

1,3-Butadiene Hydrogenation on Single Crystals of Platinum

II. Sulfur Poisoning of Pt(110)

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The sulfur deactivation of Pt(110) for the 1,3-butadiene hydrogenation and H_2-D_2 equilibration reactions at 323–423 K and ~400 Torr pressure were investigated. It was observed that each sulfur atom poisons one dissociation site for hydrogen without changing the mechanisms of the reactions occurring on the sites remaining free of sulfur. An isotherm of sulfur adsorption was obtained at 373 K during the hydrogenation reaction. This curve indicates that the butadiene molecules adsorbed under the steady-state conditions of hydrogenation significantly decrease the binding energy of sulfur on platinum (15–20%). As a general conclusion of this study, it appears that the deactivation behavior of sulfur for a catalytic reaction involving unsaturated hydrocarbon depends on the adsorption strength of the hydrocarbon and on its concentration on the surface. © 1987 Academic Press, Inc.

INTRODUCTION

In Part I (1), we have described results concerning the mechanism of 1,3-butadiene hydrogenation on Pt(110) and the role of carbon on the surface deactivation. The experiments were performed at pressures of 200–400 Torr and the H_2-D_2 equilibration rate was measured during the hydrocarbon hydrogenation. The surface was characterized before and after the reaction by LEED and AES. Using the same equipment and the same experimental approach, we have also studied the poisoning by sulfur. This has been the subject of two preliminary notes (2), and is the main topic of this paper.

In the present study we have performed two kinds of experiment. In the first, the sulfur was preadsorbed on the surface, and then the catalytic activity and the selectivity were measured as a function of the sulfur coverage. Such an approach, familiar to specialists using UHV surface science techniques, gives the possibility of correlating the activity and the selectivity with the

surface concentration and possibly with the arrangement of the atoms (or molecules) adsorbed on the surface. From the shape of the deactivation curve one can discern whether the effect of an impurity is strictly restricted to the occupied sites (pure site blocking effect) or can be extended to the neighbor sites (electronic or ligand effect). Electronic effects induced by sulfur have already been clearly shown in the case of H_2-D_2 equilibration on platinum single crystals (3). In the second series of experiments, the surface was poisoned from the gas phase containing the reaction mixture and a known amount of H_2S . This second approach provides data which are particularly interesting for catalysis specialists who wish to know the critical level of impurity in the gas phase under which the activity and the selectivity remain acceptable.

By combining both approaches, the surface coverage of the impurity at a given temperature can be obtained as a function of the H_2S pressure in the gas phase. This curve represents the isotherm of sulfur ad-

sorption under the real conditions of the catalytic reaction.

EXPERIMENTAL

As mentioned above, the apparatus and the experimental procedure have already been described in detail (1). Consequently we shall only recall here the main characteristics of this study. The catalytic reaction was performed in a closed circulating system. The reactants and the products of the reaction were analyzed by gas chromatography. At the same time, by using an equal amount of H_2 and D_2 , the rate of HD formation, which gives, under the steady-state conditions, the rate of H_2 dissociation, was continuously recorded by mass spectrometry. Sulfur was preadsorbed from H_2S under the same conditions as those previously for the study of the poisoning of the H_2 - D_2 equilibration reaction on platinum single crystals (3). The sulfur concentration was measured for each reaction by AES, the calibration of the sulfur Auger peak being made by a radiochemical technique based on the use of ^{35}S . On Pt(110), sulfur gives a series of LEED patterns which correspond to well-defined structures. Models for these structures have already been proposed (4). After the catalytic reaction and the gas removal, the surface was again characterized by AES and LEED. The reaction was performed under the following conditions:

$$\begin{aligned} 20 \leq P_{H_2}/P_{C_4H_6} \leq 60 \\ (H_2-D_2 \text{ equimolecular mixture}) \\ 323 \text{ K} \leq T \leq 423 \text{ K.} \end{aligned}$$

Under these conditions the order with respect to hydrogen is equal to unity for both the hydrogenation and the equilibration reactions and equal to zero with respect to butadiene.

RESULTS

Sulfur Poisoning

1. *Deactivation curves.* Caution was needed to obtain deactivation curves be-

cause of the following experimental features. When starting from a surface precovered with sulfur, the latter was observed to desorb during subsequent butadiene hydrogenation at temperatures around 373 K and above. During sulfur desorption, the hydrogenation rate progressively increases until it reaches a stationary value. Consequently, the deactivation curves shown in Fig. 1 have been obtained by plotting the reaction rate under steady-state conditions as a function of the sulfur coverage measured immediately after the catalytic test. Whatever the temperature, the reaction rate linearly decreases when the sulfur coverage increases.

The same linear relationship has been found between the rate of H_2 - D_2 equilibration reaction and the sulfur coverage.

It was also observed that whatever the sulfur coverage (i) the activation energies of both reactions studied were the same, as illustrated in Fig. 2 for the hydrogenation reaction, and (ii) the product distribution was identical.

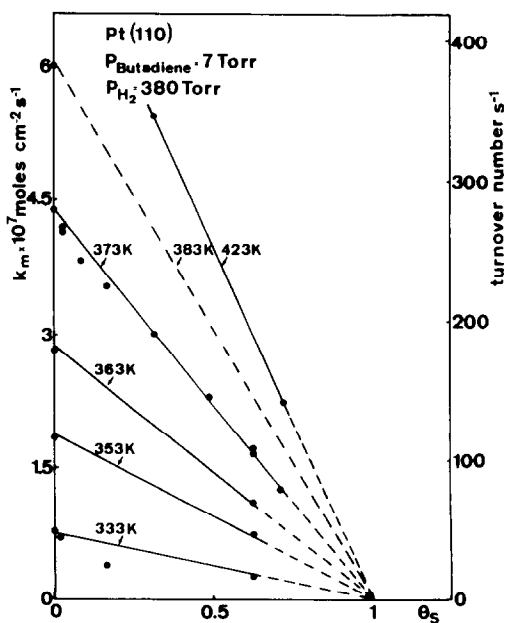


FIG. 1. Variation of the hydrogenation rate (turnover frequency) as a function of sulfur coverage (θ_s) at various temperatures.

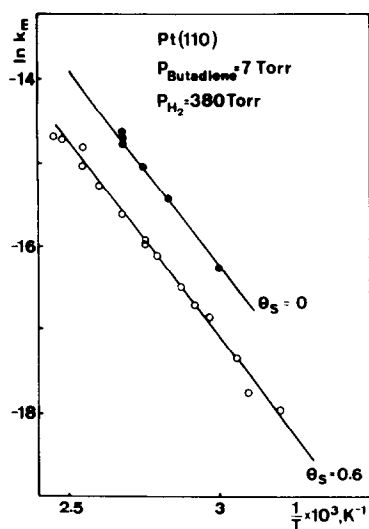


FIG. 2. Arrhenius plots giving the apparent activation energy of the hydrogenation reaction for the clean surface ($\theta_s = 0$) and sulfur-covered surface ($\theta_s = 0.6$).

The surface characterization by LEED and AES after the reaction has provided very useful additional data. First, the well-defined LEED pattern of adsorbed sulfur was no longer present after the butadiene hydrogenation but was replaced by a diffuse $p(1 \times 1)$ pattern. This indicates that sulfur was disorganized during the catalytic reaction. Second, the same amount of carbon was measured whatever the sulfur surface concentration. This corresponds to the first saturation level observed by butadiene adsorption from the gas phase, namely one butadiene molecule per two platinum atoms (1). The existence of this saturation state for butadiene on the surface under reaction conditions is consistent with the fact that the rate of butadiene hydrogenation does not depend on the partial pressure of butadiene in the gas phase.

2. *Adsorption isotherm of sulfur.* Some experiments have shown that the reaction rate under steady-state conditions depends on the residual partial pressure of H_2S in the gas phase, i.e., on the sulfur coverage θ_s at equilibrium. In order to obtain the relationship between θ_s and P_{H_2S} (isotherm of

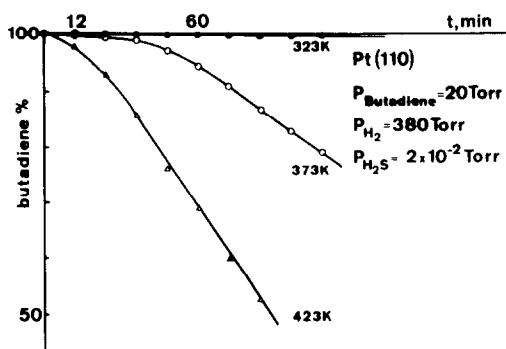


FIG. 3. Decrease in butadiene concentration in the gaseous phase as a function of time at various temperatures.

adsorption), a series of experiments has been performed under the following conditions. The surface was first saturated by sulfur and then exposed to a gas mixture containing butadiene, hydrogen, and a known pressure of H_2S . The hydrogenation rate was measured as a function of time. As one can see in Fig. 3, at 373 and 423 K the hydrogenation rate (proportional to the slope of the curves) is at first very low, and then progressively increases to reach a constant value. From this value, and using the curve of Fig. 1 as a calibration of the surface sulfur concentration, the isotherm of Fig. 4 has been drawn. The reversibility of the sulfur adsorption during buta-

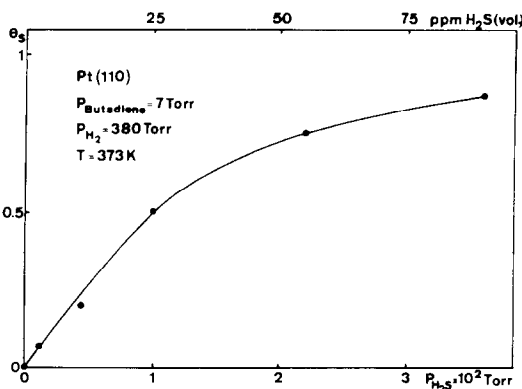


FIG. 4. Adsorption isotherm of sulfur on Pt(110) determined during the hydrogenation reaction of butadiene at $T = 373$ K.

diene hydrogenation was checked by starting from a clean metal surface.

This latter was not the case in pure hydrogen in this range of temperature (5).

DISCUSSION

The deactivation curves of Fig. 1 indicate that:

(i) each sulfur atom deactivates one site both for the equilibration reaction and for the butadiene hydrogenation,

(ii) the presence of one sulfur atom on a given site does not affect the catalytic activity or the selectivity of the neighbor sites (pure site blocking effect),

(iii) the extrapolation of the deactivation curves shows that complete deactivation would occur for a critical sulfur coverage of one sulfur atom per platinum atom (such a coverage could not be obtained by sulfur preadsorption from pure H_2S).

This poisoning behavior is quite different from what has been observed either for the methanation reaction on Ni(100) (6) or for the H_2 - D_2 equilibration (3) performed on the same surface in the absence of butadiene. In the latter case both electronic and site blocking effects were induced by sulfur and total poisoning occurred at lower sulfur coverage ($\theta_s = 0.8$). The reversibility of the isotherm of sulfur adsorption at a temperature as low as 373 K is also a new feature induced by the catalytic reaction. All these observations indicate that butadiene which is the most abundant species on the surface is determining in the mechanism of poisoning by sulfur. In Part I, we arrived at the conclusion that the most likely sites for butadiene molecules were the valley sites on the Pt(110) surface and that hydrogen dissociation occurred on other sites initially assumed to be the bridge sites on the top layer of platinum. In the absence of precise data concerning the location of butadiene molecules, another mechanism has been proposed in Ref. (2). From these new conclusions, we propose the following scheme. Starting from an or-

dered sulfur-covered surface, sulfur atoms are removed by butadiene molecules from hollow sites to the sites of hydrogen dissociation on which they are randomly adsorbed. A fraction of the initial sulfur coverage is desorbed leaving a level of adsorption related to the partial pressure of H_2S in the gas phase.

This mechanism is consistent with all the experimental features which are summarized below:

1. Sulfur atoms as well as butadiene molecules are preferentially adsorbed in the high coordination sites in the valleys of Pt(110) (4).

2. Under steady-state conditions sulfur does not change either the mechanism of butadiene hydrogenation (same activation energy, same selectivity) or the carbon surface coverage.

3. Sulfur deactivation is one site per one atom for the H_2 - D_2 equilibration as well as for the butadiene hydrogenation, both reactions requiring the hydrogen dissociation as an intermediary step.

4. When the surface is initially saturated with sulfur, an induction time is observed before the stationary state is reached.

The displacement of sulfur which is tightly bonded to platinum may appear surprising; however, the decrease in the binding energy resulting from the change in the adsorption sites for sulfur can be largely compensated by the energy gain due to the butadiene adsorption in the hollow sites.

The adsorption isotherm provides additional information on the sulfur-sulfur interactions and on the decrease in the sulfur-metal binding energy induced by the butadiene. It is a Langmüir-type isotherm, indicating that the sulfur-sulfur interactions are negligible. This is in agreement with the fact that each sulfur atom blocks one dissociation site for hydrogen. The extrapolation to 373 K of the isotherms established by McCarty *et al.* (7) between 478 and 898 K on dispersed platinum indicates a P_{H_2S}/P_{H_2} ratio of 10^{-9} in-

stead of 10^{-5} leading to half-coverage. This represents four orders of magnitude lower than that observed in our experiments. In fact, based on the location of the adsorption isotherm in the scale of H_2S partial pressures, platinum, covered by butadiene, behaves more like silver than like clean platinum. To determine the heat of sulfur adsorption, we have performed some experiments at various temperatures. These experiments were not entirely conclusive. At 323 K preadsorbed sulfur is irreversibly fixed on the surface during the butadiene hydrogenation. Between 323 and 423 K, the isotherms of adsorption do not significantly move in the scale of H_2S partial pressures. This indicates that the heat of adsorption from H_2S is quite low. From the free energy of adsorption and assuming a reasonable value for the entropy term, a rough estimation of the heat of adsorption can be made. The standard free energy of adsorption is given by the relation

$$\Delta G_T^\circ = RT \ln \frac{P_{H_2S}}{P_{H_2}}$$

At 373 K and $\theta_s = \frac{1}{2}$, $P_{H_2S}/P_{H_2} = 2 \times 10^{-5}$ which gives

$$\Delta G^\circ (373 \text{ K}) = 33.5 \text{ kJ mol}^{-1}$$

As mentioned above, the (100) face of silver presents a comparable affinity for sulfur. On this face $\theta_s = \frac{1}{2}$ for $P_{H_2S}/P_{H_2} = 1.6 \times 10^{-5}$. If we assume the same entropy term as the one of Ag(100)-S we find

$$\Delta G^\circ (373 \text{ K}) = 33 \text{ kJ mol}^{-1}$$

Taking into account the heat of H_2S formation from $\frac{1}{2}S_2$ and H_2 (-89 kJ mol^{-1}) and the heat of S_2 dissociation (422 kJ mol^{-1}) one finally finds for the binding energy of the sulfur atom on Pt(110) during the butadiene hydrogenation

$$E_b = 211 + 122 = 333 \text{ kJ mol}^{-1}$$

If the heat of adsorption from H_2S were negligible, as suggested by the small influence of the temperature on the position of

the isotherm, we would have found $E_b = 300 \text{ kJ mol}^{-1}$. The comparison with the value found on Pt/ Al_2O_3 (386 kJ mol^{-1}) for about the same surface coverage shows a decrease in the binding energy of the order of 15 to 20% depending on the choice for the entropy term.

The nature of the sulfur-containing species may also be questioned. $(HS)_a$ species instead of $(S)_a$ can be considered; in fact the desorption of sulfur to give H_2S in the gas must involve the formation of the transient species $(HS)_a$ and may involve a change of the adsorption site, from a highly to a less coordinated site. However, we do not have any experimental proof that $(HS)_a$ instead of S_a is the most abundant sulfur-containing species during the butadiene hydrogenation.

CONCLUSIONS

This study has shown that during butadiene hydrogenation:

- (i) the electronic or ligand effect usually observed in sulfur poisoning (3) does not exist,
- (ii) the sulfur-metal binding energy is decreased by 15 to 20%,
- (iii) the sulfur atoms are reversibly adsorbed contrary to what occurs in pure hydrogen at the same temperature and pressure; this gives the possibility of establishing the first isotherm of sulfur adsorption under real catalytic conditions.

A mechanism based on the displacement of sulfur by butadiene molecules onto the sites of hydrogen dissociation has been proposed which is consistent with most of our experimental observations.

The results give a new insight into the mechanism of sulfur poisoning and can be extended to other systems involving hydrocarbons.

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