5-2).
Figure F-6a. TPR spectra of acetylene adsorbed on Pd/alumina at 203K (Table 5-3).
Figure F-6b. TPR spectra of acetylene adsorbed on Pd/alumina at 203K (Table 5-3).
Figure F-7a. TPR spectra of acetylene adsorbed on Pd/alumina at 243K (Table 5-3).
Figure F-7b. TPR spectra of acetylene adsorbed on Pd/alumina at 243K (Table 5-3).
Figure F-8a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (1st. run, Table 5-4).
Figure F-8b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (1st. run, Table 5-4)
Figure F-9a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (2nd. run, Table 5-4.)
Figure F-9b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (2nd run, Table 5-4).
Figure F-10a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (3rd. run, Table 5-4).
Figure F-10b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (3rd. run, Table 5-4).
Figure F-11. TPD spectra of acetylene adsorbed on Pd/alumina at 223K (Table 5-5).
Figure F-12. TPR spectra of ethylene adsorbed on Pd/alumina at 203K (Table 5-6)
Figure F-13. TPR spectra of ethylene adsorbed on Pd/alumina at 298K (Table 5–6).
Figure F-14a. TPR spectra of acetylene with preadsorbed CO on Pd/alumina at 223K (20.0 Pa CO, Table 6-1).
Figure F-14b. TPR spectra of acetylene with preadsorbed CO on Pd/alumina at 223K (20.0 Pa CO, Table 6-1).
Figure F-15a. TPR spectra of acetylene with postadsorbed CO on Pd/alumina at 223K (20.0 Pa CO, Table 6-1).
Figure F-15b. TPR spectra of acetylene with preadsorbed CO on Pd/alumina at 223K (20.0 Pa CO, Table 6-1).
Figure F-16a. TPR spectra of acetylene with postadsorbed CO on Pd/alumina at 223K (73.2 Pa CO, Table 6-1).
Figure F-16b. TPR spectra of acetylene with postadsorbed CO on Pd/alumina at 223K (73.2 Pa CO, Table 6-1).

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Figure F-17. TPR spectra of ethylene with preadsorbed CO on Pd/alumina at 203K (20.0 Pa CO, Table 6-2).
Figure F-18a. TPR spectra of acetylene adsorbed on carbon-deposited Pd/alumina at 223K (Table 6-3).
Figure F-18b. TPR spectra of acetylene adsorbed on carbon–deposited Pd/ alumina at 223K (Table 6–3).
Figure F-19a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (Pd dispersion = 16.7%, Table 7-3).
Figure F-19b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (Pd dispersion = 16.7%, Table 7-3).
Figure F-20a. TPR spectra of acetylene adsorbed on Pd/1%K-alumina at 223K (Table 7-3).
Figure F-20b. TPR spectra of acetylene adsorbed on Pd/1%K-alumina at 223K (Table 7-3).
Figure F-21a. TPR spectra of acetylene adsorbed on Pd/2%K-alumina at 223K (Table 7-3).
Figure F-21b. TPR spectra of acetylene adsorbed on Pd/2%K-alumina at 223K (Table 7-3).

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Figure F-22a. TPR spectra of acetylene adsorbed on Pd/4%K-alumina at 223K (Table 7-3).
Figure F-22b. TPR spectra of acetylene adsorbed on Pd/4%K-alumina at 223K (Table 7-3).
Figure F-23a. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (catalyst dispersion = 36.2%, Table 7-3).
Figure F-23b. TPR spectra of acetylene adsorbed on Pd/alumina at 223K (catalyst dispersion = 36.2%, Table 7-3).
Figure F-24a. TPR spectra of acetylene adsorbed on 1%K-Pd/alumina at 223K (Table 7-3).
Figure F-24b. TPR spectra of acetylene adsorbed on 1%Pd/alumina at 223K (Table 7-3).
Vita

The author, Yeung Ho Park was born in Daejon, Korea on April 27, 1956. He graduated from Daejon High School in 1974.

In February 1978, he received a B.S. Degree in Chemical Engineering from Seoul National University in Seoul, Korea. He also received a M.S. Degree in Chemical Engineering from the same school in August, 1982. In August, 1984 he came to the United States to study in Ohio University, Athens, Ohio, where he received another M.S. Degree in Chemical Engineering. In August, 1985 he entered into the doctoral program in Chemical Engineering of Louisiana State University.

He is married to Soon Nim Choi in November, 1982 and has a boy.

At present, he is a candidate for the degree of Doctor of Philosophy in Chemical Engineering.
Candidate: Yeung Ho Park

Major Field: Chemical Engineering

Title of Dissertation: A Study on the Effects of Additives on Selective Hydrogenation of Trace Acetylene over Palladium Catalysts

Approved:

[Signatures]

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

March 12, 1991