JOURNAL OF CATALYSIS 86, 417–426 (1984)

The Effect of Catalyst Treatment on the Selective Hydrogenation of Acetylene over Palladium/Alumina

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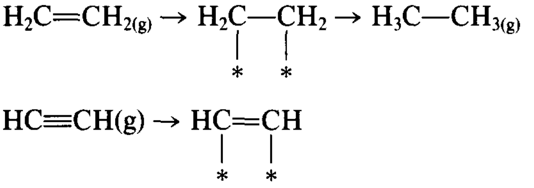
Received August 16, 1982; revised January 17, 1983

Hydrogenation of acetylene in an artificial acetylene–ethylene–deuterium mixture on three types of 0.04% Pd on alumina catalysts has been investigated. The effect of regeneration with oxygen, the hydrogenation temperature, ethylene fouling, and the effect of hydrogen vs deuterium were studied. It was established that supported palladium behaves similarly to the previously studied palladium black [Margitfalvi, J., Guczi, L., and Weiss, A. H., *J. Catal.* **72,** 185 (1981)] concerning the effect of carbonaceous deposits which affect the amount of surface hydrogen available for the formation of ethylidyne species. This form is responsible for the diminished selectivity. All factors removing this hydrogen result in an increased selectivity.

INTRODUCTION

The hydrogenation of acetylene has been the target of numerous studies (*1, 2*) because of both its commercial and fundamental significance. Traces of acetylene, typically 0.35 wt%, must be reduced to less than 5 ppm in order to meet ethylene polymerization specifications. Acetylene hydrogenation over 0.04–0.4 wt% Pd on Al_2O_3 is the favored industrial process as the acetylene concentration can be sufficiently reduced while the undesirable hydrogenation of ethylene to ethane is minimized.

By using idealized conditions to elucidate reaction paths and mechanisms, and ^{14}C-labeled acetylene and ethylene in the presence of deuterium, we have found (*3, 4*) that acetylene hydrogenation produces ethylene, ethane, and C_4^+ oligomers (the precursors to the "green oil" often found in industrial processes), while ethylene hydrogenation produces only ethane. The consecutive route from associatively adsorbed acetylene and ethylene to ethane proceeds as follows over Pd black:



$$H_2C{=}CH_{2(g)} \rightarrow \underset{*}{\underset{|}{H_2C}}{-}\underset{*}{\underset{|}{CH_2}} \rightarrow H_3C{-}CH_{3(g)}$$

$$HC{\equiv}CH(g) \rightarrow \underset{*}{\underset{|}{HC}}{=}\underset{*}{\underset{|}{CH}}$$

Acetylene is adsorbed so strongly that its adsorption is irreversible; ethane is adsorbed so weakly that its desorption is irreversible. Both acetylene and ethylene are adsorbed on the same sites, although adsorbed acetylene in effect prevents the adsorption, and therefore the subsequent hydrogenation of ethylene. In the industrial situation, acetylene concentrations are sufficiently low for both acetylene and ethylene to adsorb on the surface and undergo simultaneous hydrogenation there.

Adsorbed acetylene exists in a second form, the ethylidyne species, as demonstrated by Somorjai *et al.* (*5*). Hydrogen is stripped from dissociatively adsorbed acetylene, supplying hydrogen atoms on the catalyst surface which can then react with acetylene to form this species, which is responsible for the direct formation of ethane from acetylene. Note that the hydrogen atoms dissociated from the acetylene can,

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0021-9517/84 $3.00

and do, participate in subsequent reactions, contrary to the findings of Bond and Wells (*2*), but in agreement with those of McGown *et al.* (*7, 8*). Because the formation of this ethylidyne species requires a large population of neighboring active sites, the sites must be physically separated in order to increase selectivity.

A third form of acetylene also exists on the catalyst surface, namely C_2H_x ($x < 2$). Al-Ammar and Webb (*6*) calculated its bulk composition on supported Pd to be $C_2H_{1.4}$. This species is responsible for the formation of C_4^+ oligomers and the carbonaceous deposits on the catalyst surface. Thomson and Webb (*9*) proposed that it exists in a primary adsorption layer and acts as a transfer medium, supplying hydrogen for hydrogenations to the associatively adsorbed species which exist in a secondary adsorption layer.

The proportion of these three species on the surface may substantially control the overall selectivity, and their ratio can be affected by different factors.

Industrially, CO is used for catalyst modification and selectivity control. It occupies, and so blocks, the sites that are responsible for the formation of ethane. McGown *et al.* (*8*) studied the kinetics of selective acetylene hydrogenation in a spinning basket reactor and found that although CO inhibited both the consumption of acetylene and the formation of ethane, it inhibited the formation of ethane to a greater extent and therefore increased the selectivity.

Selectivity can also be altered in other ways, such as the choice of catalyst support, the mode of Pd deposition, or by catalyst aging (*4, 10*). Weiss *et al.* (*10*) studied catalyst selectivity and deactivation at 298 K over Pd on various supports. While supports had no activity of their own for either acetylene or ethylene hydrogenation, they were found to have a pronounced effect on the selectivity of the system. The most selective catalyst–support system was a commercial Pd on α-Al_2O_3. Other supports, in order of decreasing selectivity, were carbon fiber, silica fiber, and Carbosieve B. Peripherally and uniformly deposited Pd exhibited the same activity and only slightly different selectivities, indicating that the surface process was being studied, and that pore diffusion was not rate controlling.

In this report, we relate this background information to different types of 0.04% Pd on Al_2O_3 catalysts. We shall describe the effects of catalyst pretreatment on both selectivity and activity using deuterium labeling, and discuss these effects in terms of an overall reaction mechanism.

EXPERIMENTAL

Experiments on supported Pd catalysts were carried out in a batch reactor system similar to that described earlier (*3*). This system was made entirely of glass with Teflon valves and connections. It consisted of three parts: (i) a gas mixing section, 95 ml, (ii) a reactor which contained the catalyst, 35 ml, and (iii) a manometer connection, 10 ml. A magnetic circulation pump controlled by a square-wave generator circulated the gases over the catalyst at 5 ml/sec. The system operated at ambient temperature and a total pressure of 13.3 kPa.

A sampling valve with a 2 ml loop was used to sample the circulating gas mixture. All samples were separated in a Varian Aerograph series 1400 temperature programmed gas chromatograph, using a 1.0 m × 6.3 mm column packed with Carlo Erba activated alumina. The system operated isothermally at 323 K until both ethane and ethylene eluted, followed by a programmed rate of 20 K/min, to an upper limit between 435 and 475 K, depending upon the amount of C_4 compounds formed.

The effluent from the column was split in half (1 : 1), one going to a flame ionization detector (FID) for quantitative analysis, the other to a DuPont 21-490 mass spectrometer (MS) for deuterium distribution analysis. The FID output was recorded on a strip chart and integrated with a Chinoin Instrument Digint 31 Computing Integrator. The detectable limit for reaction rates was found to be about 10^{-9} mol s^{-1} g_{cat}^{-1}. MS peaks were measured manually and deuterium distributions calculated with the MASPEC computer program (Hungarian Academy of Sciences) which is based on C–H fragmentation factors and allows for naturally occurring ^{13}C.

The reaction mixture used was 9 : 1 : 40 of acetylene : ethylene : deuterium (C_2H_2 : C_2H_4 : D_2), respectively. Both the ethylene and acetylene were 99.95% pure by gas chromatography. Hydrogen and deuterium were purified by diffusion through a heated silver–palladium thimble when used for hydrogenation (deuteration) or catalyst regeneration, and by diffusion through a nickel catalyst and flow over molecular sieves at liquid nitrogen temperature when used for initial catalyst reduction.

Three catalysts were used in these experiments, all of which were 0.04 wt% Pd on Al_2O_3. These were the commercial catalyst ICI-38-3 (Type I), described by McGown *et al.* (*7*), and two catalysts prepared in the laboratory on γ-alumina having a surface area of 90 m^2/g. The Pd on these catalysts was peripherally deposited from a solution of $PdCl_2$ in ethanol–acetone and dried. One (Type II) was calcined at 875 K for 1 hr after impregnation; the other (Type III), was not calcined. All three catalysts were composed of 3 × 5 mm pellets.

Typically, 0.5 g of catalyst was charged to the reactor at a time. It was first treated with oxygen, then purged with nitrogen and reduced with either hydrogen or deuterium, all at 101 kPa and flow rates of about 0.5 ml/sec.

RESULTS

The activity of the catalysts is expressed as the conversion of acetylene in moles s^{-1} g_{cat}^{-1} units. Selectivity (S) is defined as:

$$S = \frac{R_{C_2H_4}}{R_{C_2H_4} + R_{C_2H_6}}$$

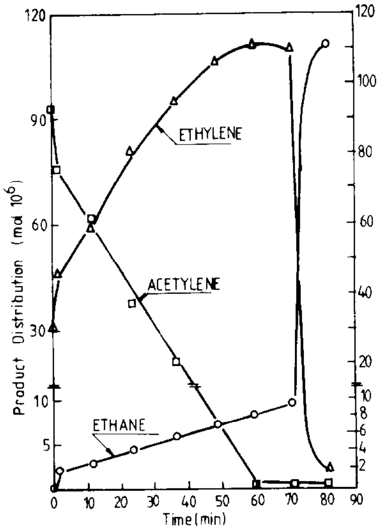


FIG. 1. Concentration of acetylene (□), ethylene (△); and ethane (○) vs time on Type II catalyst using a 15 : 5 : 81 C_2H_2 : C_2H_4 : H_2 mixture at 298 K.

where $R_{C_2H_4}$ = net rate of ethylene production, moles s^{-1} g_{cat}^{-1} and $R_{C_2H_6}$ = net rate of ethane production, moles s^{-1} g_{cat}^{-1}.

Figure 1 shows that the reaction usually exhibited three distinct phases which is typical for each catalyst. In a brief initial period, the reaction is rapid, forming both ethylene and ethane, though often with poor selectivity. In the second phase, the rates of acetylene consumption, and ethylene and ethane production are all constant. The third phase begins when acetylene hydrogenation is almost complete, and in this region approximates to the industrial situation. This behavior is analogous to that reported by McGown *et al.* (*7*) in a similar batch reaction study.

In the initial period (0 to 2 min in Fig. 1), the reaction rate is high, while selectivity is low and apparently dependent on catalyst pretreatment.

In the constant rate period (2 to approximately 60 min in Fig. 1), hydrogenation of acetylene is the primary reaction. The selectivity is usually high, and is characteristic of changes occurring in the catalyst. In this study, selectivity, activity, and other parameters are evaluated from data taken during this period. Finally, the acetylene partial pressure drops sufficiently and the rapid hydrogenation of ethylene begins.

Normally operating conditions were monitored in the constant rate phase of the reaction, during which time most of the data were gathered, and from them selectivity and activity values were calculated.

Frequently, C_4 and higher hydrocarbons (C_4^+) were detected in the product gases. The first to appear were butenes, initially only in small fractions of a percent, but in more abundance as the acetylene partial pressure decreased. Upon complete consumption of the acetylene, the butenes were rapidly hydrogenated to butane.

Experiments were made to elicit the influence of (i) oxygen treatment, (ii) hydrogen vs deuterium, (iii) catalyst aging, and (iv) high temperature ethylene pretreatment, on catalyst selectivity.

Oxygen Treatment

Initial O_2 treatment was at 475 K for 30 min, followed by purging with N_2 for 5–10 min while heating from 475 to 575 K. Next, the catalysts were reduced in either H_2 or D_2 for 2 hr at 575 K. Finally, the catalysts were evacuated to less than 10^{-2} Pa at temperatures of 575 to 775 K for 30 min, then cooled to room temperature under vacuum prior to reaction.

Treatment of a fresh sample with only H_2 reduction produced a less active catalyst than with O_2 oxidation followed by reduction. For example, the acetylene consumption rate, $R_{C_2H_2}$, increased from 4×10^{-8} to 7×10^{-7} mol s^{-1} $g_{cat}{}^{-1}$ at 343 K, and from $<10^{-9}$ to 8×10^{-8} at 303 K with a simultaneous change of selectivity values of 0.89 and 0.95 for H_2 or O_2–H_2 treated samples, respectively.

Table 1 shows the effect of evacuation temperature after initial catalyst oxidation and reduction on the selectivity during the initial stage of the reaction. This period may comprise initiation of the various surface species and intermediates on the catalyst. With evacuation at 575 K, there is a large initial formation of ethane, while at 715 and 775 K, the initial reaction is highly selective to ethylene. This suggests that the higher evacuation temperatures result in the removal of some portion of the hydrogen that is either adsorbed or chemisorbed on the catalyst surface and that would otherwise have been active in the hydrogenation process.

TABLE 1

Effect of the Temperature of Evacuation on the Initial Yield (in the First Minute) at the Start of a Batch Reaction with a 9 : 1 : 40 $C_2H_2 : C_2H_4 : H_2$ Mixture with 13.3 kPa Total Pressure on Type III Catalyst

Temperature of evacuation (K)	Initial yield (moles/g_{cat})	
	Ethane	Ethylene
575	1.5×10^{-5}	1×10^{-6}
715	4.4×10^{-6}	3×10^{-5}
775	4.2×10^{-6}	4×10^{-5}

The effects of oxidation temperature on activity and selectivity are summarized in Table 2. This shows the acetylene hydrogenation rate at 298 K increasing from 8×10^{-9} to 6×10^{-8} mol s^{-1} $g_{cat}{}^{-1}$ when the oxidation temperature is increased from 473 to 533 K, with a corresponding selectivity increase from 0.87 to 0.93.

Hydrogen vs Deuterium

The hydrogenation of acetylene (and of ethylene) utilizes hydrogen or deuterium

TABLE 2

Effect of Regeneration Temperature on the Reaction at 298 K with $C_2H_2 : C_2H_4 : H_2$ Mixture in 9 : 1 : 40 Ratio at 13.3 kPa Total Pressure, Using Type III Catalyst

Temp (K)	Activity $R_{C_2H_2}$ (mol s^{-1} $g_{cat}{}^{-1}$)	Selectivity $\frac{R_{C_2H_4}}{R_{C_2H_6} + R_{C_2H_4}}$
473	8×10^{-9}	0.87
525	3×10^{-8}	0.90
553	6×10^{-8}	0.93

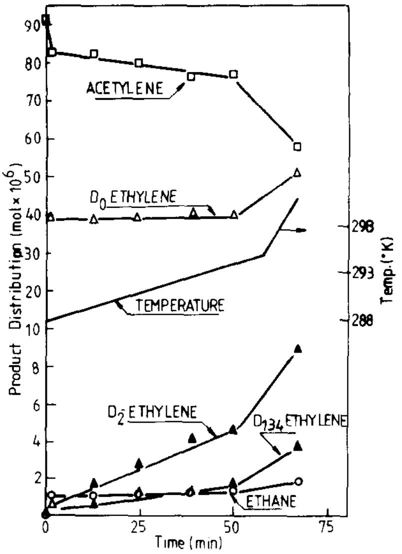


FIG. 2. Consumption of acetylene, formation of ethane and deuterated ethylene on Type II catalyst using a 3 : 1 : 16 $C_2H_2 : C_2H_4 : D_2$ mixture.

mainly from the gas phase. However, when conditions are changed by a rapid temperature increase, hydrogen from another source, either adsorbed on the surface or dissociated from acetylene, is utilized. Figure 2 shows the changes which occurred in the total number of moles of each species present in the system, including the deuterium distributions in ethylene. In this particular experiment, hydrogen was used in the initial reduction of the catalyst, while deuterium was used as the reactant in the system. During the constant rate period, the temperature increased slightly, from 291 to 295 K. The rate of formation of ethylene-d_0 was zero after the initiation phase, but increased when a temperature jump was made at 55 min. There was also an increase in the total ethylene rate of formation during this period.

Most importantly, however, the source of hydrogen for the production of ethylene-d_0 was either from acetylene dissociation, or adsorbed hydrogen on the catalyst from the initial reduction, as deuterium was used in the gas phase. Other work (*11*), in which the deuterium distributions of the C_4 compounds produced were calculated, has shown that hydrogen dissociated from acetylene can react in this system.

Table 3 shows the effects of the use of hydrogen and deuterium on catalyst activity. When only D_2 was used for reduction, regeneration, and reaction, the reaction rate was very low, approximately 3×10^{-9} mol sec^{-1} g_{cat}^{-1}, while the use of only H_2 produced a much higher rate, 1.2×10^{-7} mol sec^{-1} g_{cat}^{-1} (B vs C). This is a factor of 40 difference. Table 3 also shows the following points.

(i) When used as a reactant, H_2 resulted in a rate eight times greater than did D_2 (B vs E). This is much larger than the 1.4–1.6 isotope factor reported by Inoue and Yasumori (*12*) for the same reaction.

(ii) All else being equal, the difference between the use of H_2 or D_2 for reduction after regeneration is not significant (B vs F, D vs E).

(iii) Initial catalyst reduction with H_2 resulted in approximately five times greater activity than with D_2 (A vs B, C vs D).

The effective difference between H_2 and D_2 was only in the catalyst activity. There was no significant difference in selectivity in any case.

Catalyst Aging

The Pd/Al_2O_3 catalyst activity usually improved with age during the first few experiments, and was stable thereafter (see Fig.

TABLE 3

Effect of D_2 vs H_2 on the Rate of Reaction Measured at 298 K: Catalyst of Type II Reacted with 3 : 1 : 16 Mixture of $C_2H_2 : C_2H_4 : D_2(H_2)$ at T = 298 K

	D_2 or H_2 used for			Rate × 10^7 (mol s^{-1} g_{cat}^{-1})
	Pretreatment	Reduction after regeneration	Reaction	
A	D_2	H_2	H_2	0.33
B	H_2	H_2	H_2	1.2
C	D_2	D_2	D_2	0.03
D	H_2	D_2	D_2	0.2
E	H_2	H_2	D_2	0.15
F	H_2	D_2	H_2	1.0

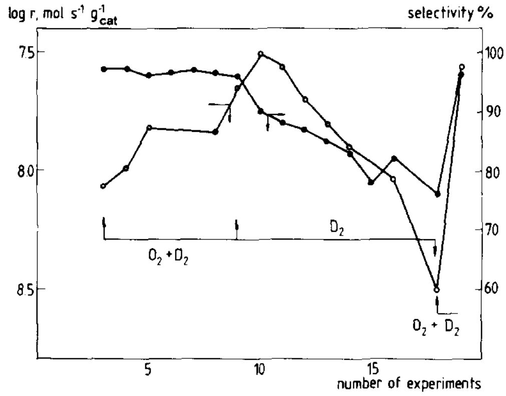


FIG. 3. The effect of $O_2 + D_2$ vs D_2 treatment as a function of the number of experiments on activity and selectivity on Type I catalyst with a 3 : 1 : 16 $C_2H_2 : C_2H_4 : D_2$ mixture.

3). Selectivity of the catalysts which were regenerated with O_2, while not a very stable indicator, did not show any trends with age. This may be contrasted with previous studies (*7, 10*) where selectivity decreased sharply on aging of Pd catalysts that were not regenerated with O_2. After 25 experiments on one sample of Type I catalyst, with oxidation and reduction after each experiment, the ratio of ethylene to ethane production rates remained close to 20. McGown *et al.* (*7*) reported that on the same catalyst, but without oxidation between experiments, this ratio decreased from 15–20 to about 2–3 after only four experiments.

Ethylene Fouling

After several reactions and regenerations had been carried out on one sample of catalyst, it was fouled with ethylene in the following way. Fifty Torr of ethylene was circulated over the catalyst at 363 K for 1 hr. The catalyst was then regenerated as before with O_2, H_2, and evacuation at 575 K. The resulting activity of the next experiment was approximately one-third of that observed prior to the fouling, with a corresponding selectivity decrease from 0.95 to 0.93. However, after another regeneration cycle, both the activity and selectivity had returned to their original values. Thus, the effect of ethylene fouling was serious, but reversible, at a temperature typical of commercial front end selective hydrogenations.

Kinetics

Referring back to Fig. 1, the reactions on the 0.04% Pd/Al_2O_3 catalysts of Type I and Type II follow similar courses as those reported for Pd black (*11*), except that in the latter case, the initiation phase is not present. Figure 4 shows deuterium distributions as percentage in ethylene species, which are also quite similar to those reported in Fig. 6 of Ref. *11* in which Pd black was used.

The effect of hydrogen partial pressure on the hydrogenation reaction is related to the initial hydrogen pressure. In any given experiment, the reaction was zero order in hydrocarbon reactants while acetylene was present. However, the reaction was first order, or greater, with respect to the initial hydrogen pressure (see Fig. 5).

Figure 6 shows an Arrhenius plot for Type II Pd/Al_2O_3 catalyst. The reaction rate constants were calculated assuming a first order dependence on initial hydrogen pressure and a zero order dependence on hydrocarbon partial pressure. The activation energy above 298 K is 41.8 kJ/mol.

This effect is analogous to that reported by Rennard and Kokes (*13*) for the hydro-

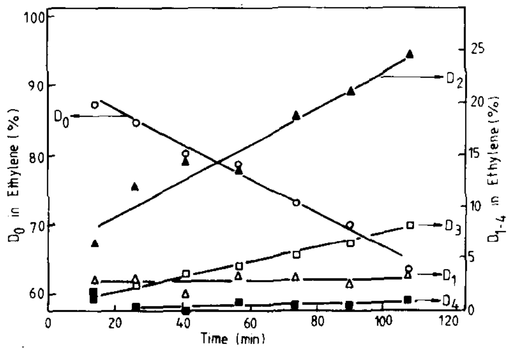


FIG. 4. Deuterium distribution in ethylene formed vs time in reaction with 9 : 1 : 40 $C_2H_2 : C_2H_4 : D_2$ mixture on Type I catalyst at 288 K.

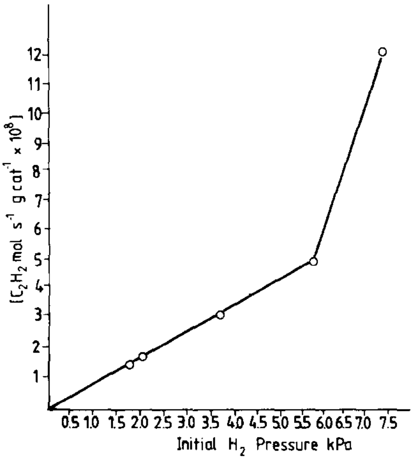


FIG. 5. Rate of acetylene consumption vs p_{H_2} in the reaction with 3 : 1 C_2H_2 : C_2H_4 mixture on Type II catalyst at 298 K.

genation of ethylene on palladium hydride in which they described the kinetics in terms of a first order rate constant dependent only on the initial content of hydrogen in the palladium and zero order in gas phase hydrogen. Analogously to the present results, the initial hydrogen pressure dictates the amount of hydrogen absorbed by the palladium. As a consequence, the rate is dependent upon the hydrogen content in the Pd and the kinetics appear to be dependent upon initial hydrogen pressure.

The selectivity tended to increase with decreasing hydrogen partial pressure. However, this can only be reported as a trend, as the selectivity reproducibility was poor in these experiments.

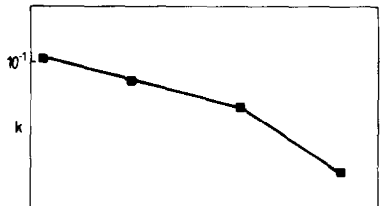


FIG. 6. Arrhenius plot for reaction in 3 : 1 : 16 C_2H_2 : C_2H_4 : D_2 mixture at 8 kPa total pressure on Type II catalyst. K = rate of C_2H_2 consumption/initial H_2 pressure.

DISCUSSION

In our earlier work on palladium black (*11*), we obtained evidence that there was only one type of active palladium site operating. The behavior of the site is different at high vs low concentration of acetylene (in ethylene). In the former case, acetylene is so strongly adsorbed relative to ethylene that it dominates the surface. As was shown for an industrial mixture on the same catalyst (*14*), as long as the full coverage of the surface with regard to acetylene is maintained, ethylene is not hydrogenated on palladium and a drop in the overall selectivity is due to the hydrogenation of ethylene on a support-oligomer site. On the other hand, reactions are different from those in which acetylene partial pressure is so low that ethylene can also competitively adsorb on the surface. It is clearly indicated in Fig. 1 where at about 70 min a dramatic change in hydrogenation selectivity is observed: at this stage the acetylene coverage is abruptly decreased and ethylene is also adsorbed on the metal site; thereby the rate of ethylene hydrogenation is increased resulting in a sharp drop in the overall selectivity. This effect of supported palladium is more pronounced than on Pd black (*11*) because of the distance between Pd sites.

Another difference in the supported catalyst is the high deactivation rate relative to that of Pd black. This is due to accumulation of oligomers and carbonaceous deposits within the pores which is not a problem with Pd black. It was shown in Ref. (*3*) that the oligomer on Pd black is produced from acetylene not ethylene, and in this present study C_4, C_6, and C_8 species were observed.

The well known "oxygen effect," also observed here, is probably due to combustion of carbonaceous materials from the vicinity of the active sites. Without oxygen regeneration the activity decline observed here is a function of time. These phenomena are reflected in kinetics, too. In Table 4 oxygen-treated catalysts of Types I–III

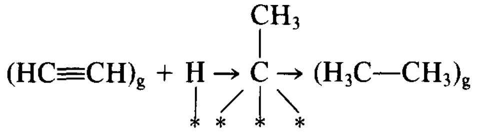
TABLE 4

Comparison of Activity and Selectivity of Different Catalysts in Acetylene Hydrogenation

Catalyst type	T (K)	$P_{C_2H_2}$ (kPa)	$P_{C_2H_4}$ (kPa)	P_{H_2} (kPa)	Measured rate (mol s^{-1} g_{cat}^{-1})	S	Corrected rate[a] (mol s^{-1} g_{cat}^{-1})
I[b]	293	0.41	19.5	0.82	4.36×10^{-9}	0.74	2.18×10^{-8}
I[c]	298	1.33	5.32	2.66	1.75×10^{-8}	0.92	1.97×10^{-8}
II	293	2.0	0.66	4.1	2.51×10^{-8}	0.95	2.51×10^{-8}
III	283	2.0	0.66	4.1	2.62×10^{-8}	0.97	4.8×10^{-8}

[a] Rate is corrected to 4.1 kPa H_2 and 293 K assuming rate equation of $r = kP_{H_2} \exp(-10{,}000/RT)$.
[b] Measured by McGown *et al.* (*5*).
[c] Measured in our laboratory.

show similar activity, but considerably higher selectivity, than Type I catalyst without oxygen treatment. In order to explain the change of selectivity we may use the formation of ethylidyne species suggested by Somorjai *et al.* (*5*) by the reactive type of acetylene adsorption (*11*). The criteria for the presence of this species are the presence of hydrogen atoms on the surface and three palladium sites in a given geometrical arrangement. In fact, by increasing the evacuation temperature (see Table 1), hydrogen can be removed from the surface



$$(HC{\equiv}CH)_g + \underset{*}{H} \rightarrow \overset{CH_3}{\underset{* \;*\; *}{C}} \rightarrow (H_3C{-}CH_3)_g$$

and thus an increased selectivity can be observed. The same effect can be shown by increasing the oxidation temperature (see Table 2). In this latter case the carbonaceous deposits can be removed to a larger extent than at low temperature. The presence of carbonaceous deposit results in increased hydrogen coverage as shown by Szymerska and Ratajczykowa (*15*) on Pd film. The same phenomenon was shown by Boudart *et al.* (*16*) on the platinum/carbon system. Consequently, at elevated temperature, the more carbonaceous deposits that can be removed, the less hydrogen coverage will be present. As a result of the smaller amount of hydrogen available a higher selectivity is observed.

As previously pointed out the amount and the source of hydrogen on the palladium surface are important and control the activity and selectivity as well. At low hydrogen coverage we have high selectivity but low activity at steady state (see Fig. 3) but if the surface polymer is allowed to build up, activity and selectivity decrease; the former does so because a part of the active site is covered, the latter, because hydrogen coverage becomes too high. It is important to consider the different possibilities for the hydrogen source at different stages of the reaction.

Concerning unsupported palladium, the β-hydride phase, which has a close relationship to both the activity and the selectivity, may be formed. Thus, Palczewska (*17*) showed for acetylene hydrogenation that in parallel with the formation of the hydride phase there is a simultaneous increase in the rate of acetylene hydrogenation and a drop in selectivity. Similarly, Janko *et al.* (*18*) found that the rate of hydrogenation increased 10-fold after the formation of the hydride phase. Based upon the results obtained by Rennard and Kokes (*13*) for ethylene hydrogenation on palladium hydride, we may assume that the diminished selectivity in acetylene hydrogenation is caused by the increased rate of ethylene hydrogenation. However, Palczewska (*17*) showed that ethylene hydrogenation is poisoned by the formation of palladium hydride. Thus, we may conclude that hydrogen in hydride participates in the formation of ethylidyne species which are transformed only to ethane, thereby causing the diminished selectivity. Consequently, all factors which can influence the amount of palladium hydride on the surface sensitively affect the selectivity by influencing the proportion of the ethylidyne species.

Unfortunately, the presence of hydrogen in hydride form is not unambiguously proved. Nevertheless, Scholten and Konvalinka (*19*) showed that the hydride phase is present on 0.5% Pd on alumina possessing particle size less than 1.5 nm. In our case, the difference in the rate of acetylene hydrogenation by using hydrogen vs deuterium (see Table 3, lines B and F) might be due to the formation of palladium hydride if hydrogen is present, and the absence of palladium deuteride when deuterium is present (formation of deuteride is thermodynamically unfavored, see Ref. *20*).

However, the above interpretation contradicts the experimental fact that in the presence of deuterium only the catalytic activity decreased whereas the selectivity is the same as that in hydrogen. In order to explain this finding it has to be considered that in the initial stage of hydrogenation, deuterium has no effect because a large amount of ethylene-d_0 is formed. In agreement with the phenomena obtained on Pd black, on supported palladium, hydrogen is dissociated from acetylene and used for hydrogenation. This is further proven by experiments in which temperature is increased because here ethylene-d_0 also increases, indicating that more hydrogen participates in the hydrogenation (see Fig. 2). The effect of deuterium is, therefore, rather due to a structural change of the catalyst because the use of deuterium in place of hydrogen in the initial treatment affects the catalytic activity to a large extent; i.e., the catalyst "remembers" whether this treatment was carried out in hydrogen or in deuterium (compare A to B and C to D in Table 3). The effect of deuterium is negligible in the regeneration state. Moreover, the carbonaceous deposit aids the formation of the hydride phase (*15*); therefore, the decrease in activity is always accompanied by a decline in selectivity.

In summary, the catalyst pretreatment mainly influences the amount of surface hydrogen. All factors which decrease the surface hydrogen diminish the catalytic activity and increase the selectivity. Surface oligomers increase the hydrogen coverage; thus activity increases, but selectivity decreases. Part of the acetylene dissociates its hydrogen which participates in the hydrogenation. Deuterium treatment probably alters the structure of the palladium catalyst.

ACKNOWLEDGMENTS

The authors express their appreciation to the Petroleum Research Fund of the American Chemical Society, the National Science Foundation (Grant INT 7918395), and the Hungarian Academy of Sciences for their support of this research, and to Mr. S. LeViness of the Worcester Polytechnic Institute for useful discussions and assistance in preparing this report.

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