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Influence of Adsorbed Sulfur on the Catalytic Activity of Platinum in the Ethylene Hydrogenation Reaction

The development of a radioactive-tracer method for measuring very small quantities of sulfur adsorbed on a metallic surface and recent surface-analysis techniques have permitted our laboratory to acquire the first thermodynamic and structural data concerning sulfur adsorption on several metals (*1, 2*). Sulfur is well-known as a catalyst poison for metals (*3, 4*). In this note the fundamental character of sulfur adsorption on a polycrystalline platinum surface, the regeneration by hydrogen of the same surface after poisoning by sulfur, and the effects of adsorbed sulfur on catalytic activity will be considered.

METHODS

A detailed description of the apparatus used in this study has been given in previous papers (*5, 6*). There has been only one slight modification, which is the addition to the flow reactor of a gas chromatograph. All the experiments were performed on a cylindrical sample of polycrystalline platinum (99.999% purity) whose dimensions were approximately r = 2.5 cm and h = 4 cm.

For adsorption and desorption studies, the sample was annealed at 1200°C for 12 h in high-purity flowing hydrogen at a pressure of 1 atm. It was then transferred to the reaction apparatus and heated once more in high-purity flowing hydrogen at the same pressure but at 800°C. The hydrogen pressure was then set at 0.2 atm for adsorption. The sample was exposed to a $H_2/H_2^{35}S$ mixture admitted from a side tube and heated at the adsorption temperature, typically for 1 or 2 h. After formation of a sulfur monolayer on the platinum surface, in order to study desorption, the sample was heated for several hours in a continuous flow of high-purity hydrogen at different temperatures (150 to 400°C). From time to time, the surface radioactivity was measured.

The same polycrystalline sample was used to study the catalysis of ethylene hydrogenation. The partial pressures of the reaction mixture were 30 Torr ethylene with 270 Torr hydrogen. The first set of hydrogenation reactions was made on "clean" platinum. The sample was first annealed in high-purity oxygen at 400°C and then in high-purity flowing hydrogen at 450°C. Verification of total sulfur removal from the surface was obtained by counting. There was, however, no possibility of controlling the cleanliness of the surface with respect to carbon or oxygen. For the hydrogenation reactions on sulfur-poisoned platinum catalyst, sulfurization was carried out by means of adsorption isotherms. After adsorption of sulfur to yield partial or total coverage on the platinum surface, the catalytic mixture ethylene/hydrogen was introduced and the first chromatographic analysis recorded. The extent of hydrogenation versus time was monitored at three temperatures for three different coverages.

RESULTS AND DISCUSSION

Adsorption Isotherms

Figure 1 shows the sulfur adsorption isotherms for three temperatures, 350, 400, and 450°C. As for other metal/sulfur systems studied previously (*7, 8*), we assume that for pressure ratios of $P_{H_2^{35}S}/P_{H_2}$ above 10^{-3} the weight of adsorbed sulfur reaches a maximum value of 43.7×10^{-9} g/cm², i.e., 8.2×10^{14} atom/cm². This saturation value was considered to signify the formation of a

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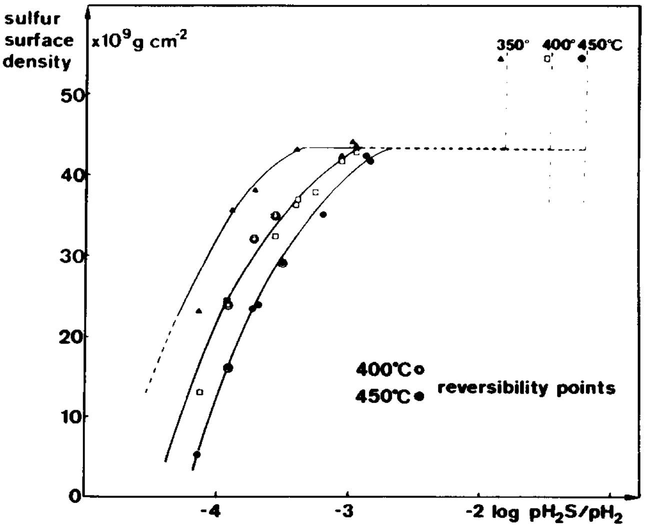

FIG. 1. Adsorption isotherms of sulfur-35 on polycrystalline platinum at 350, 400, and 450°C.

sulfur monolayer and was defined as a reference level for degree of coverage ($\theta = 1$ is equivalent to $\theta = 43.7 \times 10^{-9}$ g/cm^2). Under similar conditions, Berthier *et al.* (*9*) obtained a value of 8×10^{14} atom/cm^2 and Heegemann *et al.* (*10*) 6.6×10^{14} atom/cm^2 on polycrystalline platinum.

When the pressure ratio $P_{\mathrm{H}_2^{35}\mathrm{S}}/P_{\mathrm{H}_2}$ was reduced, the weight of adsorbed sulfur was also reduced. The transition from monolayer to small coverages when the pressure is reduced depends only on the mechanism of chemisorption. This phenomenon in the case of platinum takes place over a large range of pressures. It suggests possibly weak lateral forces of interaction between adsorbed atoms and it is also a consequence of the heterogeneity of the surface. As in the case of silver (*7*), the slope of the isotherms was not influenced by the adsorption temperature.

For both the isotherms at 400 and 450°C, the weight of adsorbed sulfur was found to be dependent only the final partial pressure of hydrogen sulfide $\mathrm{H}_2^{35}\mathrm{S}$. The "reversibility" points are also represented in Fig. 1. In contrast, reversibility was not observed at 350°C because of the very slow reduction kinetics at this temperature (see below).

The results shown in Fig. 1 allowed calculations of thermodynamic values in relation to the adsorbed sulfur. An approximate value for the adsorption energy of -46 ± 10 kJ/mole can be derived, which is in good agreement with the values obtained by Heegemann *et al.* (*10*) on single crystals of platinum.

Reduction of Adsorbed Sulfur by H_2

After adsorption of a sulfur monolayer, desorption was monitored at 150, 200, 250, 350, 400, and 450°C. For each temperature, the weight of adsorbed sulfur versus time of reduction is shown in Fig. 2, from which the following observations are evident:

1. There was no reduction in the adsorbed monolayer coverage at 150°C up to 20 h.
2. In contrast, at 450°C reduction was complete within only 1 h. This result has consequently been used to obtain a "clean" platinum surface (concerning sulfur).
3. Between 200 and 400°C, reduction was incomplete. This corresponds to very slow kinetics.

The results may be compared with those of McCarty *et al.* (*11*) which showed variations in the adsorption enthalpy with the

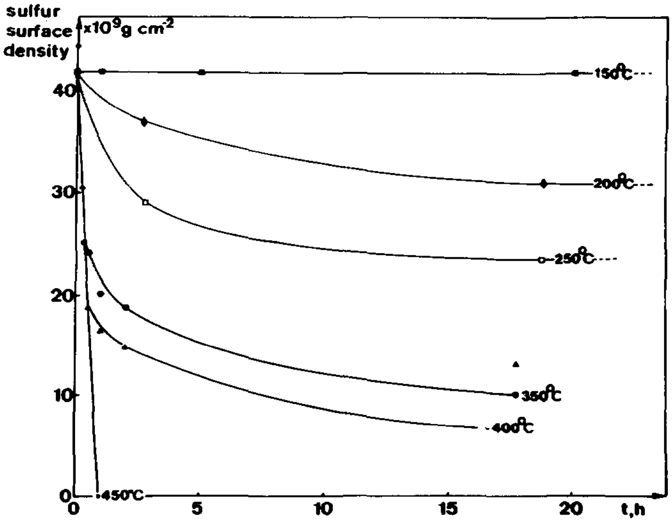

FIG. 2. Reduction by hydrogen of sulfur adsorbed on polycrystalline platinum at various temperatures.

degree of coverage of the surface by sulfur. This could explain the existence of the steps on the desorption curves in Fig. 2. Moreover, Berthier *et al.* (*9*) and Heegemann *et al.* (*10*) found, by TDS studies on single crystals of platinum, that the desorption temperature changed suddenly at a specific degree of coverage. They suggested that there were lateral forces of interaction between the adsorbed atoms, transmitted through the metal, and that these forces were in particular present for high degrees of coverage by sulfur. These forces, by weakening the sulfur/metal bonding, would enhance the desorption process. It must be recognized, however, that a polycrystalline sample was used here and therefore there are likely to be adsorption sites with different affinities for sulfur.

The results show that, by working at temperatures below 250°C, the degree of coverage by sulfur of the surface is constant, even after several hours. This fact was exploited for the hydrogenation reaction described in the next section.

Ethylene Hydrogenation

Catalytic test on "clean" platinum. Figure 3 shows the percentage of ethane formed versus time for three temperatures of hydrogenation, 25, 55, and 100°C. The three, reproducible curves have the same shape, depending on the temperature, there is a more or less rapid increase in the amount of ethane up to a constant level corresponding to the end of the reaction. The turnover frequency, defined as the ratio of the number of molecules of reacted ethylene to the product of time and number of accessible platinum atoms, was calculated on the hypothesis that all platinum atoms are accessible and by taking an average density between the three low indexed faces, (100), (110), and (111). The results are given in Table 1.

It is evident from Fig. 3 and Table 1 that the hydrogenation rate increases with the temperature, particularly between room temperature and 55°C and that in each case it is possible to obtain complete hydrogenation of ethylene. Moreover, the slope of each curve is constant, indicating that the reaction has a zero order with respect to ethylene, as described in the literature (*12*).

Catalytic tests on platinum carrying adsorbed sulfur. For a sulfur coverage of $\theta_1 = 30.4 \times 10^{-9}$ g/cm^2, i.e., a two-thirds monolayer (Fig. 4), there was no hydrogenation

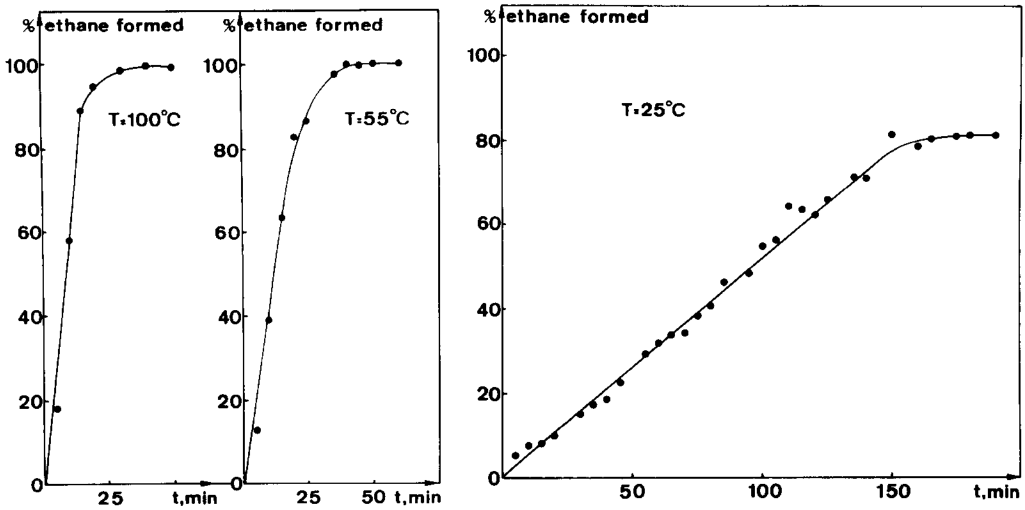

FIG. 3. Ethylene hydrogenation on "clean" platinum at 25, 55, and 100°C.

of ethylene at room temperature even up to 70 min. At 55°C, the hydrogenation was limited; a plateau was soon reached after 30 min and 1.2% ethane was produced. Under the same conditions, 15% ethane was produced on clean platinum. At 110°C, complete hydrogenation was observed but the conversion rate was slower than that on clean platinum.

In contrast to the former case, for a coverage $\theta_2 = 8.4 \times 10^{-9}$ g/cm^2, i.e., a one-fifth monolayer (Fig. 5), over all test temperatures, the hydrogenation was complete. The turnover frequencies were calculated for each temperature and are shown in Table 1.

TABLE 1

Turnover Frequencies for Ethylene Hydrogenation on Clean Platinum and on Platinum Carrying Adsorbed Sulfur at a Coverage of $\theta_2 = 8.4 \times 10^{-9}$ g cm^{-2}.

T (°C)	Turnover frequency (s^{-1})	
	Clean Pt	With adsorbed sulfur (θ_2)
25	4.4	21
55	35	28
100	46.6	70

CONCLUSIONS

The experimental results suggest a double role for the sulfur adsorbed on platinum in ethylene hydrogenation, namely a promoter at low degrees of coverage and an inhibitor for higher degrees of coverage when sulfur becomes a poison for the metallic catalyst. A complete interpretation of this work would require, at any reaction time, a thorough knowledge of the surface state, the conditions of adsorption of sulfur, hydrogen, and ethylene, and the exact amount of each element in the gas mixture. These factors could not be controlled in the present study and most of the studies to date concerning the adsorption conditions of ethylene and hydrogen on platinum have been carried out on single crystals (*13*) or on particulates (*14*) and, thus, cannot be used in the present case. It is, however, possible to postulate several models:

1. There is a deactivation by the poison only for the occupied adsorption sites and no interactions with the sulfur-free surface.
2. Chemisorption changes the properties of the metallic atom involved in the poison/

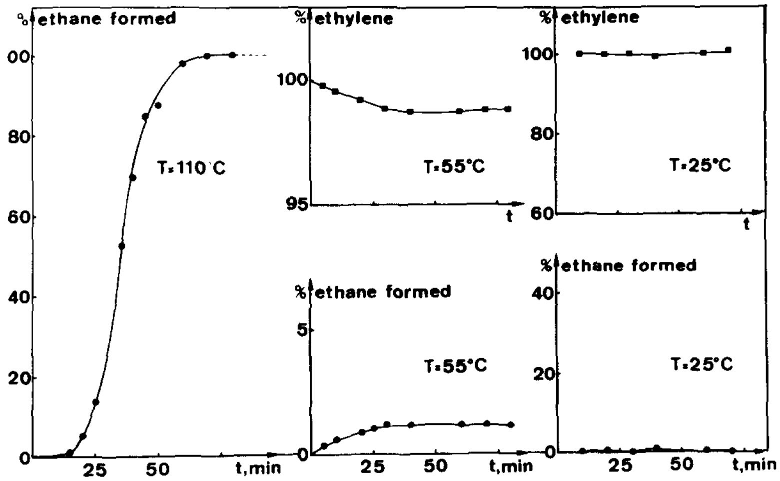

FIG. 4. Ethylene hydrogenation on platinum with a coverage by sulfur of 30.4 × 10^{-9} g/cm^2, i.e., a two-thirds monolayer.

metal bond, particularly its bonding with the neighboring metallic atoms. The electronic effect so caused would be transmitted through the metal and would thus modify the neighboring sites.

3. When the interaction between the metal and the adsorbed atom is very strong, the metal–metal bonding can also be modified; it is thus possible to obtain new surface structures due to the increased mobility of surface atoms (*15*).

It is difficult to select between these three postulated models, each of which is likely to occur in different proportions. This is quite similar to the phenomenon shown by Pradier *et al.* on platinum for the exchange reaction $H_2 \cdot D_2$ (*16*). The maximum rate for this reaction corresponded to an amount of

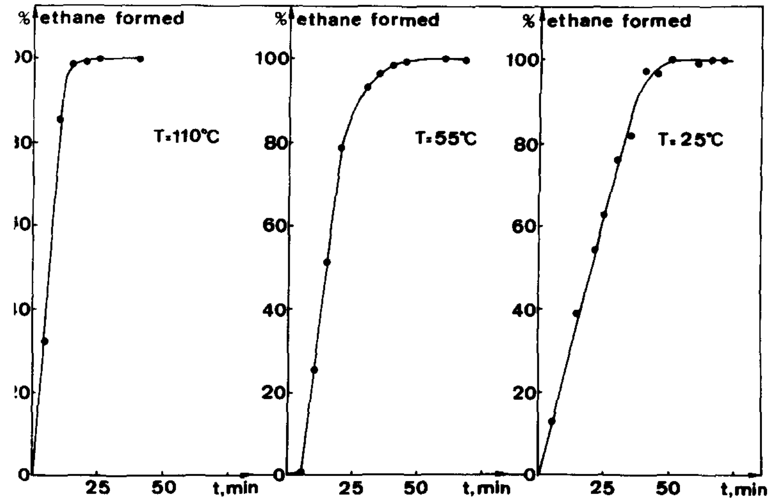

FIG. 5. Ethylene hydrogenation on platinum with a coverage by sulfur of 8.4 × 10^{-9} g/cm^2, i.e., a one-fifth monolayer.

adsorbed sulfur equal to one atom of sulfur for nine atoms of platinum, which is exactly the amount obtained in this investigation in the θ_2 case. For this degree of coverage, there should be an equilibrium between the negative effect of the blocking of reaction sites and the positive electronic effect of adsorbed sulfur on neighboring sites. Above this coverage, the blocking effect is stronger and the surface is completely deactivated compared with "clean" platinum.

ACKNOWLEDGMENT

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