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Reactions of Acetylene during Hydrogenation on Pd Black Catalyst

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Deuteration of trace amounts of acetylene in the presence and absence of ethylene has been studied on Pd black catalyst in a continuous flow reactor. At nonsteady state the Pd black catalysts showed very low selectivities, whereas higher selectivities were obtained at steady state. Pretreatment with air and H_2 yielded a catalyst with higher selectivity than the same catalyst treated only with H_2. The order in acetylene pressure passed from positive to negative with increasing $p_{C_2H_2}$ both in the presence and absence of ethylene. The deuterium distribution of the ethylene formed showed that hydrogen originating from acetylene also took part in the hydrogenation reaction; thus, part of the acetylene dissociatively adsorbed on the surface. Using $[^{14}C]C_2H_2$ it was demonstrated that at low acetylene partial pressure the main route of acetylene hydrogenation was the formation of ethane, ethylene, and C_4 hydrocarbons. Using $[^{14}C]C_2H_4$ it was also shown that at certain level of acetylene partial pressure the formation of ethane from ethylene was completely terminated. The observed kinetic data are discussed and it is suggested that different surface species such as dissociatively and associatively adsorbed acetylene as well as ethylidyne species are present on the palladium surface. Experimental conditions, such as catalyst pretreatment and partial pressure of the reactants, can influence the relative concentrations of these surface species and can also change the routes of surface reactions, leading to different reaction products from acetylene. The reaction mechanism proposed is discussed based on different organometallic and spectroscopic evidence published recently.

1. INTRODUCTION

Acetylene hydrogenation on metal catalysts has been the subject of extended studies (*1*, *2*). Palladium was found to be the most active and selective catalyst among the transition metals (*3*, *4*). One of the characteristic features of acetylene hydrogenation is a sudden decrease of selectivity when the hydrogen-to-acetylene ratio exceeds a certain value (*5*). Bond and Wells (*6*) have also reported that the rate of acetylene hydrogenation was altered on ethylene addition.

The selectivity phenomenon is a crucial point in this reaction, especially when a mixture of acetylene and ethylene is hydrogenated. Using ^{13}C-labeled acetylene and deuterium, McGown *et al.* showed (*7*) that similarly to the finding of Bond and Wells (*6*), ethylene is not an inert diluent in the initial stage of the reaction and they also demonstrated (*8*) that, with higher amounts of added ethylene, the rate of acetylene hydrogenation became lower. At higher ethylene partial pressures the fraction of acetylene dimerized was also reduced except at low levels of acetylene.

On the other hand, Al-Ammar *et al.* showed (*9*–*11*) with a ^{14}C-tracer study that ethylene adsorption and hydrogenation occurred in the presence of acetylene. No displacement of ^{14}C-labeled ethylene by acetylene was observed.

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By studying the hydrogenation of acetylene–[^{14}C]ethylene mixture in the presence of deuterium it was clearly demonstrated (*12*) that at the initial stage of the reaction ethane was directly formed from acetylene. That is, under a given condition, formation of ethane cannot be influenced by lowering the ethylene hydrogenation activity of the palladium black catalyst. It was proposed that initially the surface was monopolized by acetylene and subsequently, after the acetylene partial pressure had decreased, ethylene could be competitively adsorbed in significant quantities.

The observed selectivity is always subject to the influence of experimental conditions. Thus, on aging, Weiss *et al.* (*13*) found that the selectivity of acetylene deuteration to ethylene in the ethylene–acetylene mixture decreased as a function of time as the catalyst aged. Activity for acetylene conversion remained constant, but that for deuterium conversion increased to accommodate the additional ethane formed. The decrease in selectivity with aging observed (*13*) might have been correlated with the slow buildup of the β-Pd hydride phase, which has been suggested to be responsible for a decrease in selectivity of acetylene hydrogenation (*14, 15*). The hydrogen in the hydride phase is provided by the dissociative adsorption of acetylene. It has been suggested that dissociatively adsorbed species are involved in the formation of permanently retained acetylenic species which are responsible for activity decrease (*11*).

On the basis of data from hydrogenation of unsaturated hydrocarbons on metals (*16*), it was proposed (*11*) that hydrogenation takes place by a hydrogen transfer mechanism between a dissociatively adsorbed C_2H_x species and associatively adsorbed acetylene. The latter forms an overlayer on the dissociatively adsorbed acetylene.

However, we should not neglect the importance of the different surface species formed by interaction of acetylene with the metal surface and their role in the final selectivity of a palladium catalyst. Indeed, a clean metal surface is capable of activating both acetylene and ethylene to form multiple-bonded carbyne and carbene-type surface complexes as shown by different methods, viz., LEED (*17*), UPS (*18, 19*), and ELS (*20*).

The main goal of the present study is to elucidate the participation of the various surface intermediates in the selective hydrogenation of acetylene on palladium catalyst. The intrinsic selectivity of this metal is highly influenced by the experimental condition, the reactant ratio, the pretreatment, and reaction in the nonsteady and steady states. We shall use the Double-Labeling Method (DLM) developed earlier (*12*), modified for flow system studies.

2. EXPERIMENTAL

Acetylene deuteration was carried out in a conventional continuous flow reactor at atmospheric pressure at 273 K. All parts of the reactor manifold were of stainless steel. The reactor, 8 mm o.d., 6 mm i.d., made of Pyrex glass, was equipped with two Teflon valves attached to the manifold by two ball joints. The catalyst (18 mg Pd black supplied by Strem Chemicals) was inserted between two glass-wool plugs. Under our reaction conditions the reactor could be considered as a back-mixed flow reactor. All reaction rates, except when it is stated otherwise, were measured under steady-state conditions.

Helium carrier gas (Air Products) and deuterium (Matheson) were deoxygenated by a Deoxo catalytic unit and dried over columns of molecular sieve 5A and Drierite before introduction into the reactor. Hydrocarbons (CP-grade ethylene and purified acetylene, both supplied by Matheson) were dried before entering the reactor. A constant flow rate of 1 ml/s was kept through the catalyst bed in all hydrogenation reactions. The flow rates of helium and ethylene were regulated with precision needle valves and measured with a bubble flowmeter. Acetylene and deuterium flow rates were fixed by stainless-steel capillaries Hamilton syringes. Six-way sampling valves before and after the reactor were used for samples. Analysis of the reaction products, including all C_4 hydrocarbons formed, was made by gas chromatography, using a 3.2×10^{-3}-m × 1.2-m (1/8 in. × 4.0 ft) SS phenyl isocyanate on Porasil C column.

In the ^{14}C-labeled experiments a 2.4-m-long column was used for better ethane–ethylene separation. The carrier gas, helium, had a flow rate of 0.25 ml/s. The effluent from the GC column was split in the ratio 5 : 1 to the mass spectrometer (MS) and flame ionisation detector (FID). Deuterium distribution of ethane, ethylene, and acetylene was measured by a Dupont 29-491 double-focusing mass spectrometer. A Nuclear Chicago, Tracerlab Versamatic V Scaler, model O-47 proportional counter was used for ^{14}C radioactivity measurements. In these experiments the effluent from the GC column was split in the ratio 10 : 2 : 1 going to the proportional counter (PC), mass spectrometer (MS), and flame isonisation detector (FID). Radioactive acetylene ([1, 2-^{14}C]acetylene, 58.0 mCi/mmol) and ethylene ([1,2-^{14}C]ethylene, 109 mCi/mmol) purchased from New England Nuclear, were used in the double-labeling experiments. The radioactive gases were introduced to the reaction mixture using a syringe pump equipped with a back-flush gas-tight Hamilton syringe. The latter was connected with Teflon tubing to the gas manifold into the reactor. Before use, the radioactive gases were diluted with nonradioactive ethylene or acetylene, respectively.

Before each series of experiments the following standard procedure was carried out to regenerate the catalyst. First, deposits on the catalyst were burnt off by heating the catalyst in air at 573 K for 1.8×10^4 s. Then the catalyst was treated with flowing 2 : 1 He : D_2 mixture, $1.5–1.7 \times 10^{-2}$ ml/s for 5.4×10^4 s at 533 K. After deuterium treatment the catalyst was cooled in the 59 : 1 He : D_2 mixture (flow rate: 1 ml/s). The deuterium content of the gas mixture in the cooling period had no influence on the steady-state reaction rates in the hydrogenation experiment. Any other changes at higher temperatures had a significant influence on the steady-state reproducibility. Two types of catalyst were distinguished: catalyst without air pretreatment, type I, and catalyst with air pretreatment, type II.

In special cases, during the catalyst regeneration procedure at 533 K, small amounts ($0.8–1.6 \times 10^{-5}$ ml/s) of ethylene or acetylene were introduced into the mixture of helium and deuterium by the previously mentioned syringe pump equipped with a back-flush gas-tight syringe (catalyst, type III).

3. RESULTS

The activity of the catalysts was evaluated on the basis of either the rate of conversion of acetylene or the rate of formation of reaction products per gram of catalyst. The reaction of acetylene with deuterium over palladium at 273 K gave ethane, ethylene, butane, 1-butene, *cis*-2-butene, and *trans*-2-butene. No butadiene was found. No analyses were made for higher hydrocarbons such as C_6 and C_8. The higher-molecular-weight products amount to 5–20% of the acetylene reacted. For this reason, two selectivities are defined, the commonly used ratio and the one which takes into account the formation of C_4 hydrocarbons. These are

$$S_1 = \frac{r_{C_2H_4}}{r_{C_2H_4} + r_{C_2H_6}} \quad \text{and}$$

$$S_2 = \frac{r_{C_2H_4}}{r_{C_2H_4} + r_{C_2H_6} + r_{C_4H_x}},$$

where

$r_{C_2H_4}$ = net rate of ethylene production, mol/g_{cat} s,

$r_{C_2H_6}$ = net rate of ethane production, mol/g_{cat} s,

$r_{C_4H_x}$ = net rate of total C_4 production mol/g_{cat} s.

3.1 Reaction in Nonsteady State

Steady state was reached within 1–3 h after reactant flow was started, depending on the type of catalyst and on the deuterium and acetylene partial pressures.

Immediately following the introduction of acetylene into the reactor, an extremely fast acetylene consumption was observed. Figure 1 shows such results for catalyst type I. At the same time the rates of formation of ethylene and ethane were also initially high and S_1 selectivity was extremely low (Fig. 1). The acetylene consumption and the ethylene and ethane formation decreased and the selectivity increased as the reaction system approached the steady state. Stopping the acetylene flow after steady state had been reached resulted in an unexpected large increase in the rates of formation of ethane and ethylene and the S_1 selectivity drastically decreased.

The deuterium distribution of ethylene formed in this experiment is also presented in Fig. 1. There is a significant difference in the deuterium distribution at the very beginning of the reaction where $C_2H_2D_2$ predominates and at steady state where C_2H_3D and $C_2H_2D_2$ are about equal. This suggests that hydrogen dissociated from acetylene is also reactive. The ethylene-d_0 content slightly increased as the reaction proceeded. Only the ethylene-d_1 showed considerable increase, but the percentage of ethylene-d_2, -d_3, and -d_4 decreased while approaching steady state. After disconnecting the acetylene flow a significant increase in ethylene-d_2 and a parallel decrease in ethylene-d_0 were obtained (Fig. 1). The mean deuterium number for ethylene was about 1.90–1.95 and 1.75–1.80 initially and at steady state, respectively. After disconnecting acetylene it increased again to 1.85–1.90.

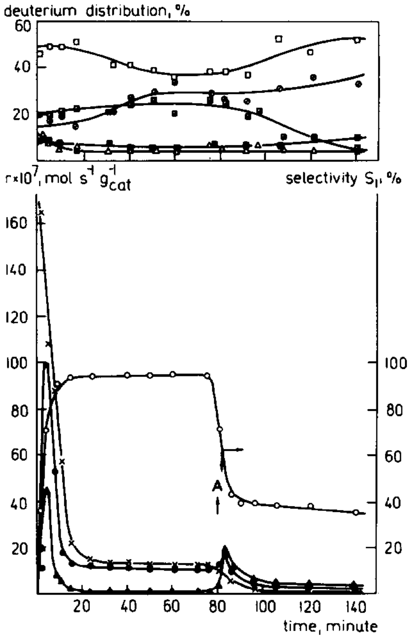


FIG. 1. Lower set of curves: Rates of acetylene deuteration (×) and formation of ethylene (●) and ethane (▲), and selectivity (S_1) data (○) under nonsteady-state and steady-state conditions, as well as after disconnecting acetylene flow (A). Experimental conditions: Pd black without air treatment (type I), $p_{C_2H_2}$ = 0.29 kPa, p_{D_2} = 1.91 kPa. Upper set of curves: Deuterium distribution of the ethylene formed in acetylene deuteration under non-steady-state and steady-state conditions, as well as after disconnecting acetylene flow. Symbols: ◪—C_2H_4; ⊘—C_2H_3D; □—$C_2H_2D_2$; ■—C_2HD_3; △—C_2D_4.

The same experiment was repeated but with introducing acetylene without deuterium in the reaction mixture. Fast reaction was detected after acetylene introduction with 90% selectivity in ethylene. However, after a few minutes the overall acetylene consumption became very low. The source of hydrogen in this case was partly the deuterium adsorbed during the catalyst regeneration procedure, and partly the hydrogen which originated from acetylene via its dissociative adsorption.

3.2. Kinetics of Acetylene Hydrogenation

The results obtained on catalyst type I (catalyst regenerated in He : D_2 mixture at 530 K) are shown in Fig. 2. The reaction was first order with respect to D_2 only at relatively low deuterium pressures. Above 3 kPa there was a considerable deviation

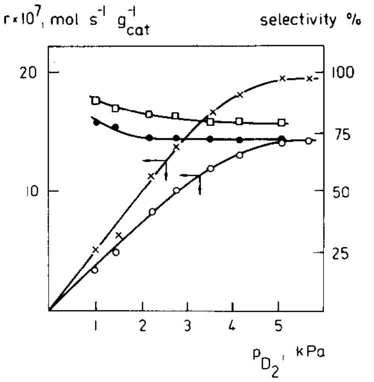


FIG. 2. Rate dependence of acetylene hydrogenation (×) and ethylene formation (○) and selectivity data (S_1—□; S_2—●) on deuterium partial pressure. Experimental conditions: Pd black without air treatment (type I), $p_{C_2H_2}$ = 0.25 kPa.

from the first-order dependence. Both S_1 and S_2 selectivities were low (initially 90 and 80%, respectively) and they decreased slightly with increasing deuterium partial pressure.

Catalyst type II gave higher selectivities (Fig. 3, S_1 = 98%, S_2 = 90%, initially). The kinetic behavior of the reaction was first order with respect to deuterium. No deviation was observed up to 5 kPa D_2 partial pressure (Fig. 3).

The rate of acetylene consumption on both catalysts I and II passed through maxima (Fig. 4) with increased acetylene partial pressure. On catalyst II the maximum in the rate of acetylene consumption vs acetylene partial pressure was shifted to the lower acetylene pressures and rates over this catalyst were inhibited by acetylene itself to a greater extent. Both selectivities were extremely low at small (~0.05 kPa) acetylene partial pressures for both catalysts, namely, about 50%. With further decrease in acetylene partial pressure below 0.05 kPa we were unable to achieve any steady-state reaction rate as a very fast catalyst deactivation took place.

Deuterium distribution of ethylene, the main product formed, is shown in Figs. 5 and 6 vs acetylene and deuterium partial pressures, respectively. All of the ethylene species were formed. Increased deuterium pressure gave rise to the formation of ethylene-d_2 species, while ethylene-d_0 and -d_1 decreased. The opposite phenomenon was observed when acetylene partial pressures increased, i.e., ethylene-d_2 decreased and

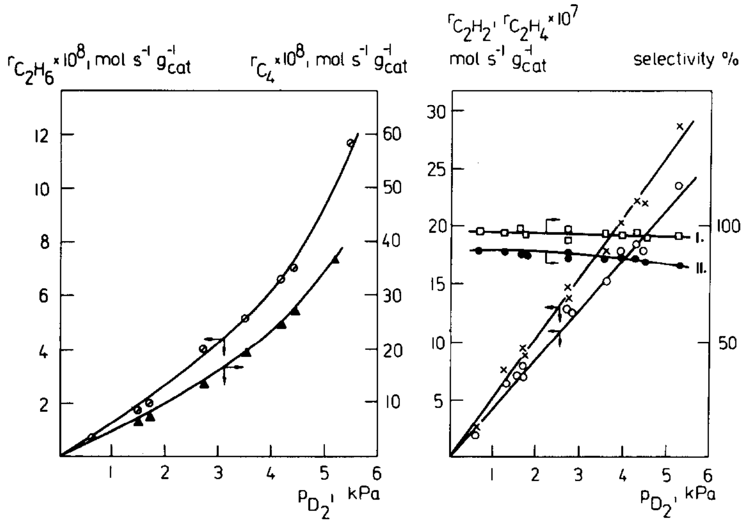


FIG. 3. Selectivity dependence (S_1—□, S_2—●) rate dependence of acetylene hydrogenation (×) and of formation of ethylene (○), ethane (⊘), and C_4 (▲) on deuterium partial pressure. Experimental conditions: Pd black, with air pretreatment (type II), $p_{C_2H_2}$ = 0.27 kPa.

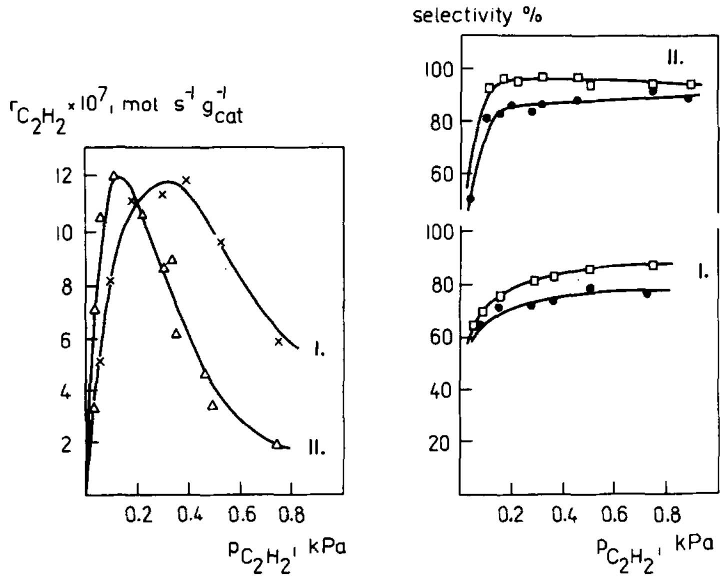


FIG. 4. Rate and selectivity dependence of acetylene hydrogenation on acetylene partial pressure over different Pd black catalysts. Experimental conditions: I. Pd black, without air pretreatment (type I), II, Pd black, with air pretreatment (type II), p_{D_2} = 1.95 kPa; for symbols of S_1 and S_2, see Fig. 3.

ethylene-d_0 and -d_1 increased, again confirming the direct utilization of hydrogen from acetylene. In both series ethylene-d_3 and -d_4 were also formed in small amounts.

Figure 4 compares selectivity data obtained on the two catalysts. There is about 15% lower selectivity on type I catalyst. This may be attributed to the carbonaceous content of the catalyst. The deuterium treatment alone is probably insufficient to clean the surface from polymeric residues.

The effect of carbonaceous deposits on the selectivity can be further supported by acetylene and ethylene pretreatment by adding a small amount of acetylene and ethylene continuously during the regeneration. In both cases the catalysts became less active, both selectivities were low

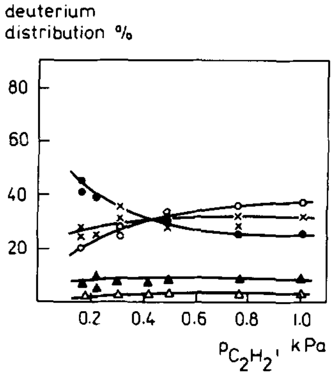


FIG. 5. Deuterium distribution dependence of ethylene formed as a function of acetylene partial pressure. Experimental conditions as in Fig. 4, catalyst type II. Symbols: C_2H_4—○; C_2H_3D—×; $C_2H_2D_2$—●; C_2HD_3—▲; C_2D_4—△.

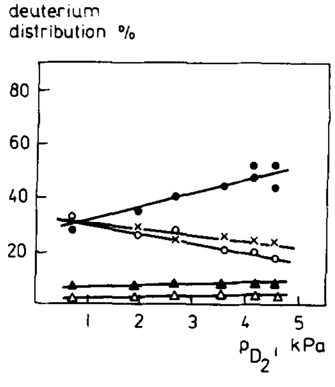


FIG. 6. Deuterium distribution dependence of ethylene formed as a function of deuterium partial pressure. Experimental conditions as in Fig. 3, catalyst type II. Symbols: see Fig. 5.

($S_1 < 70\%$; $S_2 < 52\%$), and the C_4 formation was significant. These experiments support our previous observations that high C_4 formation correlates with poor reproducibility and instability of our catalyst. Similar results were obtained aging the catalyst. Here the initial low S_1 selectivity somewhat increased but the S_2 selectivity decreased slightly.

3.3 Kinetics of Acetylene Hydrogenation in the Presence of Ethylene

The influence of deuterium partial pressure on acetylene hydrogenation in the presence of ethylene at 4 : 1 ethylene–acetylene ratio and at fixed inlet acetylene partial pressure of 0.29 kPa are shown in Figs. 7a–d. The rate of acetylene consumption at 273 K was found to be *higher* in the presence of ethylene below 4 kPa D_2. In the presence of ethylene, the first-order kinetics with respect to deuterium are not maintained above 4 kPa D_2, and the reaction rate becomes almost independent of the deuterium partial pressure at higher deuterium partial pressures. Above 4 kPa deuterium partial

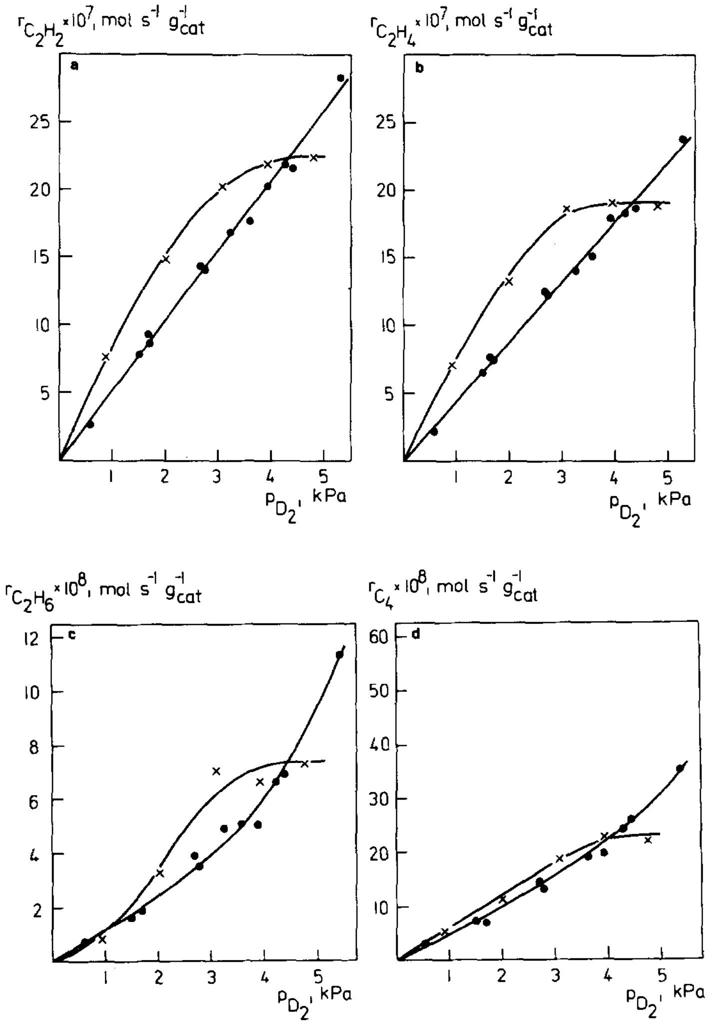


FIG. 7. Rate dependence of acetylene consumption (a) and ethylene (b), ethane (c), and C_4 formation (d) on deuterium partial pressure in the presence (×) or absence (●) of ethylene. Experimental conditions: Pd black with air treatment (type II), $p_{C_2H_2} = 0.29$ kPa, $p_{C_2H_4} = 1.25$ kPa.

pressure the rate of acetylene hydrogenation is lower in the presence of ethylene than in its absence. Lowered reaction rates were also reported in the presence of ethylene by McGown *et al.* (*8*). Their study utilized higher deuterium partial pressures than ours. We have found that a characteristic influence of the added ethylene is the higher S_2 selectivities; $r_{C_2H_4}$ increased, while r_{C_4} was almost constant in the presence of ethylene. Figure 7 shows that, at deuterium pressure below 4 kPa, the presence of ethylene increased the rates of consumption of acetylene and of production of ethylene, ethane, and C_4.

Note that the rate behaviors of ethylene, ethane, and oligomer production are all similar to that of acetylene conversion in the presence of ethylene, suggesting that under these conditons, at least, acetylene is the sole source of all of these products.

A set of experiments was then made at a fixed D_2 pressure of 3.2 kPa and a C_2H_2 pressure of 0.27 kPa, by varying C_2H_4 pressure (Fig. 8). On increasing the ethylene partial pressure both the rates of consumption of acetylene and of formation of ethane increased with parallel decrease in the rate of C_4 hydrocarbon formation.

The influence of acetylene partial pressure on the hydrogenation of the ethylene–acetylene mixture was studied at 1.93 kPa of deuterium, where the effect of ethylene addition was so pronounced (see Fig. 9). In these series of experiments the ratios of $C_2H_4 : C_2H_2$ were varied from 100 : 1 to 1 : 1 at fixed ethylene partial pressure of 1.01 kPa.

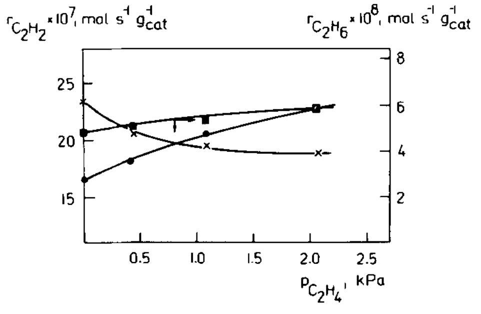


FIG. 8. Rate dependence of acetylene consumption (●) and ethane (■) and C_4 formation (×) on ethylene partial pressure. Experimental conditions: Pd black with air treatment (type II), $p_{C_2H_2} = 0.27$ kPd, $p_{D_2} = 3.2$ kPa.

As shown in Fig. 9, the rate of acetylene consumption passes through a maximum. The maximum rate is higher in the presence than in the absence of ethylene.

Under our standard hydrogenation conditions ($P_{D_2} = 1.93$ kPa, $p_{C_2H_4} = 1.01$ kPa) ethylene could be hydrogenated with extremely high rate with a conversion above 90% unless the acetylene pressure was high. On increasing the amount of added acetylene a very fast inhibition of the ethylene hydrogenation took place (Fig. 10) and above a certain level of acetylene partial pressure hydrogenation of ethylene was completely terminated. With increasing acetylene partial pressure in the presence of ethylene both S_1 and S_2 selectivities were higher than in the absence of ethylene.

3.4. ^{14}C-Labeled Experiments

In the experiments where both acetylene and ethylene were hydrogenated, it was impossible to distinguish the origin of ethane formed and to calculate the rates of formation of ethane from ethylene and from acetylene. Using ^{14}C-labeled acetylene we confirmed that at very low acetylene concentration the main reaction route for acetylene is the direct formation of ethane, i.e., the presence of ethylene did not change the reaction paths of acetylene hydrogenation. Radioactivity data of all reaction products and unreacted acetylene are shown in Table 1. At low acetylene partial pressure the total radioactivity of the ethane is much higher than that of the ethylene, which shows that at low acetylene partial pressure the main route is the acetylene hydrogenation to ethane and C_4 formation. Increasing acetylene partial pressure changed the distribution of the species produced from acetylene. This series of experiments gave us information about the direct route of acetylene to ethane but it did not tell us anything about the ethylene hydrogenation.

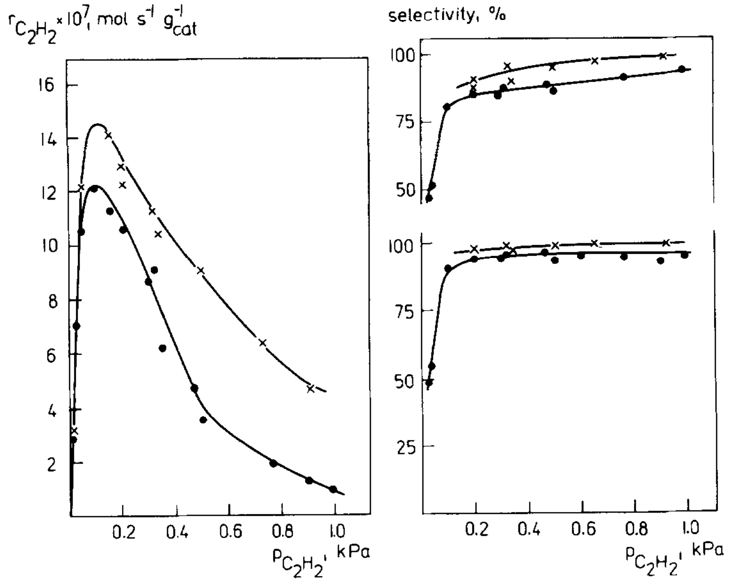


FIG. 9. Rate dependence of acetylene hydrogenation and selectivity data on acetylene partial pressure in the presence (×) an absence (●) of ethylene. Experimental conditions: Pd black with air treatment (type II), p_{D_2} = 1.95 kPa, $p_{C_2H_4}$ = 1.01 kPa.

Labeled ethylene was therefore used in the hydrogenation of ethylene–acetylene mixture. At lower acetylene partial pressures ethylene was converted to ethane as can be seen from the radioactivity data (lower set of data in Table 1); however, by increasing the concentration of acetylene the formation of ethane from ethylene was completely terminated. No acetylene or oligomers come from ethylene.

No essential differences can be found in the deuterium distribution in comparison to those where acetylene was used alone. The main features are:

TABLE 1

^{14}C-Labeled Experiments

$p_{C_2H_2}$ (kPa)	$r_{C_2H_2}\times 10^7$ (mol/g_{cat}s)	$r_{C_2H_6}$ (mol/g_{cat}s)	Total radioactivity (mCi)			
			C_2H_6	C_2H_4	C_2H_2	C_4
			Set 1[a]			
0.0076	1.707	200.4	4.110	0.762	0.210	0.708
0.0446	9.705	116.6	3.140	1.113	1.027	0.483
0.1373	17.350	3.53	0.602	1.628	3.100	0.460
0.1689	22.512	2.72	0.447	1.751	3.043	0.551
			Set 2[b]			
0.0446	9.51	27.00	4.981	5.820	0.00	0.00
0.0776	13.08	17.49	2.015	8.203	0.00	0.00
0.1363	16.38	2.64	0.00	10.780	0.00	0.00

[a] Acetylene is labeled (5.8 mCi/mmol); $p_{C_2H_4}$ = 1.08 kPa, p_{D_2} = 1.94 kPa.
[b] Ethylene is labeled (10.8 mCi/mmol); $p_{C_2H_4}$ = 1.435 kPa, p_{D_2} = 1.94 kPa.

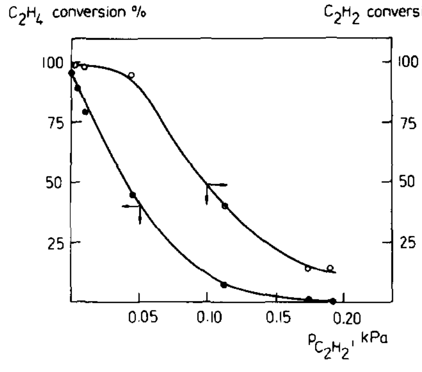


FIG. 10. Influence of acetylene partial pressure on the hydrogenation conversion of ethylene (●) and acetylene (○). Experimental conditions: Pd black with air treatment (type II), p_{D_2} = 1.91 kPa, $p_{C_2H_4}$ = 1.01 kPa.

(i) there was no deuterium in the non-reacted acetylene;

(ii) the mean deuterium content of C_4 formed varied between 4.5 and 6.5.

4. DISCUSSION

In our previous paper (*12*) we have established that under special experimental conditions acetylene and ethylene are separately hydrogenated. Ethylene and ethane are formed via a different pathway from acetylene. However, these results refer to a single composition of ethylene and acetylene and thus the general effect of the experimental condition could not be elucidated. This is why the experimentation described in this paper was adopted. The behavior of the system in nonsteady state, as well as the kinetics of acetylene hydrogenation in the absence and in the presence of added ethylene, helps us to understand the selectivity phenomena observed.

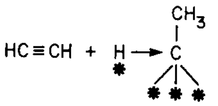
The existence of C_2H_x ($x < 2$) species may be confirmed in the non-steady-state experiments. Bare palladium surface (Pd is considered a bare surface even if deuterium gas is adsorbed on it) is extremely active but nonselective, because after acetylene introduction the rates of formation of all reaction products were high, but acetylene consumption was faster than production of (ethane + ethylene), i.e., $r_{C_2H_2} > (r_{C_2H_4} + r_{C_2H_6})$ as shown in Fig. 1. In this build-up period part of the acetylene is dissociatively adsorbed on the surface to produce C_2H_x ($x < 2$) species as possible precursors to the carbonaceous overlayer formation (*10*) and surface protium. The protium from the C_2H_2 may form a surface hydride phase (such as β-PdH) which is active in acetylene hydrogenation (*15*). Under the same condition Pd–deuteride does not exist (*21*). It can be seen from the deuterium distribution data that after acetylene introduction the relative amounts of ethylene-d_2, ethylene-d_3, and ethylene-d_4 decrease at the expense of ethylene-d_0 and ethylene-d_1 (see Fig. 1) as protium atoms are furnished from acetylene dissociation.

After disconnecting the acetylene flow the reverse process occurs, i.e., deuterium from the gas phase is taken up by the surface and used for hydrogenation.

One may argue against the dissociation of hydrogen atoms from acetylene at chemisorption furnishing protium atoms to the surface. Instead, we may assume the formation of associative adsorption of acetylene followed by additional surface exchange involving an alkenyl type of intermediate with adsorbed deuterium atoms. If it were so, the amount of protium should have decreased because adsorbed deuterium atoms would have been displaced by acetylene during the course of its buildup. However, we obtained the opposite effect, i.e., the increase of protium concentration resulted in an increase of ethylene-d_0 in the gas phase at higher acetylene pressures.

The rapid decrease in the rates may be due to the blocking of active sites by C_2H_x and oligomer. C_4 formation gives evidence that this species is formed from acetylene as is indicated by radioactive measurements (see Table 1). The high deuterium content in C_4 hydrocarbons reported earlier (*12*) and observed also in this study supports our suggestion with respect to the role of C_2H_x species in the oligomerization reactions.

The high rate of ethane formation on bare surface and after disconnecting the acetylene flow indicates that formation of its surface precursor was highly favoured. In the previous paper (*12*) we suggested a special form of surface intermediate originally proposed by Oliver and Wells (*22*) to operate in the direct formation of ethane. One can see from the non-steady-state experiments that at low acetylene coverage low selectivity may be caused by the direct acetylene-to-ethane reaction using this species. However, the route by which this species is formed includes a carbenyl-type intermediate which can also be easily converted simultaneously to ethylene, as reported in the previous paper (*12*). Here we suggest another ethane precursor which is produced by a reactive adsorption of acetylene using surface d atoms and a one-step rearrangement:



$$\mathrm{HC{\equiv}CH} + \underset{*}{\mathrm{H}} \longrightarrow \overset{\mathrm{CH_3}}{\underset{*\,*\,*}{\mathrm{C}}} \qquad (1)$$

The triple-bonded form is called an ethylidyne species. Direct evidence was obtained by Kesmodel *et al.* (*17*) for this species on a Pt surface. This species requires three vicinal surface atoms which are available only at low coverage. Moreover, organometallic evidence also exists for this reaction (*22–26*). As soon as this species is formed it can be desorbed only as an ethane molecule.

Consequently, we suggest three types of adsorbed species which exist at the same time on the surface:

(1) dissociative form, C_2H_x ($x < 2$);

(2) associative form, which is the precursor of ethylene;

(3) reactive form to produce ethylidyne species which is responsible for the direct ethane formation.

The proportions of these species depend on the experimental conditions, nature of catalysts, pressure of reactants, and temperature.

We will show that these three species will adequately explain all the experimental results obtained in the steady-state runs.

In this stage instead of the usually observed negative- or zero-order dependence on acetylene, at low acetylene partial pressures a positive order with respect to acetylene partial pressure was found. With increasing acetylene pressure more and more surface sites are occupied with dissociative, associative, and reactive forms; the overall rate of reaction therefore increases. Since the number of free sites decreases, the proportion of surface processes requiring more vacant sites becomes relatively less important; thus selectivity increases. As mentioned earlier, the deuterium distribution of the products provided further evidence that besides ethane and ethylene formation, dissociation of acetylene also takes place. Indeed, on increasing the acetylene partial pressure the amounts of ethylene-d_0 and ethylene-d_1 increased continuously, and thus the role of protium originating from acetylene became more pronounced. There is a more important conclusion that even at higher acetylene partial pressure part of the acetylene is dissociatively adsorbed on the Pd surface supplying hydrogen atoms for the overall hydrogen pool.

Beyond the maximum the rates of formation of all products decrease, and the selectivity further increases. One of the possible explanations is that the deuterium coverage decreases via the displacement of D atoms by acetylene and, due to the first-order dependence on deuterium pressure, the rate decreases. Since the number of vacant sites drastically diminished there is practically no ethane formation.

When reaction is carried out in the presence of ethylene for modeling the practical conditions, the observations are as follows:

(i) the acetylene rate is more deuterium dependent at small pressures of deuterium and then becomes independent of it at higher deuterium pressure,

(ii) the rate of acetylene consumption in the presence of ethylene also passes through a maximum with no effect of ethylene presence before the maximum and with a higher rate in the presence of ethylene after the maximum,

(iii) both selectivities (S_1 and S_2) are higher above 0.1 kPa acetylene partial pressure,

(iv) before the maximum the main route for acetylene deuteration is the simultaneous reaction to both ethylene and ethane (see Table 1). Ethylene hydrogenation to ethane also takes place. Beyond this maximum the rate of ethane formation decreases by two orders of magnitude and ethylene hydrogenation is completely terminated.

Even at low pressures of acetylene the ethylene conversion continuously decreases (see Fig. 10). At ~0.2 kPa C_2H_2, which corresponds to the maximum in Fig. 9, no reaction of ethylene to ethane occurs. Below this pressure range the selectivity is very low since at low surface coverage acetylene is mostly in a highly dissociative and reactive form. In this sequence, no difference can be seen with respect to ethylene presence or absence.

Although ethylene hydrogenation is completely terminated, it is still adsorbed on palladium black according to ^{14}C-tracer experiments by the Glasgow group (*10, 11*).

Since ethylene is adsorbed on the surface, it must hinder somewhat the highly dissociative and reactive adsorption of acetylene. There is the consequence that first, in the presence of ethylene the surface is covered by C_2H_x residues to a lesser extent, this giving more free sites to the deuterium adsorption on the surface. The increased deuterium coverage results in an enhanced rate of acetylene deuteration. Second, because of the diminished amount of adsorbed species via dissociative adsorption, as a precursor of C_4, enhanced selectivity S_2 is obtained, that is, despite the increased deuterium coverage, C_4 formation is prevented. In the absence of ethylene, deuterium increases C_4 production.

Since not only S_2 but also S_1 increases, the presence of ethylene on the surface influences the degree of reactive adsorption which leads to ethane formation. Because of the comparatively large space requirements (*17*) for the formation of ethylidyne as precursor to an ethane molecule, ethylene adsorption may block part of these sites; consequently the amount of ethane formed decreases, and S_1 thus increases.

Since C_4 hydrocarbons can be formed only from acetylene, their formation requires that the two adsorbed species be at an appropriate distance from each other. In the presence of chemisorbed ethylene the probability for these two species to be close to each other is lower, resulting in higher S_2 selectivity.

The presence of carbonaceous deposit and its influence can be shown by the drastic decrease in activity in the nonsteady state, by pretreatment with ethylene (type III) and by the absence of air treatment (type I). In this latter case the carbonaceous species built up during the reaction cannot be completely removed.

On the catalyst without air treatment (type I) and the catalyst prepared in the presnce of ethylene (type III) the carbonaceous overlayer can alter the adsorption and surface concentration of both hydrogen and acetylene. On the basis of data obtained on platinum (*27*) we can postulate that on the Pd surface covered by a carbonaceous overlayer the hydrogen coverage is higher than on a bare surface. Consequently, the acetylene coverage may be lowered and formation of ethane and C_4 hydrocarbons is favoured. The change in hydrogen order on catalyst type I (see Fig. 2) also suggests an involvement of hydrogen coverages in the different behavior of catalyst types I and II.

Analogously to the rate dependence of acetylene consumption vs acetylene partial pressure the rate of C_4 formation on acetylene partial pressure passes through a maximum.

About 5–20% of acetylene reacted was converted to C_4 hydrocarbons, which is within the range reported by McGown *et al.* (*8*). We found that the production of C_4

species increased on increasing deuterium partial pressure, at all acetylene partial-pressure levels, and no butadiene was formed under our experimental conditions. In our experiments the amount of *cis*-2-butene formed was higher than that of trans-2-butene. The C_4 hydrocarbons had higher deuterium numbers than that of *trans*-2-butene. The C_4 hydroformation from acetylene. We consider that, at least partly, the dissociatively adsorbed acetylene is responsible for the C_4 formation. The lower S_2 selectivities on catalyst with carbonaceous overlayer, as well as lower S_2 selectivities obtained in aging experiments, indicated that both the surface hydrogen and the carbonaceous species may have been involved in the C_4 formation.

5. GENERAL CONCLUSION

Our present data are in good agreement with earlier batch studies on acetylene deuteration where a direct route for ethane formation via a concerted mechanism was suggested (*12*). In this study we propose that the strongly adsorbed surface species containing a methyl group is responsible for the direct ethane formation. Formation of this carbyne-like $\equiv C—CH_3$ ethylidyne species is favoured by accessible multiple sites, available only at low acetylene coverages, and at high hydrogen partial pressure, and its formation should be a fast one-step process and can be considered as reactive chemisorption.

The dissociative adsorption of acetylene is supported by the lower mean-deuterium number in the ethylene formed. We have direct evidence that hydrogen resulting from acetylene dissociative adsorption participates in the hydrogenation. The hydrooligomerization reactions resulted in C_4 formation and the aging phenomena. The strong inhibition of all surface reactions by acetylene itself indicates that deuterium atoms can be removed from the surface and Θ_D decreases.

Dissociatively adsorbed C_2H_x species reacting by the hydrogen transfer mechanism proposed by Thomson and Webb (*16*) and Al-Ammar and Webb (*10, 11*), may be responsible for the deactivation phenomena and for the progressive formation of permanently retained oligomeric species on the catalyst surface.

The most important statement is that, although ethylene can be hydrogenated at low acetylene pressure, acetylene is hydrogenated to ethane and ethylene in a parallel way regardless of the presence of added ethylene. At higher acetylene pressure hydrogenation of ethylene completely ceases and at the same time acetylene is converted only to ethylene. Here it is possible to explain the increase of selectivity on addition of CO (*8*). CO chemisorption decreases the number of sites responsible for the formation of ethylidyne or sterically hinders the surface reaction leading to that surface species. Thus even at low acetylene content ethane formation is strongly reduced.

The results suggest that in the development of a more selective catalyst, the research must aim at altering the catalyst itself, independently of the experimental condition. Even at low acetylene pressure, both ethylene and acetylene hydrogenations simultaneously take place and this can be only marginally altered by experimental conditions.

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REFERENCES

1. Bond, G. C., and Wells, P. B., *in* "Advances in Catalysis and Related Subjects," Vol. 15, p. 91. Academic Press, New York/London, 1963.
2. Wells, P. B., "Surface and Defect Properties of Solids," Vol. 1, p. 24. Specialist Periodical Reports, The Chemical Society, London, 1972.
3. Bond, G. C., "Catalysis by Metals," p. 281. Academic Press, New York, 1962.
4. Bond, G. C., and Wells, P. B., *J. Catal.* **5**, 65 (1966).

5. Bond, G. C., Dowden, D. A., and Mackenzie, N., *Trans. Faraday Soc.* **54,** 1537 (1958).
6. Bond, G. C., and Wells, P. B., *J. Catal.* **4,** 211 (1965).
7. McGown, W. T., Kemball, C., Whan, D. A., and Scurrell, M. S., *J. Chem. Soc. Faraday Trans. I* **73,** 632 (1977).
8. McGown, W. T., Kemball, C., and Whan, D. A., *J. Catal.* **51,** 173 (1978).
9. Al-Ammar, A. S., Thomson, S. J., and Webb, G., *J. Chem. Soc. Chem. Commun.*, 323 (1977).
10. Al-Ammar, A. S., and Webb, G., *J. Chem. Soc. Faraday Trans. I* **74,** 195 (1978).
11. Al-Ammar, A. S., and Webb, G., *J. Chem. Soc. Faraday Trans. I* **74,** 657 (1978).
12. Guczi, L., LaPierre, R. B., Weiss, A. H., and Biron, E., *J. Catal.* **60,** 83 (1979).
13. Weiss, A. H., Gambhir, B. S., LaPierre, R. B., and Bell, W. K., *Ind. Eng. Chem. Process Des. Dev.* **16,** 352 (1977).
14. Palczewska, W., *in* "Advances in Catalysis and Related Subjects," Vol. 24, p. 245. Academic Press, New York/London, 1975.
15. Palczewska, W., "Proceedings, Conference on Supported Metal Catalysts, Novosibirsk, 1978," in press.
16. Thomson, S. J., and Webb, G., *J. Chem. Soc. Chem. Commun.*, 526 (1976).
17. Kesmodel, L. L., Dubois, L. H., and Somorjai, G. A., *J. Chem. Phys.* **70,** 2180 (1979).
18. Demuth, J. E., *Chem. Phys. Lett.* **45,** 12 (1977).
19. Demuth, J. E., *Surf. Sci.* **84,** 315 (1979).
20. Ibach, H., and Lehwald, S., *J. Vac. Sci. Technol.* **15,** 407 (1978).
21. Lewis, F. A., "The Palladium Hydrogen System," Chap. 8. Academic Press, New York, 1967.
22. Oliver, R. G., and Wells, P. B., *J. Catal.* **47,** 364 (1977).
23. Sutton, P. W., and Dahl, L. F., *J. Amer. Chem. Soc.* **89,** 261 (1967).
24. Sheldrick, G. M., and Yesinowski, J. P., *J. Chem. Soc. Dalton Trans.*, 873 (1975).
25. Seyferth, D., *Advan. Organomet. Chem.* **14,** 98 (1976).
26. Fachinetti, G., Pucci, S., Zanazzi, P. F., and Methong, U., *Angew. Chem. Int. Ed. Engl.* **18,** 619 (1979).
27. Móger, D., Besenyei, G., and Nagy, F., *React. Kinet. Catal. Lett.* **8,** 189 (1978).