Hydrogenation of Ethylene over Platinum (111) Single-Crystal Surfaces

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Abstract: The hydrogenation of ethylene with both hydrogen and deuterium was studied over (111) platinum single-crystal surfaces under a total pressure of 110 torr and a temperature range of 300-370 K. An activation energy (E_a) of 10.8 ± 0.1 kcal/mol and kinetic orders with respect to hydrogen and ethylene partial pressure of 1.31 ± 0.05 and -0.60 ± 0.05, respectively, were observed. The deuterium atom distribution in the product from the reaction with D_2 peaks at 1-2 deuterium atoms per ethane molecule produced, similar to what has been reported for supported catalysts. The reaction takes place on a partially ordered carbon covered surface, where the carbonaceous deposits have a morphology similar to that of ethylidyne. However, this ethylidyne does not directly participate in the hydrogenation of ethylene, since both its hydrogenation and its deuterium exchange are much slower than the ethane production. A mechanism is proposed to explain the experimental results.

Although many chemisorption studies have been carried out using surface science techniques, such as Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS), the direct application of their results to interpret catalytic processes is not straightforward. One of the problems is that most of these studies are carried out over clean surfaces and under ultra-high vacuum conditions. The catalytic reactions, on the other hand, generally take place on surfaces covered with adsorbed species, and at several atmospheres of reactant gases. Then, the intermediates in the reactions need not necessarily be related to the chemisorbed states of the reactants under vacuum conditions. Here, we attempt to find the relationship between the chemisorption process that occurs on clean surfaces and the mechanism of the catalytic reaction under high pressures for the case of the hydrogenation of ethylene over platinum surfaces.

Since its discovery by Sabatier and Senderens in 1897,[1] the hydrogenation of ethylene over high surface area metallic catalysts has been extensively studied. However, up to now, the mechanistic details of the surface reaction are still unknown. In contrast, appreciable research effort has focused on the adsorption of ethylene on clean metallic surfaces under vacuum and ultra-high vacuum conditions.[2,3] On (111) single-crystal faces of most noble metals, alkenes are believed to lose one hydrogen atom at around room temperature and form stable alkylidyne species on the surface.[4]

In the present work, the kinetic parameters for the hydrogenation of ethylene with hydrogen and deuterium were obtained on the Pt (111) crystal surface and were in the range of those reported for supported platinum catalysts.[5] Evidence was obtained that partially hydrogenated carbonaceous deposits (most probably including ethylidyne fragments) cover the surface during reactions but do not participate directly in the reaction mechanism. Also important is the fact that, from LEED evidence, the carbonaceous fragments were at least partially ordered after the high-pressure reactions, and it is, to the best of our knowledge, the first case where the presence of ordered overlayers during catalytic reactions is reported. Finally, we propose that the hydrogenation reaction takes place on top of these carbonaceous residues instead of on the clean platinum surface. A mechanism involving ethylidene moities as intermediates is proposed to explain the specific details on how hydrogen incorporates into the ethylene molecule.

Experimental Section

All of the experiments were carried out in an ultra-high vacuum (UHV)/high-pressure apparatus designed for combined UHV surface analysis and high-pressure studies using small-area catalyst samples, as described in detail in previous publications.[6] This system is equipped with four-grid electron optics for LEED and AES, an ion gun for crystal cleaning, a quadrupole mass spectrometer, and a retractable internal isolation cell that constitutes part of a microbatch reactor in the 10^{-2}–10-atm pressure range. The reaction cell and the external recirculation loop were connected to an isolatable pressure gauge, a stainless steel bellows pump for circulation, and a gas chromatograph sampling valve. Hydrocarbon conversion was monitored with a HP3880 gas chromatograph equipped with a 6 ft × $^1/_8$ in. Chromosorb 104 column.

A platinum single crystal (99.998% purity) was cut to within 1° of the (111) orientation by using standard procedures. The resulting thin disc (≤ 0.5 mm thick) had about 1.5-cm^2 total area, of which less than 30% was polycrystalline (the edges of the crystal and the supporting wires). The crystal was spot-welded to a rotatable manipulator by using a series of platinum, gold, and copper supports,[7] which enabled the crystal to be heated to about 1400 K without significant heating of any other part of the reaction chamber. Both crystal faces were cleaned by repeated argon ion sputtering, oxygen treatment, and annealing, until a well-defined (1 × 1) LEED pattern was observed, and no Ca, Si, P, O, S, or C impurities were detected by AES. Research purity ethylene (Matheson, 99.98% purity), prepurified hydrogen (Matheson, 99.99% purity), and deuterium (Matheson, >99.5% atomic purity) were used as supplied. Extra dry nitrogen (Matheson, 99.9% purity) was passed over a molecular sieve trap before use.

In order to perform high-pressure experiments, the reaction cell was closed, enclosing the clean crystal within the high-pressure loop, which was then pressurized to about 150 torr with H_2 for about 1 min to cool the sample to room temperature. AES analysis at this point never showed more than 10% carbon on the surface. The cell was then evacuated, and ethylene, hydrogen (or deuterium), and, if necessary, nitrogen (to maintain a constant total pressure) were sequentially introduced to the desired pressures. Circulation was started, and the crystal was heated to the reaction temperature. The whole process took about 2-3 min. The reaction temperature was continuously regulated to within ±2 K by using a precision temperature controller and a chromel–alumel thermocouple spot-welded to one face of the crystal. The temperature calibration was

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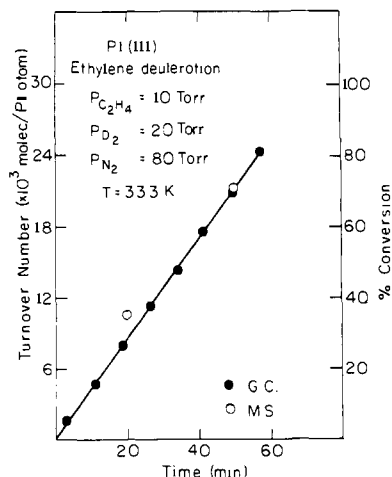
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Figure 1. Product accumulation curve as a function of time for ethylene hydrogenation to ethane over Pt (111) single-crystal surfaces. $T = 333$K, $P_{C_2H_4} = 10$ torr, $P_{D_2} = 20$ torr, $P_{N_2} = 80$ torr. The product was measured by gas chromatography (●) and mass spectrometry (O).

carefully checked by using a isobutane–isobutene equilibrium mixture, as explained in detail in ref 8.

The product formation was followed by gas chromatography, mass spectrometry, or both. Initial reaction rates were determined graphically from the slopes of product accumulation curves as a function of time. They were reproducible within 5%. Blank experiments using platinum surfaces covered with graphitic carbon that formed upon heating the crystal in an hydrocarbon atmosphere at 750–800 K showed a low level of background catalytic activity, never higher than 10% of the activity measured for clean platinum.

For the deuteration experiments, the deuterium distribution was obtained mass spectrometrically. During reactions, the gas mixture was leaked to the vacuum chamber at a rate of about 50 mm^3/min, so that a base pressure of about 1×10^{-7} torr was maintained inside the main chamber, and mass spectra in the 1–50-amu range were recorded periodically. The electron energy of the ionizer was set to 70 V. The composition of the mixture was obtained by deconvoluting the data between 26 and 36 amu using spectra for the pure gases reported in ref 9. The spectra for pure ethylene and ethane were similar to those obtained by using the experimental spectrometer ionizer settings. As a further check on the reliability of this procedure, kinetic studies were performed simultaneously with both mass spectrometric and gas chromatographic detection. The agreement between the two techniques was excellent, as shown by the example in Figure 1.

After completion of the reaction, the crystal was cooled to room temperature, the loop evacuated to below 10^{-3} torr by using a sorption pump, and the cell opened, to expose the sample to ultra-high vacuum. The resulting surface was examined by using LEED, AES, and also thermal desorption spectrometry (TDS), monitoring the H$_2$ (2 amu) or D$_2$ (4 amu) evolution.

Results

The hydrogenation of ethylene to ethane using both hydrogen and deuterium was investigated over the flat close-packed platinum (111) surface at temperatures between 300 and 373 K. The total pressure of the gases was kept constant at 110 torr by adding nitrogen to the reaction mixture when necessary. The standard reaction conditions were pressures of 10 torr of ethylene and 20 torr of hydrogen (or deuterium), unless indicated otherwise. A typical product accumulation curve, determined as a function of reaction time, is shown in Figure 1. The reaction rates, which were constant up to high conversion (see Appendix), were calculated from the slopes of these plots. Arrhenius plots of the initial rates of hydrogenation using both hydrogen and deuterium are shown in Figure 2 and yield activation energies of 10.8 ± 0.1 kcal/mol. The reaction exhibits a normal isotope effect: the reaction with hydrogen is about 1.3 times faster than with deuterium. The dependences of the rates on H$_2$ and C$_2$H$_4$ partial pressures were also studied. The data is sumarized in Table I. From these, the following kinetic equation was obtained:

$$\text{rate} = (8 \pm 4) \times 10^8 \exp[-(10.8 \pm 0.1)/(RT)]P_{C_2H_4}{}^{(-0.60 \pm 0.05)}P_{H_2}{}^{(1.31 \pm 0.05)}$$

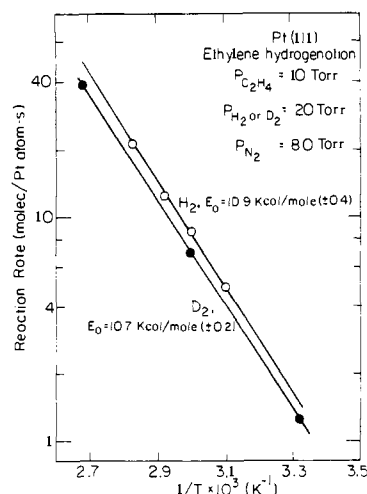**Figure 2.** Arrhenius plots for ethylene hydrogenation with H$_2$ and D$_2$ over Pt (111). $P_{C_2H_4} = 10$ torr, P_{H_2} or $P_{D_2} = 20$ torr, $P_{N_2} = 80$ torr.
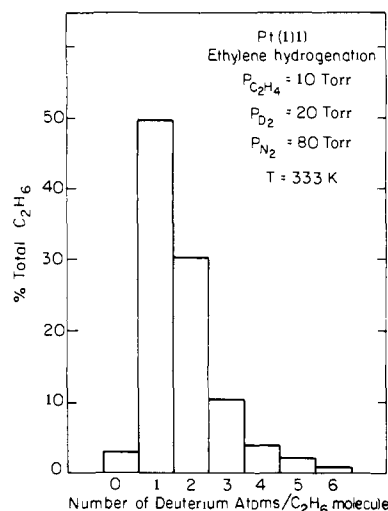

Figure 3. Deuterium atom distribution in the resulting ethane from the hydrogenation of ethylene with deuterium over Pt (111). Same conditions as Figure 1.

Table I. Pressure Dependence of the Initial Reaction Rates of Ethylene Hydrogenation over Platinum (111) Single-Crystal Surfaces

$P_{C_2H_4}$, torr	P_{D_2}, torr	T, K	rate, molecule/(Pt atom s)
10	10	300	0.42
10	20	300	1.24
10	100	300	7.95
10	10	333	2.63
10	20	333	6.80
10	40	333	17.53
10	100	333	⩾65
20	20	333	4.56

where the rate is expressed in molecule/(Pt atom·s), R is the gas constant ($R = 1.987 \times 10^{-3}$ kcal/(mol·K)), T is the reaction temperature in degrees Kelvin, and P_{H_2} and $P_{C_2H_4}$ are the hydrogen and ethylene partial pressures in atm, respectively.

For reactions with deuterium, the product distribution in the resulting ethane was studied mass spectrometrically. A typical distribution is shown in Figure 3. Most of the ethane contains either one or two deuterium atoms per molecule, although products up to d_6 are also present. From these distributions, an average number of deuterium atoms per ethane molecule, M, can be calculated. Figure 4 shows the change of this average as a function of reaction time for a typical case. As can be seen, M increases slightly with time due to the exchange of deuterium in the ethylene.
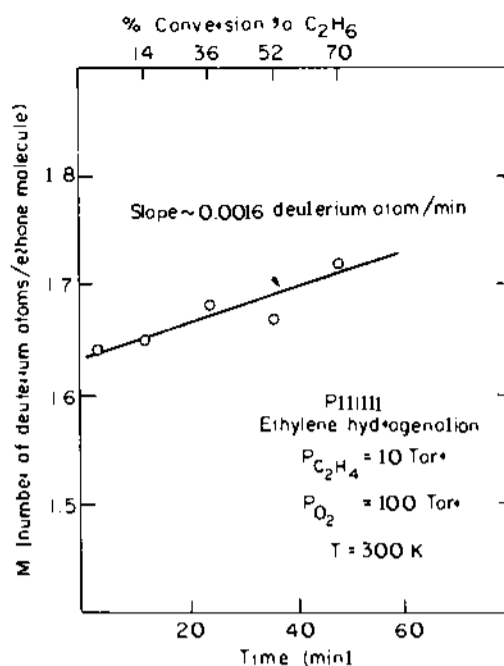
Figure 4. Average number of deuterium atoms incorporated per ethane molecule produced (M) as a function of time of reaction for the hydrogenation of ethylene with deuterium over Pt (111). $T = 300$ K, $P_{C_2H_4}$ = 10 torr, P_{D_2} = 100 torr.
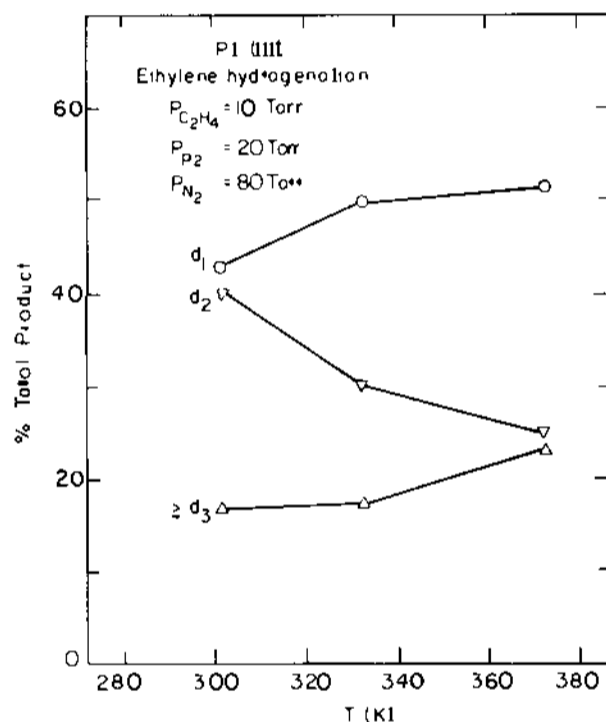

Figure 5. Temperature dependence of the deuterium atom distribution in the resulting ethane from the deuterium of ethylene over Pt (111). Same conditions as in Figure 2.

Table II. Pressure Dependence of the Deuterium Atom Distribution in the Resulting Ethane from the Ethylene Hydrogenation with D_2 over Platinum (111) Single-Crystal Surfaces[a]

P_{D_2}, torr	composition, %				
	d_0	d_1	d_2	d_3	d_4
20	0	45	39	11	2
100	0	43	46	6	4

[a] $T = 300$ K, $P_{C_2H_4}$ = 10 torr.

The rate of this side reaction can be estimated from the slope in the figure to be about 25% of the rate of hydrogenation (see Appendix for details). The deuterium distribution also changes as a function of temperature (Figure 5) and deuterium partial pressure (Table II).

The reaction did not exhibit self-poisoning (within the experimental error) under the reported conditions. After completion of a reaction, and evacuation of the cell, a second run with a fresh reaction mixture yields similar reaction rates. An experiment was performed in which the crystal was saturated with ethylene (1 min at 2 × 10⁻⁷ torr, that is, 12 L exposure) before closing the reaction cell and starting the reaction. Again, the activity was equal to that obtained when starting with a clean platinum surface.
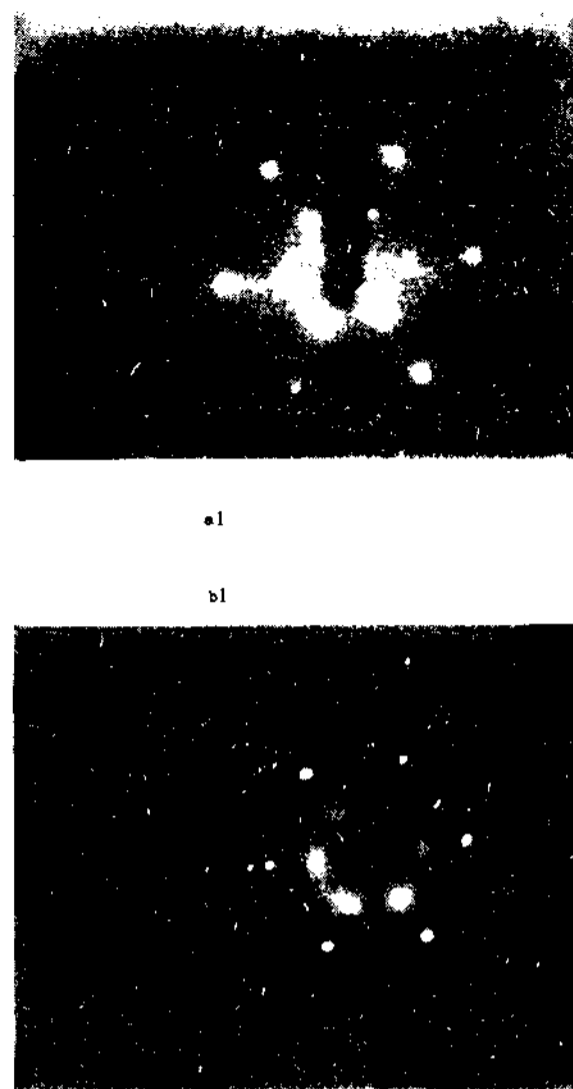

Figure 6. (a) (2 × 2) LEED pattern resulting from the adsorption of ethylene on a Pt (111) surface at room temperature and UHV conditions. (b) Diffuse (2 × 2) LEED pattern obtained after ethylene hydrogenation reactions over Pt (111) surfaces at 300–370 K. Electron energy ~70 eV.
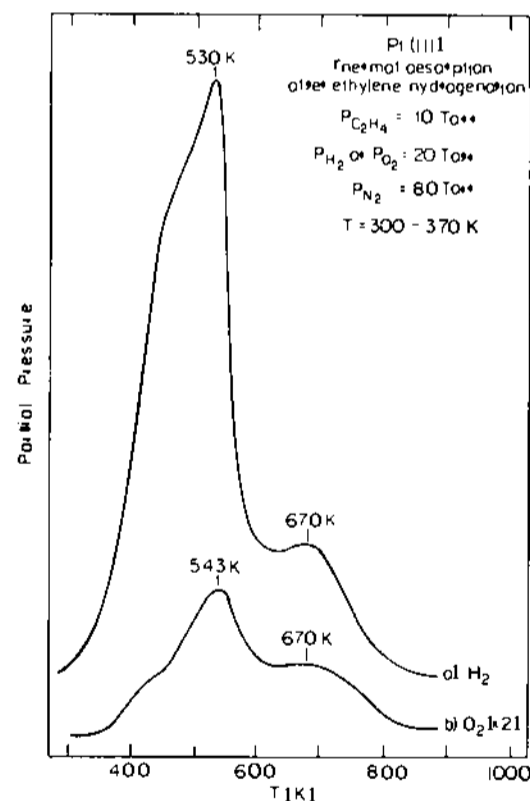

Figure 7. (a) TDS (2 amu) after ethylene hydrogenation with H_2. (b) TDS (4 amu) after ethylene reaction with D_2. Reactions over Pt (111) surfaces, $T = 300$–370 K, same conditions as Figure 2. Heating rate ~40 K/s.

LEED pictures of the platinum (111) surface were taken after each reaction. A poorly ordered (2 × 2) pattern was always obtained. This is shown in Figure 6, together with the pattern resulting from room-temperature exposure of the clean surface to ethylene, which leads to the formation of ethylidyne.[4]

Hydrogen (2 amu) and deuterium (4 amu) TDS were obtained after reactions by heating the crystal at a constant rate of ~40 K/s, and recording the desired partial pressure by using the mass spectrometer. Examples are shown in Figure 7. These desorption

Table III. Comparison of Ethylene Hydrogenation Kinetic Parameters for Different Platinum Catalysts

catalyst	log rate^a	a^b	b^b	E_a, kcal/mol	ref
platinized foil	1.9	−0.8	1.3	10	11
platinum evaporated film	2.7	0	1.0	10.7	12
1% Pt/Al$_2$O$_3$		−0.5	1.2	9.9	5
platinum wire	0.6	−0.5	1.2	10	13
3% Pt/SiO$_2$	1.0			10.5	14
0.05% Pt/SiO$_2$	1.0	0		9.1	15
Pt (111)	1.4	−0.6	1.3	10.8	our work

^{a} Rate in molecule/(Pt atom s), corrected for the following conditions: $T = 323$ K, $P_{C_2H_4} = 20$ torr, $P_{H_2} = 100$ torr. ^{b} Orders in ethylene (a) and hydrogen (b) partial pressures.

profiles, which exhibit maxima at 530 and 670 K, were similar to those obtained from adsorbed ethylidyne.[4] The only new feature in the spectra is the shoulder at about 450 K, due to desorption of coadsorbed hydrogen (or deuterium). The upper spectrum was obtained after a series of reactions of ethylene with H$_2$, between 300 and 370 K, whereas the lower spectrum was obtained after similar reactions, but with D$_2$. To compare the spectra, it should be pointed out that the mass spectrometer sensitivity to H$_2$ is about 1.7 times that of the sensitivity to D$_2$. The 4-amu (D$_2$) TDS for reactions with D$_2$ are very similar to that at 2 amu (H$_2$) using H$_2$ as a reactant, except that the area under the deuterium peak is about 10–20% of the area under the hydrogen peak. However, the sum of areas under the 2- and 4-amu curves after deuteration equals the areas under the 2-amu TDS trace when the reaction is performed with H$_2$.

The Auger spectra indicated that the amount of carbon on the surface after reactions did not change significantly with reaction temperature or hydrogen partial pressures. The average value for the $I_C(273$ eV$)/I_{Pt}(237$ eV$)$, where I is the Auger intensity peak-to-peak height, was always 0.74 ± 0.20. This represents an atomic ratio of $\theta_C = 0.46$ carbon atoms/Pt atom,[10] or roughly one carbon atom for every two platinum atoms. These carbon residues are partially hydrogenated, with a hydrogen to carbon ratio (obtained by measurement of the H$_2$ TDS area and the C/Pt AES ratio) very close to that for ethylidyne (that is, 1.5 H atoms/C atom).

Discussion

The hydrogenation of ethylene using either hydrogen or deuterium on Pt (111) single-crystal surfaces was found to have an activation energy of 10.8 kcal/mol and orders of 1.31 with respect to hydrogen (or deuterium) and −0.60 with respect to ethylene partial pressures. The reaction also displays a normal isotope effect, the reaction with hydrogen being about 1.3 times faster than that with deuterium. All these kinetic data compares favorably with results reported previously by other workers on supported platinum catalysts (Table III). For instance, most of the reported activation energies lie between the values of 9 and 11 kcal/mol.[11-15] Bond and co-workers studied the reaction of ethylene with deuterium over different platinum catalysts and reported reaction rate orders in hydrogen and ethylene partial pressures of 1.2 and −0.5, respectively.[15,16] They also reported a deuterium distribution in the resulting ethane that qualitatively agrees with that obtained in our work. Also, the hydrogenation reaction over five different types of catalysts was essentially structure insensitive. In that respect, it is of interest to note that the absolute reaction rates obtained here for the platinum single crystals are within the range of those reported in the literature already cited for supported high surface area polycrystalline platinum catalysts.

The AES spectra after reactions always reveal the presence of surface carbon. Furthermore, when reactions were started on
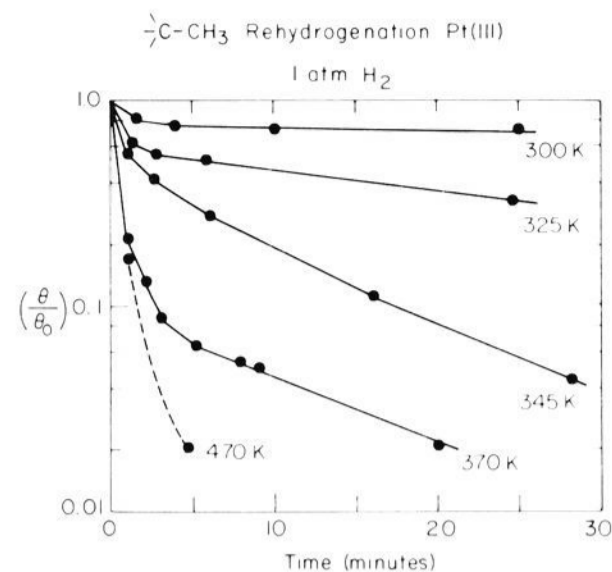
(15) Schlatter, J. C.; Boudart, M.; *J. Catal.* **1972**, *24*, 482.
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Figure 8. Radiotracer decay curves illustrating the rehydrogenation of [^{14}C]ethylidyne species chemisorbed on Pt (111) single-crystal surfaces.

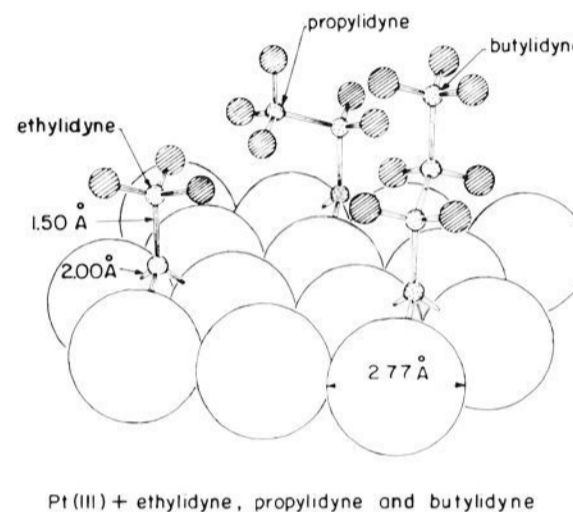Pt (111) + ethylidyne, propylidyne and butylidyne

Figure 9. Atomic surface structure for alkylidyne species adsorbed on Pt (111) single-crystal surfaces.

surfaces covered by hydrocarbon fragments, either by retaining the carbonaceous deposits from previous reactions or by predosing the surface to ethylene under UHV conditions, the rates were identical with those when starting with a clean surface. In addition, the hydrogenation of these fragments is much slower that the rates of ethylene hydrogenation (Figure 8 and ref 20), but no reaction self-poisoning was detected during the experiments (i.e., over several hours). These observations suggest that the hydrogenation reaction takes place on a surface covered with partially hydrogenated carbon fragments. The (2 × 2) LEED pattern obtained after reactions, the shape of the H$_2$ TDS spectra that results from the thermal decomposition of these adsorbates, and the similar kinetic results for the ethylene hydrogenation obtained with a clean Pt (111) surface and with a surface precovered with ethylene under UHV conditions all suggest that the carbonaceous species are, in fact, ethylidyne moieties, as obtained by dosing ethylene onto a clean Pt (111) surface in UHV.[4,17-19] According to the LEED,[4,17] UPS, TDS,[18] and high-resolution electron energy loss spectroscopy (HREELS)[19] studies, ethylene loses one hydrogen as it bonds to the (111) surface at room temperature, forming a triple bond between one of its carbon atoms and three platinum atoms, and has its carbon–carbon bond perpendicular to the surface so that the terminal carbon is a methyl group. A schematic representation of this ethylidyne is shown in Figure 9 (together with similar structures for alkylidynes derived from propylene and butene). The saturation coverage is a quarter of a monolayer, that corresponds to $\theta_C = 0.5$. One difference between the low-pressure and the high-pressure studies is the presence of a small amount of coadsorbed hydrogen in the latter case, which appears as a low-temperature shoulder in the thermal desorption spectrum of H$_2$ (Figure 7).

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(19) Skinner, P.; Howard, M. W.; Oxton, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2*, **1981**, *77*, 1203.

Since the surface is analyzed after returning the platinum crystal to UHV conditions, there is always the possibility that changes take place on the surface during the pumping process. However, it is known that ethylidyne on Pt (111) is stable between about 300 and 400 K, and experiments of repeated pressurization with H_2 and subsequent evacuation show that its composition and structure remains unchanged while restoring vacuum conditions, as checked by LEED and HREELS.[20] This implies that if any changes occur during high-pressure exposures, they are reversible. Also, since there is a high pressure of ethylene during reactions (10–20 torr) and ethylidyne rehydrogenation at room temperature is slow,[21] the platinum surface is believed to be saturated with ethylidyne during and after reactions. This fact rules out the possibility of readsorption of the residual gases: ethylene (which would produce ethylidyne as it adsorbs), ethane (which does not adsorb readily on the clean platinum surface), and hydrogen. The only possible difference in the platinum surface between the time the reactions are taking place and when the surface is analyzed is that all the overlayers of weakly adsorbed hydrocarbons are lost as they are pumped away. Optical spectroscopy techniques might be used to study the surface in situ during reactions to obtain more detailed information on the structure of this second layer.

The role of the carbonaceous deposits in the mechanism of the hydrogenation reactions is not yet well understood. Experiments with [^{14}C]ethylene have shown that the hydrogenation of ethylidyne at 1 atm H_2 is very slow at room temperature (ref 21 and Figure 8). Also, if ethylidyne were to be a direct intermediate for the hydrogenation, the reaction with D_2 should yield ethane containing at least three deuterium atoms per molecule, instead of one or two, as obtained experimentally. On the other hand, several groups have reported that ethylene self-hydrogenates over metallic surfaces, at least in the early stages of the reaction.[1] This would suggest that the carbonaceous fragments somehow facilitate the hydrogen incorporation into the ethylene. In that case, the hydrogen in the methyl group of the ethylidyne should be easy to exchange with deuterium. Salmeron and Somorjai reported that this is indeed possible under UHV conditions at 400 K and low ethylidyne coverages.[22] However, recent preliminary studies in this laboratory indicate that, in fact, very little exchange takes place at room temperature in an atmosphere of 150 torr D_2 rather than UHV conditions. Even after long D_2 exposures at temperatures as high as 370 K, the extent of exchange was never more than 40% (Figure 7). Also, work on Rh (111) surfaces using HREELS has suggested similar conclusions.[23] It seems that the rate of this deuterium exchange depends on the ethylidyne coverage, being slower at saturation coverage (that is the situation that prevails during hydrogenation reactions). Further work is under way to clarify this point.

In view of all the evidence, a main conclusion of this work is that *the hydrogenation of ethylene does not take place on the clean metallic surface but rather on top of a layer of carbonaceous fragments, which TDS, LEED, and AES results strongly suggest are composed of ethylidyne adsorbates*. The bond of unsaturated hydrocarbons to metals is too strong to allow them to desorb at room temperature, but a bond to the covering carbonaceous deposits could be, on the other hand, within the energetic range required for the catalytic reaction to take place. If that is the case, perhaps the future surface science work should focus not only on chemisorption on clean surfaces but on surfaces that have been already exposed to the reactant gases. The main problem is that the weak reversible chemisorption expected in the latter case is hard to achieve under UHV conditions. One way around this could be to work at lower temperatures, but the question still remains as to whether this is the equivalent of having higher gas pressures. Also, molecular beam experiments on covered surfaces should be helpful in elucidating the details of the chemical reactions.

(20) Koel, B.; Bent, B.; Zaera, F.; Somorjai, G. A, unpublished results.
(21) Davis, S. M.; Zaera, F.; Salmeron, M.; Gordon, B. E.; Somorjai, G. A. *J. Am. Chem. Soc.*, submitted for publication.
(22) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.
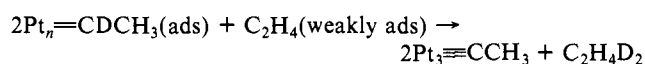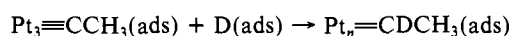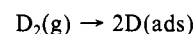(23) Koel, B.; Bent, B.; Somorjai, G. A., private communication.

Table IV. Comparison of Ethylene Hydrogenation Kinetic Parameters over Different Metals

metal	form	a^a	b^a	E_a, kcal/mol	ref
Ni	wire	0	0.97	11–15	26
	powder	−0.6	0.98	6	27
	evap film	0	1	9–10	28
	on SiO_2	−0.08	0.67	8.4	29
Pt	foil	−0.8	1.3	10	11
	wire	−0.5	1.2	10	13
Pd	thimble	0	1	5–7	30
	on SiO_2	−0.03	0.66	8.4	29
Rh	on Al_2O_3	0	1	12	31
Fe	film	−0.6	0.87	7.3	32
Ir	on Al_2O_3	−0.4	1.6	13.8	16
Ru	on Al_2O_3	−0.2	1	8.7	33
Co	on SiO_2	−0.19	0.55	8.4	29

^{a} Order in ethylene (a) and hydrogen (b) partial pressures.

Even if the reaction takes place on a covered surface, the presence of the metal still has to be important, because the reaction rates are known to change with different metals.[1] A diagram of a saturated 2 × 2 overlayer of ethylidine on the Pt (111) (using van der Waals radii for the carbon and hydrogen atom) shows that platinum atoms cannot be reached by the gaseous ethylene molecules. However, this surface is able to adsorb a small amount of hydrogen as seen by the low-temperature shoulder in the TDS. Also, hydrogen is most probably involved in the limiting step of the reaction, since this would account for the pressure dependence and the isotopic effect on the rates. It seems highly improbable that this chemisorbed hydrogen will jump from the surface to an ethylene molecule adsorbed on a second layer without the intervention of the ethylidyne in the first layer, but, on the other hand, the hydrogen atoms in the methyl group of the ethylidyne do not directly participate in the hydrogenation of the gaseous ethylene. One possible explanation that reconciles the preceeding conclusions is that the adsorbed deuterium atoms α-incorporate into the ethylidyne, forming ethylidene intermediates, which subsequently transfer the deuterium to the ethylene. Schematically, this mechanism is as follow:

$$D_2(g) \rightarrow 2D(ads)$$

$$Pt_3{\equiv}CCH_3(ads) + D(ads) \rightarrow Pt_n{=}CDCH_3(ads)$$

$$2Pt_n{=}CDCH_3(ads) + C_2H_4(weakly\ ads) \rightarrow$$
$$2Pt_3{\equiv}CCH_3 + C_2H_4D_2$$

Such an ethylidene intermediate has been proposed by Salmeron and Somorjai to explain the ethylidyne deuterium exchange under UHV conditions.[22] In their case, however, the incorporation of deuterium at the α carbon of ethylidyne is followed by β abstraction of a hydrogen atom from the methyl group, and this can be the slow step at high ethylene pressures, since it may be necessary for the ethylidyne to tilt so that the H atom can reach the surface and exchange can occur. Further work on the hydrogen transfer mechanism is under way in our laboratory to test this proposed mechanism.

Our results also indicate that the hydrogenation of ethylene over platinum (111) single-crystal surfaces is very similar to that on supported catalysts. Since the reaction takes place on a surface covered by carbonaceous deposits, we propose that the carbon deposit masks the surface structure, making the reaction surface insensitive.

The mechanism we proposed for the hydrogenation of ethylene on platinum may be extended to other metals and to other olefins. The existence of ethylidyne and its analogous propylidyne and butylidyne have been demonstrated for Pt (111) and Rh (111) surfaces.[3] On Pd (111), it has not been proven conclusively whether adsorbed ethylene forms ethylidyne or ethylidene. On Ni (111), on the other hand, the most probable specie on the surface is an acetylenic complex.[24] In all these cases, the hy-

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Table V. Ratio R_{hyd}/R^*_{hyd} as a Function of Ethylene Conversion for the Initial Conditions $P^*_{D_2} = 20$ torr and $P^*_{C_2H_4} = 10$ torr

conversion fraction of ethylene (F)	P_{D_2}, torr	$P_{C_2X_4}$, torr	R_{hyd}/R^*_{hyd}
0	20	10	1.000
0.20	18	8	0.996
0.40	16	6	1.014
0.60	14	4	1.086
0.80	12	2	1.345

drogen-transfer mechanism previously proposed for the hydrogenation could still, with small modifications, be valid. Also, the fact that most olefin hydrogenation reactions are structure insensitive and that they have similar kinetic parameter on group 8 transition-metals catalysts (see Table IV for some examples) support the previous statement about the reactions having similar mechanisms. It would be worthwhile to perform similar experiments to the ones reported here for other similar systems.

Appendix

Estimation of the Rate of Ethylene Deuterium Exchange. When kinetic studies are carried out in a batch reactor, the intermediate products accumulate with time in the reactant mixture, modifying the rate of the subsequent reactions. This is the reason why the amount of extra deuterium in the ethane coming from deuterated ethylene is not just directly proportional to the deuterium exchange rate of the ethylene. In the following appendix, we estimate this exchange rate from the data in Figure 4.

If there were no deuterium exchange of the ethylene, the deuterium content of the resulting ethane would be constant, $C_2H_{6-M'}D_{M'}$, where M' should ideally be 2, but was found experimentally to be about 1.64. However, due to the incorporation of deuterium atoms in the ethylene, M increases with time, as seen in Figure 4. The side reaction involved can be written as

$$C_2H_4 + D_2 \rightarrow C_2H_3D + HD \qquad \text{rate} = R_{exc} \qquad (1)$$

The exchange of ethane with deuterium can be ruled out as a source of deuterated ethane, since this reaction does not take place until much higher temperatures (above 550 K, see ref 25).

Will will assume in our derivation that R_{hyd} is constant, as found experimentally, since $R_{hyd} = kP_{D_2}^{1.31}P_{C_2X_4}^{-0.60}$, and the two pressure factors almost cancel out up to 80% conversion (see Table V). R_{exc} will be assumed to be either constant or linearly dependent on $P_{C_2X_4}$.

The rate of formation of ethane with an extra deuterium atom will be

$$d(P_{ed})/dt = R_{hyd}(P_{C_2H_3D}/P_{C_2X_4}) \qquad (2)$$

where P_{ed} is the partial pressure of the ethane with the extra deuterium, R_{hyd} is the rate of hydrogenation of ethylene, and X is either H or D.

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For constant R_{exc}

$$P_{C_2H_3D} = R_{exc}t - P_{ed} \qquad (3)$$

and

$$P_{C_2X_4} = P^*_{C_2H_4} - R_{hyd}t \qquad (4)$$

where the asterisk denotes initial pressure. By substitution of eq 3 and 4 into eq 2

$$\frac{d(P_{ed})}{dt} = R_{hyd}\frac{R_{exc}t - P_{ed}}{P^*_{C_2H_4} - R_{hyd}t} \qquad (5)$$

This equation is hard to solve as written, since there are some cross terms involved. However, using a Taylor series expansion about $t = 0$ and assuming that the rate of formation of P_{ed} is constant at least at the begining of the reaction, eq 5 is reduced to

$$\frac{d(P_{ed})}{dt} = \frac{R_{hyd}}{P^*_{C_2H_4}}\left[R_{exc} - \frac{d(P_{ed})}{dt}\right]\left(t + \frac{R_{hyd}}{P^*_{C_2H_4}}t^2 + \frac{R_{hyd}^2}{P^*_{C_2H_4}^2}t^3 + ...\right) \qquad (6)$$

Integrating the previous equation, substituting for the conversion fraction of ethylene to ethane, $F = (R_{hyd}t)/P^*_{C_2H_4}$, and taking the limiting case when $F \ll 1$, we get

$$P_{ed} = FR_{exc}t(1/2 + F/3 + F^2/4 + ...) \qquad (7)$$

From this, the rate of exchange is:

$$R_{exc} = (P_{ed}/Ft)(1/2 + F/3 + F^2/4 + ...)^{-1} \qquad (8)$$

If the rate of exchange is slow enough, only one deuterium per ethylene molecule will be present in the reaction mixture, and

$$P_{ed} = (M - M')R_{hyd}t = (M - M')FP^*_{C_2H_4} \qquad (9)$$

and

$$R_{exc} = [((M - M')/t)P^*_{C_2H_4}](1/2 + F/3 + F^2/4 + ...)^{-1} \qquad (10)$$

The first factor in this expression can be estimated from Figure 4 to be about 0.016 torr/min, or 1.06 molecule/(Pt atom s), and the second term varies from 2 at zero conversion to about 1 when $F = 0.95$. Since the rate of hydrogenation under the same conditions is $R_{hyd} \sim 7.95$ molecule/Pt atom s), the ratio R_{exc}/R_{hyd} lies between 0.13 and 0.25.

If R_{exc} depends linearly on $P_{C_2X_4}$, $R_{exc} = k_{exc}P_{C_2X_4}$, the only difference in eq 5 is that R_{exc} has to the be substituted by

$$R_{exc} = k_{exc}(P^*_{C_2H_4} - R_{hyd}t) \qquad (11)$$

Following the same procedure as before, we get

$$k_{exc} = [2(M - M')/t](1/2 - F/3 - F^2/4 - ...) = 0.0032 \text{ min}^{-1} \qquad (12)$$

and

$$R_{exc} = k_{exc}P^*_{C_2H_4}(1 - F) \qquad (13)$$

Then R_{exc}/R_{hyd} varies between 0.25 at $F = 0$ and 0.23 at $F = 0.5$.