

1,3-Butadiene Hydrogenation on Single Crystals of Platinum

I. Mechanism and Carbon Deactivation on Pt(110)

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1,3-Butadiene hydrogenation and H₂-D₂ exchange have been simultaneously investigated on the Pt(110) surface at 200-400 Torr pressure. The surface was characterized by Auger electron spectroscopy (AES) and LEED before and after the reaction. Depending on the hydrogen pressure, two kinetic regimes were observed. First, at high hydrogen pressure (above 130 Torr), the order of the reaction is one with respect to hydrogen and zero with respect to butadiene. The selectivity does not depend on the hydrogen pressure. The surface is covered by one butadiene molecule for every two surface atoms of platinum. As revealed by LEED analysis after reaction, the butadiene monolayer shows no structural order. Moreover, AES measurement performed at grazing incidence gives evidence for the adsorption of the butadiene molecules in the valleys of the unreconstructed (110) face. Second, below a critical hydrogen pressure (~125 Torr), the order of the reaction is two with respect to hydrogen and zero with respect to butadiene. The selectivity toward butane decreases as the hydrogen pressure decreases. The carbon concentration is higher than that in the previous case. The lower-temperature carbon deactivation seems to result from the selective poisoning of the hydrogen dissociation sites by some hydrocarbon species. A reaction mechanism is proposed according to which the rate-determining step is the hydrogenation of the half-hydrogenated product C₄H₇. © 1987 Academic Press, Inc.

INTRODUCTION

Despite a large number of studies, the mechanisms involved in catalyzed hydrogenation reactions are not well understood. Recently, model experiments performed on well-defined surfaces of single crystals have been very fruitful in providing new insights into such reactions and more generally into heterogeneous catalysis. Many attempts are now being made to use reactive gas mixtures at pressures near atmospheric or higher, in order to approach the conditions encountered in industrial applications. Unfortunately, at pressures above 10⁻⁵ Torr, the surface can no longer be characterized during the reaction by surface-sensitive techniques. However, the chemical composition and structure of the surface can be precisely determined before and after the catalytic reaction. Such a procedure allows

the initial cleanliness of the surface to be checked and gives the possibility of interpreting the catalytic activity and the selectivity with surface coverage by hydrocarbon molecules, carbon deposit, or other species. These data are fundamental to the understanding of the mechanisms involved in catalyst deactivation by self-poisoning or poisoning by specific impurities. This study concerns butadiene hydrogenation on a single crystal surface of platinum. Hydrogenation of diolefines is an important reaction in oil refining, especially in reforming. It is known that diolefines are more strongly adsorbed on metal catalysts than monoolefines and can irreversibly poison the surface. To optimize this process more data on the reaction are required. Until now, most of the work on this subject has been performed on polycrystalline metal films (1) or dispersed catalysts (2); however, one

study on butadiene hydrogenation on Pt(111) has been reported (3). A review dealing with this field has recently been published by Davis and Somorjai (4).

In this paper we describe the results obtained for butadiene adsorption from the pure gas, the kinetics of butadiene hydrogenation, and the effect of carbonaceous deposits on the activity and the selectivity. Special attention has been paid to the mechanism of carbon deposition which deactivates the surface. This work concerns the Pt(110) plane which was found to be the most active of the main low-index planes of platinum, as observed in a preliminary series of experiments.

The reaction was carried out at a total gas pressure comprised between 200 and 400 Torr in the presence of a hydrogen excess. The temperature range was 300 to 700 K. The activity and the selectivity for monoolefines (butenes) and butane were measured simultaneously. The surface was characterized before and after the reaction by LEED and Auger electron spectroscopy (AES). The AES device comprised a graz-

ing incidence ($\alpha = 15^\circ$) gun which is considered to give better precision for low coverages. By using an equal amount of H_2 and D_2 we were able to determine the rate of HD formation during butadiene hydrogenation. The H_2 - D_2 exchange by equilibration has been previously studied in our laboratory in the same range of hydrogen (or deuterium) pressure on clean and sulfur-covered platinum single crystals, including Pt(110) (5). Preliminary results on the effect of sulfur poisoning of Pt(110) on butadiene hydrogenation have been published recently (6) and additional work on this subject will be presented in a forthcoming paper.

EXPERIMENTAL

The apparatus used is shown in Fig. 1. It is mainly composed of a Low-energy diffractometer equipped with an isolation chamber. The AES analysis was performed with the grids of the diffractograph. Residual gas was analyzed by a mass spectrometer. The single crystal sample was a disk about 1 cm in diameter and 1 mm thick. It

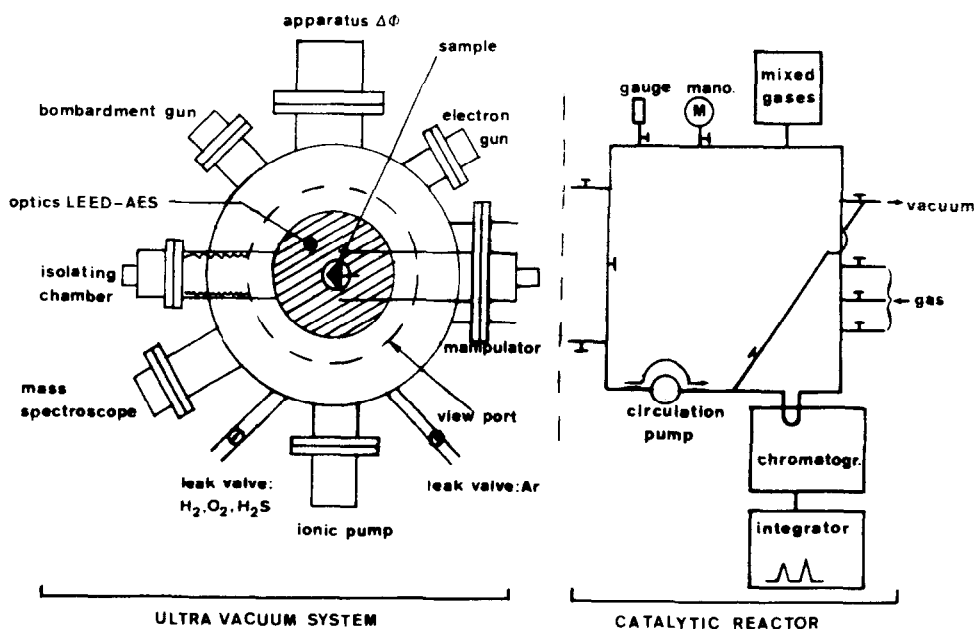


FIG. 1. Scheme of the apparatus used for the characterization of the catalyst crystal surface and for study of the reaction.

was cut at the required orientation with a precision of 1° . The surface was prepared according to a standard procedure: ion bombardments and thermal heating until the AES spectrum and the LEED pattern, characteristic of clean Pt(110), were obtained. Treatment at low pressures of pure hydrogen was used to eliminate carbon contamination. After cleaning the sample was isolated from the main chamber. The stainless steel isolation chamber was attached to a recirculation system made of Pyrex glass. Hydrocarbon reactants and products were analyzed by gas chromatography. H_2 , D_2 , and HD were continuously analyzed by a calibrated mass spectrometer.

RESULTS AND DISCUSSION

1,3-Butadiene Adsorption

Over a large range of pressure, the hydrogenation rate was found to be independent of the butadiene pressure. This observation suggests that the surface was saturated with butadiene molecules. By following the butadiene adsorption from the gas phase we expected to measure the saturation coverage and obtain useful information on the ordering of the hydrocarbon. Experiments were performed under various pressures of pure butadiene. At pressures lower than 10^{-7} Torr, the Auger peaks of C at 272 eV and Pt at 168 eV were continuously recorded. At higher pressures, the surface coverage was measured immediately after removing the gas phase.

Figure 2 shows the results obtained at a butadiene pressure of 6×10^{-9} Torr. The C_{272} Auger peak increased linearly as a function of time and reached a constant value. During this adsorption process the intensity of the Pt_{168} Auger peak very slowly decreased until saturation was reached. At higher pressures, the same kinetics of adsorption with the same saturation level were observed but the time required to reach the plateau was much shorter. For example, at a pressure of $6 \times$

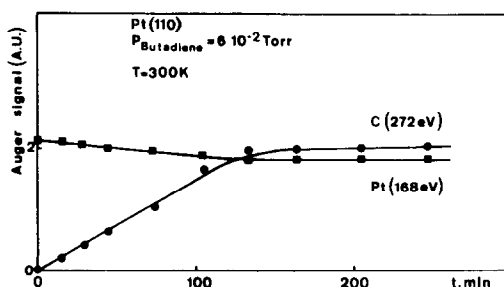


FIG. 2. Variation of Auger signal intensity for carbon (272 eV) and platinum (168 eV) as a function of exposure time at 6×10^{-9} Torr of butadiene.

10^{-2} Torr, the plateau is reached almost instantaneously. Based on a calibration established by Biberian and Somorjai with a perpendicular gun (7) and adapted by Abon *et al.* for grazing incidence (8) our calculation gives a value for the saturation level which is equal to two carbon atoms per platinum atom (2C/Pt). At $P = 6 \times 10^{-9}$ Torr this saturation state is reached within 130 min. The sticking coefficient determined from these values is $S_1 = 3.5 \times 10^{-2}$. This must be considered as a rough approximation because of the error associated with the measurement of the butadiene pressure. At this stage of the adsorption we observe a diffuse LEED pattern without any coincidence mesh with the substrate $p(1 \times 1)$.¹ This pattern disappears irreversibly at 673 K. From this saturation level, at low butadiene pressures, the carbon peak slowly increases after many hours of gas exposure.

At a pressure of 6×10^{-2} Torr the increase in the carbon Auger peak is much more rapid, as is shown in Fig. 3. Compared with the first stage of adsorption the negative slope of the curve giving the Pt_{168} Auger peak as a function of the carbon peak is markedly increased. This indicates that the Pt Auger emission is now more strongly screened than before. The second satura-

¹ The well-defined pattern mentioned in Ref. (6) has not been observed in more recent experiments and could be due to the formation of graphite.

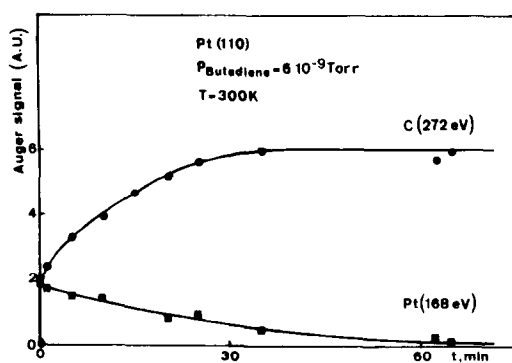


FIG. 3. Variation of Auger signal for carbon and platinum as a function of exposure time at 6×10^{-2} Torr of butadiene.

tion level was reached after 30 min of exposure. At this stage the intensity of the carbon Auger peak was about three times greater than that observed for the first plateau, indicating that the surface concentration of carbon was 6C/Pt. No clear LEED pattern was observed at this stage. As deduced from the time required to reach the second saturation level at 6×10^{-2} Torr, the mean sticking coefficient was then $S_2 = 3.5 \times 10^{-8}$, many orders of magnitude lower than S_1 . For longer exposure, the C_{272} peak continued to increase slowly until the Pt peak was nearly totally screened. The strong change in the sticking coefficient, the change in the curve for the kinetics of adsorption, and the change in the decrease in the Auger peak of platinum, all these factors strongly suggest the existence of two types of carbon deposit.

Based on the Auger results some assumptions can be tentatively made on the nature and the location of these deposits. We have seen that the hydrocarbon species adsorbed in the first stage has a poor screening effect on platinum. Such a result is likely to be compatible with an adsorption of these species in the valleys of the (110) plane. The slight decreases in the Auger emission would be mainly due to the attenuation by the hydrocarbon species of the signal coming from the platinum in the second layer. At grazing incidence of the

excitation electron beam one would expect the Auger contribution of these metal atoms to be much less important than the contribution of the metal atoms in the top-most layer. This first level saturation corresponds to one molecule of C_4H_6 for two platinum atoms and a mean surface area per molecule of 21.8 \AA^2 . This value is 25% lower than the theoretical molecular cross section determined by Gazevotti *et al.* (9). At the present time such a difference cannot be considered significant if we take into account the experimental scattering in the Auger results (of the order of 10%) and the errors in the calibration of carbon which was indirectly made by reference to results obtained on a different orientation of platinum with different equipment. We will therefore consider that in the first stage of adsorption, butadiene molecules are adsorbed flat and are lying in the valleys as shown in Fig. 4.

In the second stage of the adsorption the stronger screening effect of the hydrocarbon species on platinum seems to indicate that these species are now adsorbed on the topmost layers of platinum atoms. It also suggests another kind of bonding for the hydrocarbon molecules. Instead of the molecules lying flat we tentatively consider that the additional butadiene molecules are adsorbed as butadienyl or butylidyne species and are bonded to the surface by only one carbon atom. The saturation of the topmost layer of platinum would correspond to one species per platinum atom. However, to check the preceding conclusions more in-

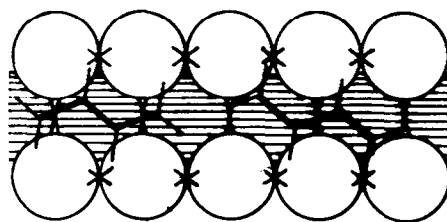


FIG. 4. Butadiene hydrogenation on Pt(110): model of the working catalyst (crosses signify sites for hydrogen dissociation).

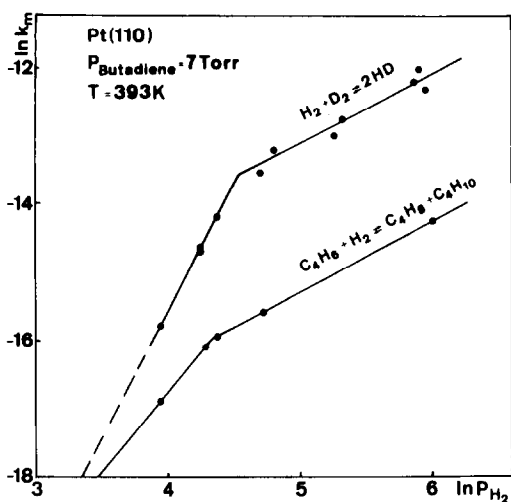


FIG. 5. Variation of rates as a function of H_2 pressure for butadiene hydrogenation and H_2 - D_2 exchange.

formation on the structural features of the bound hydrocarbon would be necessary.

B. Kinetics of Hydrogenation

In a first series of experiments performed at 393 K, the rates of butadiene hydrogenation

and of H_2 - D_2 equilibration were measured simultaneously as a function of hydrogen pressure at constant butadiene pressure (7 Torr). As shown in Fig. 5, two operating regimes are discernible with different orders in hydrogen pressure for both reactions. We shall mainly discuss here the results obtained at higher hydrogen pressures.

Under such conditions the selectivity was observed to be constant and the orders for hydrogenation and equilibration were both equal to unity with respect to hydrogen pressure. A typical curve of butadiene conversion into the various products is shown in Fig. 6. The carbon concentration, measured by AES at low conversion and after gas removal, was equivalent to one butadiene molecule for two platinum atoms (first level of saturation obtained by adsorption from pure butadiene). Such a saturation is consistent with the zero order of the reaction rate with respect to butadiene measured at the start of the reaction. It would correspond, as previously discussed, to the complete filling of the valleys of the

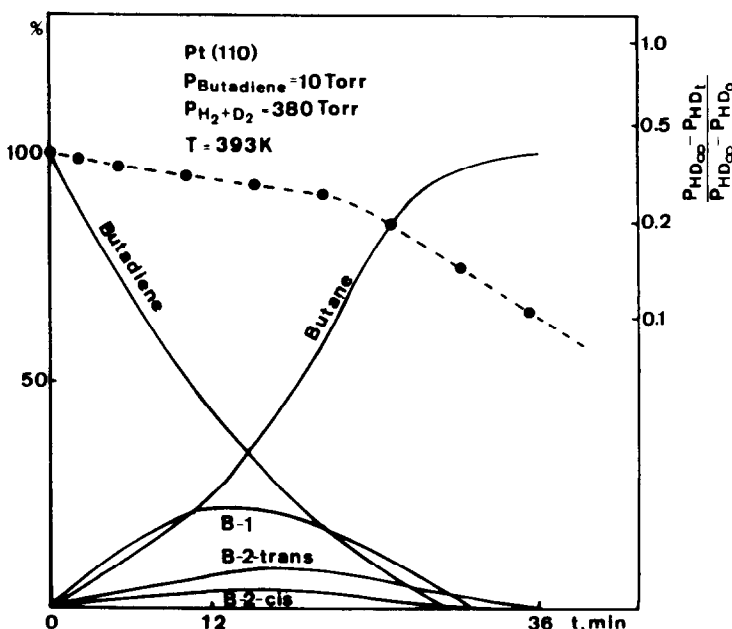
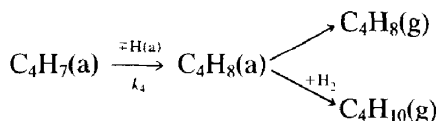
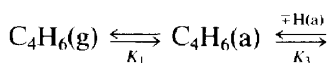
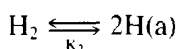


FIG. 6. Kinetics of butadiene hydrogenation, formation of reaction products, and kinetics of H_2 - D_2 equilibration measured simultaneously.

Pt(110) by the hydrocarbon molecules. As shown in the proposed model (Fig. 4), the part of the surface which remains free of hydrocarbon may provide the dissociation sites for hydrogen molecules, more particularly the bridge sites. As a matter of fact, the surface can be considered a bifunctional catalyst, one part of the surface providing the adsorption sites for butadiene molecules, and the other part the dissociation sites for hydrogen molecules. We have seen and will discuss in more detail in a forthcoming paper that the hydrogen dissociation is selectively poisoned by sulfur. This confirms the fact that hydrogen and butadiene occupy separate adsorption sites in this regime of hydrogenation.

In the same H_2 pressure regime, the influence of the temperature has been investigated for both studied reactions. The activation energies deduced from the curves in Fig. 7 are $E_a = 39.3 \text{ kJ mol}^{-1}$ for the butadiene hydrogenation² and $E_a = 16.8 \text{ kJ mol}^{-1}$ for the equilibration reaction.

The butadiene hydrogenation can be described by the following elementary steps:



Under the steady-state condition the equilibration rate gives the rate of H_2 dissociation. This rate is one order of magnitude higher than the rate of hydrogenation. Consequently, the rate-determining step of the hydrogenation reaction is not the hydrogen adsorption but more probably step 4 which corresponds to the hydrogenation of the half-hydrogenated product. Assuming that

² This value is more precise than the value (10.6 kcal mol⁻¹) reported in Ref. 6.

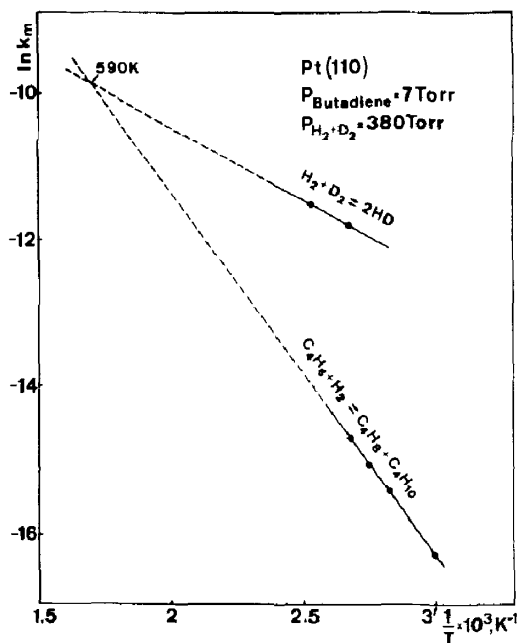


FIG. 7. Arrhenius plots for the hydrogenation and the equilibration reactions giving the temperature at which the rates are equal.

$C_4H_6(a)$ is the most abundant species, we have

$$[C_4H_6(a)] \gg [C_4H_7(a)]$$

in which $[C_4H_6(a)]$ and $[C_4H_7(a)]$ are respectively the surface concentrations of both compounds with one $C_4H_6(a)$ per two Pt atoms. With the additional assumption that all sites are active for hydrogen dissociation, the rate of the reaction is

$$\begin{aligned} r &= k_4[C_4H_7(a)] \cdot [H(a)] \\ &= k_4K_3[C_4H_6(a)] \cdot [H(a)]^2 \\ &= k_4K_3K_2 \cdot P_{H_2} \cdot [C_4H_6(a)] = K \cdot P_{H_2} \end{aligned}$$

where K_2 and K_3 are respectively the equilibrium constants for reactions 2 and 3. This rate equation is in agreement with the kinetic results.

At 373 K the rate of the equilibration reaction is 20 times lower than that on the bare Pt(110) (5). This indicates that a fraction of the dissociation (or recombination) sites is blocked by the hydrocarbon molecules. In the absence of a systematic study

of the hydrocarbon deuteration, the major mechanism of the H_2 - D_2 equilibration cannot be determined. It can be either the direct recombination between $H(a)$ and $D(a)$ or the exchange among $D(a)$, $C_4H_6(a)$, and $C_4H_7(a)$.

When a large amount of butadiene is converted, the change of order with respect to this species indicates that the surface is not saturated anymore and the equilibration rate is increased. This is in agreement with the fact that the part of the surface free of adsorbed butadiene molecules has the same behavior as the bare $Pt(110)$ with respect to the H_2 - D_2 exchange reaction.

In the low hydrogen pressure regime, the selectivity toward butane is proportional to hydrogen pressure (Fig. 8) and the order with respect to hydrogen pressure is no longer one but becomes two for the hydrogenation reaction. This order also increases for the equilibration reaction. The rate of both reactions is lower than the rate we would expect by extrapolating the results obtained at high hydrogen pressures. It was observed that the carbon surface concentration in this regime was higher than that previously and could even reach nearly the equivalent of 6C atoms per platinum atom. This latter concentration corresponds to the second level of saturation obtained by

adsorption from pure butadiene. These observations seem to indicate that the sites for hydrogen dissociation are partially poisoned by some hydrocarbon species. As previously assumed, dehydrogenated butadiene molecules such as butadienyl species may be responsible for this partial deactivation. The order of two with respect to hydrogen for the hydrogenation reaction can be explained with the same general mechanism as above, if the fraction of dissociation sites for hydrogen is no longer constant but varies proportionally with the hydrogen pressure.

C. Deactivation by Carbon

(i) *Low-temperature deactivation.* A series of catalytic tests has been performed for several values of carbon concentration obtained by butadiene adsorption at room temperature followed by treatment under vacuum at the same temperature. As seen above, it is possible by such treatments to realize various carbon deposits and there is good experimental evidence that butadiene molecules are adsorbed first in the valleys (up to one molecule per two platinum atoms), then on the topmost metal atoms (up to one molecule per platinum atom, or 1.5 molecules per platinum atom for the total amount).

As shown on the deactivation curve, two regimes are visible (Fig. 9).

(i) Up to $2C/Pt$ or $1C_4H_6/2Pt$ the same activity A_0 and selectivity as those starting from the clean surface were found. This means that even if butadiene molecules are partially dehydrogenated during the vacuum treatment, this process does not irreversibly poison the surface.

(ii) Above $2C/Pt$ the deactivation curve roughly follows the relation $A = A_0(1 - \theta_c^2)$ where θ_c is the number of butadiene molecules per platinum atom adsorbed, in the second adsorption stage, i.e., on the presumed dissociation sites for hydrogen. If butadiene molecules are adsorbed at random, the preceding relation indicates that

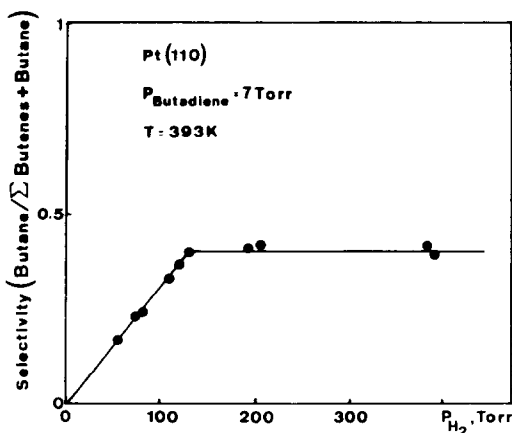


FIG. 8. Variation of the selectivity in butane as a function of hydrogen pressure.

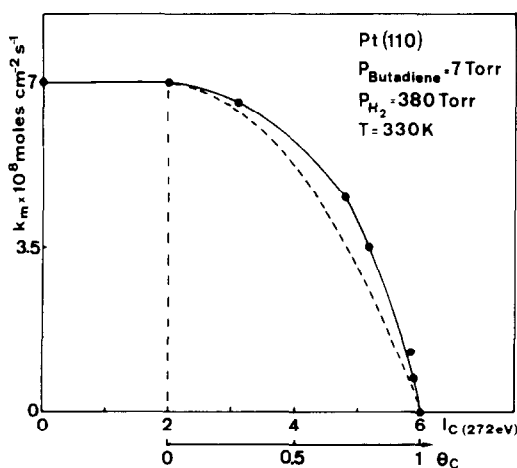


FIG. 9. Variation of the hydrogenation rate as a function of carbon coverage at $T = 330 \text{ K}$ (θ_c varying from 0 to 1 between 2 and 6 for $I_{c(272)}$). The dotted line corresponds to the curve $A = A_0(1 - \theta_c^2)$.

the deactivation of one dissociation site for hydrogen would require two butadiene molecules adsorbed on two next-neighbor sites. We finally note that complete deactivation occurs for $\theta_c = 1$ which corresponds to the second level of saturation obtained by butadiene adsorption. Contrary to the previous case, this deactivation is probably the result of some irreversible transformation of the hydrocarbon molecules adsorbed during the second stage of adsorption. We can, for example, imagine a partial dehydrogenation under vacuum with the formation of butadienyl or butylidyne radicals. It has been proved that the reactivity of partially dehydrogenated species (e.g., ethylidyne in ethylene hydrogenation (10)) is much lower than deduced from the hydrogenation rate. Vibrational spectroscopic analysis would probably be one of the most appropriate tools to differentiate between these two hydrocarbon species. The regime of butadiene hydrogenation observed at low hydrogen pressure (Fig. 5) can be tentatively explained as above by a partial deactivation of the hydrogen dissociation sites. It can be assumed that for a given hydrogen pressure, a stationary coverage of the deactivating hydrocarbon spe-

cies is reached. Such explanation would account for the higher order of the reaction rate with respect to hydrogen: a fraction of the hydrogen would be required to react slowly with the deactivating hydrocarbon species, and another fraction to hydrogenate normally the butadiene molecules.

(ii) *High-temperature deactivation.* Deactivation by carbon may also occur at high temperatures. This phenomenon is characterized by an initial rate of hydrogenation decreasing as a function of temperature, as is shown in Fig. 10. This occurs above a critical temperature $T_c = 520 \text{ K}$ (extrapolation). It was also observed that the hydrogenation rate was not constant as a function of time but was decreasing until a low stationary value was reached. After the reaction, a carbon surface concentration above the critical value of $2C/1Pt$ was always found. At high temperatures the platinum Auger peak was even totally screened, indicating the formation of a multilayer carbonaceous deposit.

We have previously assumed that at low temperatures the hydrogenation reaction was controlled by the surface reaction between adsorbed hydrogen and $C_4H_7(a)$ and with an apparent activation energy of 39 kJ mol^{-1} . By increasing the temperature, a change in the rate-determining step is to be expected when the rate of hydrogen dissociation begins to be of the same order of magnitude as the rate of hydrogenation. The temperature T'_c at which such a change of regime occurs roughly corresponds to the intersection between the curve of hydrogenation and the curve of equilibration (590 K, see Fig. 11). We note that T'_c is not very different from T_c . The agreement is even better if we consider that the departure of the normal hydrogenation curves must occur at lower temperatures than T'_c . We arrive at the conclusion that when the hydrogen supply begins to control the overall reaction, the hydrogenation of the butadiene molecules is replaced by dehydrogenation into products that are the precursors of the inactive carbon deposit.

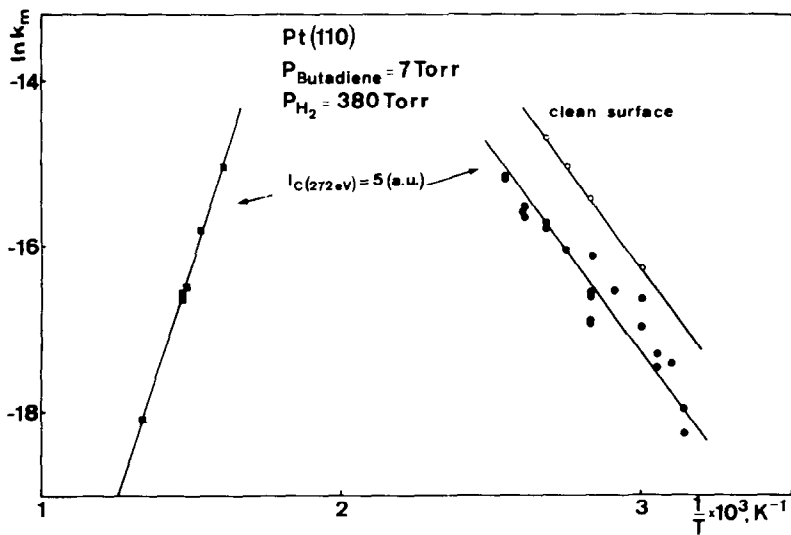


FIG. 10. Arrhenius plots giving the apparent activation energy of the hydrogenation reaction on clean surface and on carbon-covered surface ($\theta_c \sim \frac{2}{3}$).

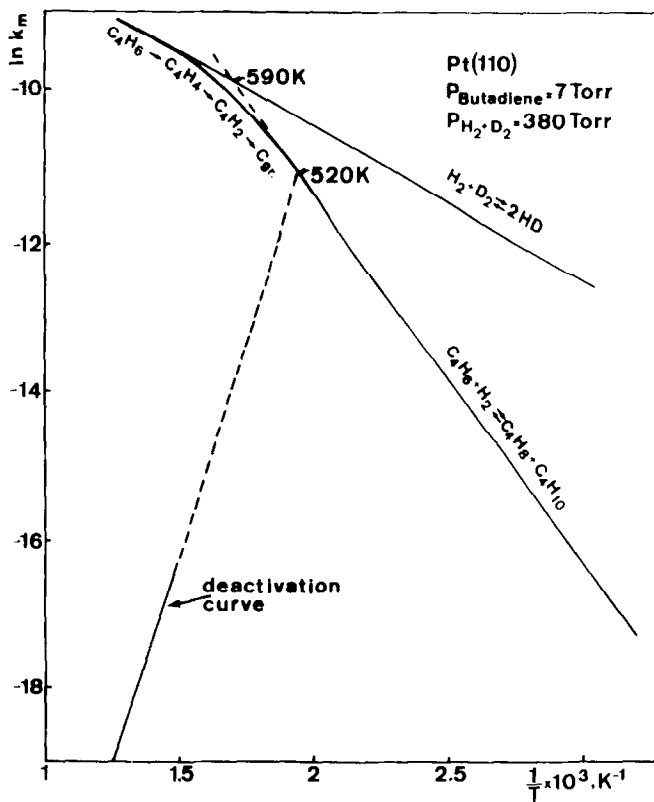


FIG. 11. Arrhenius plots of the hydrogenation and the equilibration reactions giving the temperature at which the butadiene molecules are transformed into less hydrogenated products.

In order to investigate the influence of the carbon deposit formed at high temperatures on the activation energy, a series of experiments was carried out at various temperatures starting with the same initial state of carbon contamination. As indicated by the residual activity and the measured carbon concentration, this contamination corresponded to a deposit covering about five-sixths of the surface (Fig. 10). As shown by the slope of the Arrhenius curves the activation energy remained the same for both reactions, hydrogenation and equilibration. It can be concluded that the deactivating carbon deposit does not change the electronic properties and consequently the catalytic activity of the part of the surface not covered by this deposit; also, the selectivity was observed to be unaffected by the carbon deposit.

CONCLUSIONS

By means of surface analysis before and after the catalytic reaction and simultaneous H_2 - D_2 equilibration, the butadiene hydrogenation has been studied in detail on Pt(110). Two regimes have been observed for the hydrogenation, depending on the range of hydrogen pressure employed.

Based on the results of kinetics and surface analysis we draw the following conclusions.

(1) With regard to hydrogen pressure in the range up to 400 Torr:

(i) At "high" hydrogen pressure

—butadiene is the most abundant species: under steady-state conditions the surface is covered by one butadiene molecule for two platinum atoms,

—the sites for butadiene adsorption (sites in the valleys) are different from the sites for hydrogen dissociation (probably bridge sites),

—the rate-determining step is the surface reaction between the half-hydrogenated butadiene molecules ($C_4H_7(a)$) and hydrogen atoms ($H(a)$).

(ii) Below a critical hydrogen pressure (~ 125 Torr), the sites for hydrogen dissociation are poisoned by some hydrocarbon species.

(2) Above a critical temperature the hydrogenation rate is no longer controlled by the surface reaction but by hydrogen adsorption and irreversible deactivation by carbon occurs.

(3) Deactivation by carbon formed at high temperatures does not affect the activation energy and the selectivity for the hydrogenation reaction. The residual activity is proportional to the surface free of deactivating deposit.

Since in many hydrogenation reactions the rate laws with respect to the reactants are the same as those found here at high hydrogen pressures, the proposed mechanism seems to be relevant to these reactions. In our laboratory additional work is in progress on other crystal orientations of platinum to analyze the influence of the metal structure on the mechanisms of hydrogenation. Finally, progress in the theory of the chemical bonds involving adsorbed hydrocarbons and new experimental data such as those obtained by electronic spectroscopy may provide in the future a better understanding of mechanisms of catalytic reactions involving unsaturated hydrocarbons on transition metals.

Note added in proof. The referees have drawn the attention of the authors to some critical points in this paper. In order to clarify these points, we have performed some additional AES measurements by using a cylindrical mirror analysis instead of a retarding grid analysis. These experiments have given support to the existence of two levels of saturation when butadiene is adsorbed from the gas phase. Moreover, a much lower screening effect of butadiene was observed on the platinum 168 eV Auger peak when the analysis was made at normal incidence for the excitation electron beam. These results will be reported in detail in a forthcoming publication.

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