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SULFUR POISONING AND REGENERATION OF POLYCRISTALLINE PLATINUM FOR BUTADIENE HYDROGENATION

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Simultaneous sulfur-butadiene coadsorption in the presence of hydrogen is the key to partially reactivate a sulfur-poisoned catalyst. The corresponding mechanism is analysed assuming different behavior of the surface orientations toward the butadiene-sulfur-hydrogen interactions.

1. Introduction

This study is part of a more extensive work in progress in this laboratory on the hydrogenation of diolefines over platinum [1–4]. Most experiments have been performed on single crystals at a total pressure near the atmospheric one. The surface was characterized before and after reaction by Low Energy Electron Diffraction and Auger Electron Spectroscopy. Special attention was given to sulfur poisoning which is a major problem for hydrogenation catalysts [5–10]. Results obtained on Pt(111), Pt(100) and Pt(110) for butadiene hydrogenation have shown that the efficiency of sulfur as a poison (toxicity) strongly depends on the crystalline orientation. The most unexpected result concerns the Pt(110) face [1]. On this plane, preadsorbed sulfur was observed to desorb slowly during the hydrogenation reaction at temperatures as low as 373 K contrary to what was occurring in pure hydrogen [11]. This result was ascribed to the presence of adsorbed butadiene on the surface during the catalytic reaction. By admitting a given amount of H_2S in the C_4H_6-H_2 gas mixture a stationary sulfur coverage was reached. By varying this amount, the reversible isotherm of sulfur adsorption was established. From this isotherm a decline of about 15 to 20% in the binding energy of sulfur compared to sulfur adsorbed on a butadiene free surface has been estimated.

By contrast, only partial desorption was observed on Pt(111) [3] and no desorption on Pt(100) [2]. In addition, the deactivation curves, representing the catalytic activity evolution with the sulfur coverage were quite different from one plane to another. In this paper we extend the poisoning experiments on 1,3 butadiene hydrogenation to polycrystalline platinum. Some attempts are also made to regenerate the catalyst after sulfur poisoning. Contrary to the previous cases, the surface is not characterized by AES, but the sulfur coverage is accurately measured by means of a radiochemical technique based on the use of ^{35}S.

2. Experimental

The sample is a 0.1 mm thick cylindrical platinum polycrystal (99.99% purity) of about 30 cm^2. It is first annealed at 1200 ° C for 12 hours in high purity flowing hydrogen at atmospheric pressure; then transferred into a silica tube connected to a pyrex batch reactor. This reactor, equipped with a special device for measuring *in situ* the sulfur radioactivity, has already been described [12]. In the reactor the sample is first treated in flowing oxygen at 600 ° C for 2 hours then in pure flowing hydrogen at 700 ° C for another 2 hours. After cooling to experiment temperature in flowing hydrogen a catalytic test is performed. It gives the reference activity for the sulfur-free surface.

In other cases, additional treatments in H_2S-H_2 gas mixtures were carried out after the treatment under H_2 at 700 ° C in order to poison the surface by sulfur. Their detailed conditions will be specified below. In these poisoning experiments, sulfur was labelled with ^{35}S (specific activity 148 MBq/mg) and the radioactivity of the sample was measured at room temperature in vacuum or under pure hydrogen with a Geiger Muller counter (Philips ZP 1501). The error in the sulfur coverage measured with the radioactive technique is estimated of the order of 10%. Nevertheless, the comparative error from one measurement to another is much smaller because all experiments were performed with the same sulfur calibration. In all cases, the catalytic test is performed under the following conditions: $pH_2 = 2.7 \times 10^4$ Pa, $pC_4H_6 = 3 \times 10^3$ Pa, $T = 373$ K. The gas mixture and the sample are nearly at the same temperature. Reactants and products are analyzed by gas chromatography. In order to define the turnover number TON (number of butadiene molecules reacting per platinum atom and per second) and the sulfur coverage θs (number of sulfur atom per platinum atom), the surface density of the polycrystal is calculated by taking an average density between the three low indexed planes (111)(100) and (110), assuming no reconstruction for the (100 and the (110) planes and a roughness factor of the surface equal to unity. The value thus obtained is 12.4×10^{14} platinum atoms per cm^2.

3. Results

SULFUR-FREE SURFACE

For this surface which has not been exposed to a sulfur containing gas, the initial hydrogenation rate expressed by the turnover number was found to be $N = 27\ \mathrm{s}^{-1}$ (fig. 1. curve 1). The order with respect to butadiene was zero and the order with respect to hydrogen was 0.3. The activation energy was found to be 28 ± 2 kJ mole^{-1}.

Comparison with TON measured on single crystals is not very significant because in one case (polycrystal) the gas mixture and the sample were simultaneously at the same temperature while in the other case (single crystals) only the sample was at the reaction temperature. We have checked that this difference in the experimental procedure may significantly affect the hydrogen dissociation rate and consequently the hydrogenation rate.

TREATMENT I

This treatment is the following:

$pH_2S/pH_2 = 10^{-3}$, $pH_2 = 2.6 \cdot 10^4$ Pa, $T = 723$ K, 2 hours.

After such a treatment the surface was totally inactive for butadiene hydrogenation. Additional tests performed with a H_2-D_2 mixture instead of pure H_2 showed that the H_2-D_2 exchange analyzed by mass spectrometry, and conse-

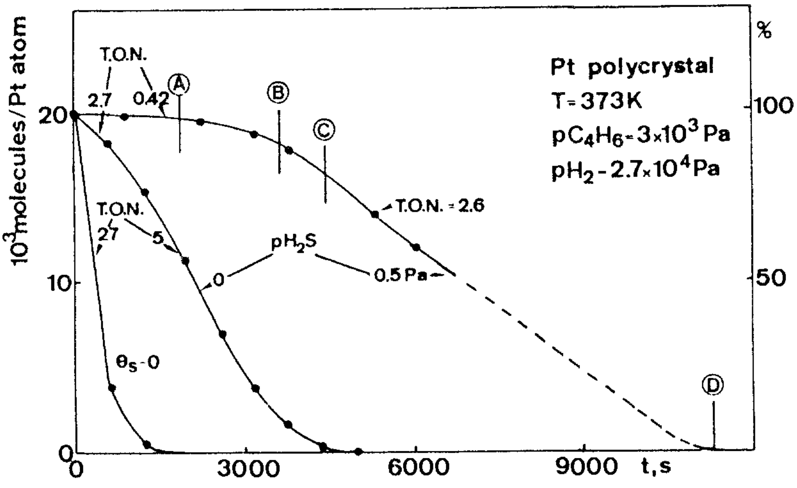

Fig. 1. Butadiene hydrogenation, – on clean surface (curve 1), – on platinum covered with co-adsorbed sulfur, the sulfur surface concentration varies from $8.2 \cdot 10^{14}$ ($t = 0$) to $7.4 \cdot 10^{14}$ at/cm^2 ($t = 4500$ s): kinetics for $pH_2S = 0$ (curve 2). – on platinum covered with co-adsorbed sulfur ($8.2 \cdot 10^{14}$ at/cm^2): kinetics for $pH_2S = 0.5$ Pa (curve 3). (A) C_2H_6S appears in the gas phase, (B) C_2H_6S no more detected, (C) $C_4H_{10}S$ appears in the gas phase, (D) $C_4H_{10}S$ no more detected.

quently hydrogen dissociation, was totally inhibited by sulfur. The surface density of adsorbed sulfur was found to be 8.2×10^{14} atoms cm^{-2}.

It corresponds to $\theta s = 0.66$. This coverage already found on polycrystalline platinum [11] corresponds to the saturation of the surface with adsorbed sulfur. By comparison, the values previously found at saturation on single crystals are respectively $\theta s = 0.5$ on Pt(111) and Pt(100) [13] and $\theta s = 0.8$ on Pt(110) [13,14].

TREATMENT II

It consists in performing the catalytic test in the presence of an additional partial pressure of H_2S in the reaction gas mixture. Two partial pressures of H_2S were admitted: 5 Pa and 12 Pa. They gave the same results: no catalytic activity, and a surface concentration of 16.4×10^{14} sulfur atoms cm^{-2} i.e exactly twice that measured after treatment I.

Partial regeneration by H_2 after treatment II

After treatment II the gas mixture (H_2-C_4H_6-H_2S) was removed at 298 K by flowing hydrogen and the reactants H_2 and C_4H_6 were readmitted into the chamber, so that the catalytic test could be performed at 373 K without any H_2S in the gas phase. But no catalytic activity was observed either, and the sulfur surface concentration remained unaltered.

At this point, butadiene was removed under a continuous flow of high purity hydrogen at 373 K. Simultaneously, significant sulfur desorption was observed as a function of time (fig. 2 curve (A)). After 15 hours under dynamic hydrogen, the

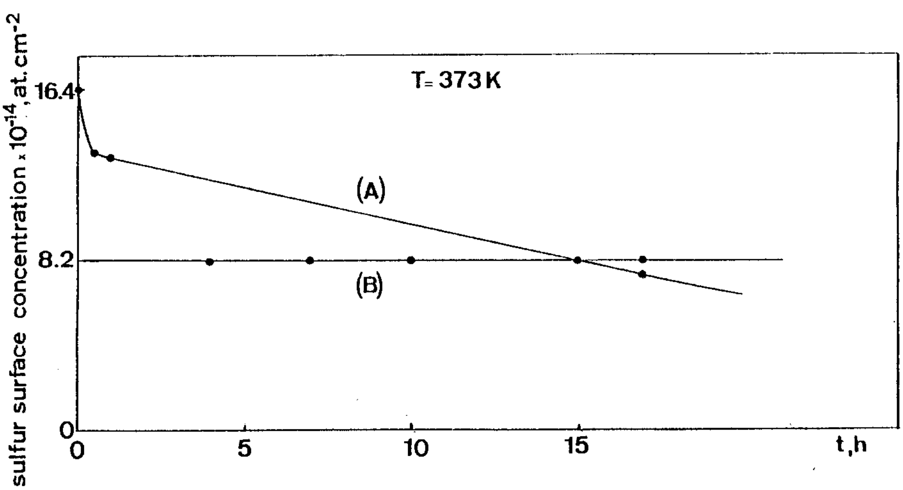

Fig. 2. Sulfur desorption kinetics under dynamic hydrogen. (A): sulfur adsorbed in the presence of C_4H_6, (B): sulfur adsorbed in a H_2/H_2S mixture.

sulfur concentration was again 8.2×10^{14} atoms cm^{-2} ($\theta s = 0.66$), and the catalytic test was then performed. Fig. 1 curve 2 shows the result.

Contrary to what was occurring after treatment I for the same sulfur coverage, the reaction rate given by the slope of this curve is no longer negligible: the TON varies from 2.7 s^{-1} (initial value) to 5 s^{-1} (stationary value). Simultaneously, the sulfur coverage varies from 8.2×10^{14} atoms cm^{-2} ($\theta s = 0.66$) to 7.4×10^{14} atoms cm^{-2} ($\theta s = 0.6$). This result indicates that the increase in the reaction rate is directly correlated with the decrease in the sulfur coverage. At $\theta s = 0.6$, about 20% of the catalytic activity of the sulfur free surface was recovered.

Partial regeneration by H_2S after treatment I

Immediately after treatment I and the subsequent catalytic test indicating no activity, butadiene was removed from the reaction gas by flowing hydrogen at room temperature. The surface was then exposed to hydrogen ($pH_2 = 2.7 \times 10^4$ Pa) containing 12 Pa of H_2S during a few minutes at 373 K. H_2S was subsequently removed from the gas phase in flowing hydrogen. At this point the sulfur coverage remained unchanged ($\theta s = 0.66$). After this process, a catalytic test performed again without H_2S in the gas mixture gave a similar result to that shown by curve 2 on fig. 1 with a 1% deviation. The TON was indeed progressing from about 2.7 to 5 s^{-1} while the sulfur coverage was decreasing from 0.66 to 0.6. This result indicated that the surface state corresponding to a 20% partial regeneration (TON 5 s^{-1} instead of 27 s^{-1}) can be obtained through two different pathways.

TREATMENT III

Another catalytic test was performed on the initially clean surface with a reaction mixture containing a partial pressure of 0.5 Pa of H_2S (treatment III). As shown on fig. 1 curve 3 the TON varies from 0.42 s^{-1} (initial value) to 2.6 s^{-1} (stationary value). During the catalytic test the sulfur coverage remained constant and equal to 8.2×10^{14} atoms cm^{-2} ($\theta s = 0.66$). This coverage exactly corresponds to that obtained directly after treatment I or after treatment II followed by the treatment in pure hydrogen during 15 h. This result indicates that at this constant coverage, sulfur is slowly converted from a nearly totally poisoning species into a less poisoning one.

During this catalytic test, sulfur containing hydrocarbons were detected in the gas phase. As indicated on fig. 1 curve 3, C_2H_6S appears after 10 minutes (A) then disappears after 60 minutes (B), $C_4H_{10}S$ appears after 75 minutes (C), and at the end of the catalytic test (D) no other sulfur compound than H_2S was detected in the gas phase. According to the gas chromatography analysis, the amounts of C_2H_6S and $C_4H_{10}S$ were about the same.

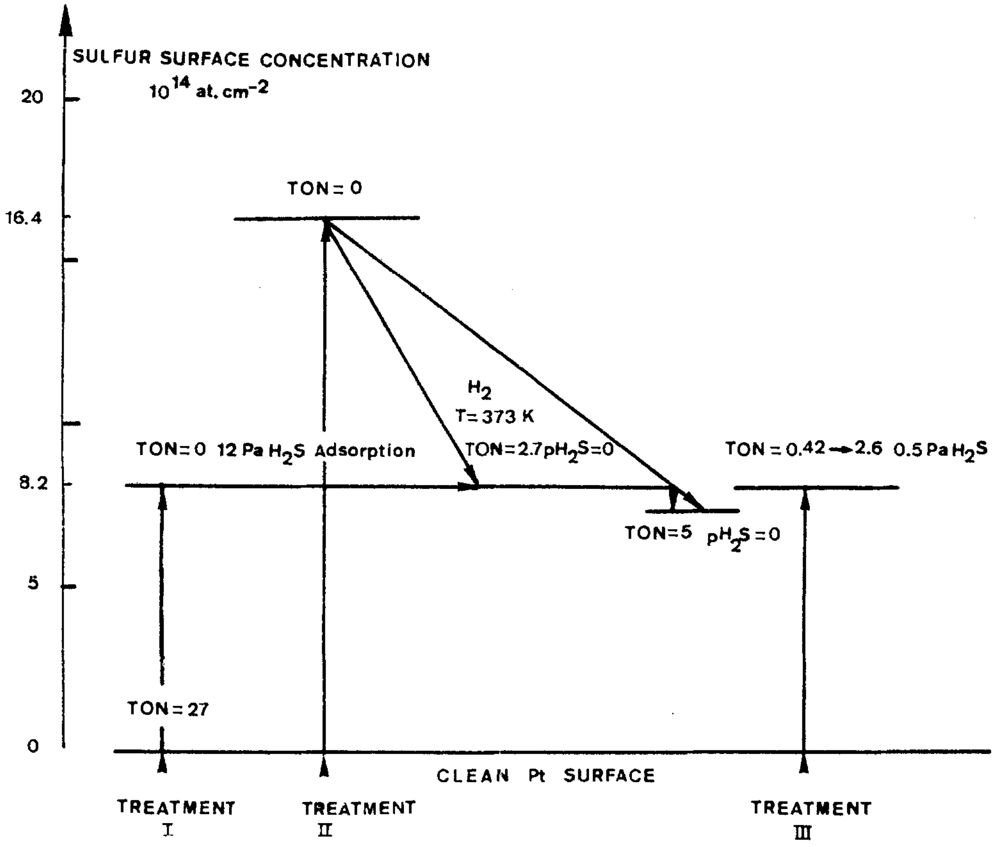

Diagram 1.

Diagram 1 summarizes the various results.

4. Discussion

To explain the experimental features of this study, we transpose to the polycrystalline sample some of the main conclusions derived from poisoning experiments on single crystals. We will consider that two categories of planes are present on the polycrystal, with the two extreme behaviors respectively observed on Pt(100) [2] and Pt(110) [1].

The first category, referring to Pt(100) faces, concerns planes on which sulfur is irreversibly fixed and acts as a permanent poison. This sulfur species will be called S_{irr}. The second category, referring to Pt(110) faces, concerns planes on which sulfur is reversibly fixed (S_{rev}), its concentration depending on the partial pressure of H_2S in the reaction gas.

We summarize below other essential features concerning S_{rev} deduced from observations made on Pt(110):
a - S_{rev} coexists on the surface with adsorbed hydrocarbon molecules (presumably butadiene)
b - S_{rev} can reach a higher coverage than S_{irr}.
c - During butadiene hydrogenation S_{rev} selectively poisons the dissociation sites for hydrogen on the basis of one per one.
We will admit that these features also characterize S_{rev} formed on the polycrystalline sample. Considering these assumptions, we propose the following interpretation of the results obtained after the various gas treatments described above.

TREATMENT I FOLLOWED BY H_2S REGENERATION

After treatment I, sulfur is adsorbed on both kinds of planes as S_{irr} at saturation coverage. As a consequence, the surface is totally poisoned for butadiene hydrogenation. Referring to previous work, S_{irr} can be identified with atomically adsorbed sulfur. [14][15].
On the "(100)" planes of the polycrystal, the catalytic test and the subsequent H_2S admission do not introduce any modification in the nature of adsorbed sulfur, probably because S_{irr} blocks the adsorption sites for butadiene as well as the dissociation sites for hydrogen as it was already observed on Pt(100). On the "(110)" planes of the polycrystal, butadiene is coadsorbed with S_{irr} during the catalytic test performed without H_2S in the gas phase. As a result, S_{irr} is then modified and transformed during the H_2S reactivation treatment into S_{rev} at constant coverage. The final activity recovered during the catalytic test performed again without H_2S in the reaction gas would be characteristic of the "(110)" planes free of sulfur, after total desorption of S_{rev}.
We now remark that the initial activity given by curve 2 on fig. 1 ($N = 2.7\ s^{-1}$) is roughly half the final activity. This result is consistent with the fact that S_{rev} originated from S_{irr} poisons at the same coverage half of the dissociation sites instead of all hydrogen dissociation sites.

TREATMENT II AND REGENERATION BY H_2

Considering the higher sulfur coverage reached after this treatment and the partial desorption of sulfur under pure hydrogen at a temperature as low as 373 K, we will admit that sulfur is adsorbed as S_{rev} during this treatment. This species would be stabilized on the whole surface by the coadsorption of butadiene occurring during the catalytic test performed with H_2S in the reaction gas. The fact that the same coverage ($\theta s = 1.32$) is obtained with 5 Pa and 12 Pa of H_2S indicated that S_{rev} has reached its saturation level. The absence of catalytic activity is easily explained if, at this saturation coverage, all dissociation sites for hydrogen are poisoned. We observe that this total poisoning occurs for a surface coverage twice that obtained with S_{irr}. It had been presumed that on Pt(110), S_{rev} could be the adsorbed radical SH: it would well explain the lower binding energy and the higher coverage as compared to sulfur atomically adsorbed (S_{irr}). Nevertheless, the definitive proof of the formation of SH radicals is still to come.

During the subsequent treatment under pure flowing hydrogen at 373 K, "(100)" and "(110)" planes behave differently.

On the "(100)" planes, half of the S_{rev} species desorb, probably through reaction with H_2 or C_4H_6. The other half would be transformed into S_{irr}, probably because butadiene, in reacting with H_2 or S_{rev}, would not stabilize any more the remaining S_{rev} adsorbed species.

On the "(110)" planes, half of the S_{rev} species desorb after a 15 hours treatment under pure hydrogen, but the remaining S_{rev} is not transformed into S_{irr}.

At this stage we find identical results to those obtained after treatment I followed by H_2S regeneration: same sulfur coverage giving same initial catalytic activity and same final activity after desorption of S_{rev}.

TREATMENT III

During this treatment, we observed an induction time prior to the steady state catalytic regime characterized by $N = 2.7\ s^{-1}$ (see fig. 1 curve 3). This number exactly corresponds to the initial rate measured after reactivation of the catalyst treated according to process I or II. The sulfur coverage calculated for this activity is 0.66. After the arguments stated above the "(110)" planes would be covered with S_{rev} at half saturation: this corresponds to the equilibrium between adsorbed S_{rev} and 0.5 Pa of H_2S in the gas phase.

Let us go back now to the induction time observed during treatment III, before reaching the steady state regime. The sulfur compounds detected in the gas phase during this lapse of time must have been formed on the catalyst before their desorption. We can notice that they appear at every change of slope of the catalytic activity curve 3 on fig. 1. The first sulfided compound to form, probably ethanethiol, can result from H_2S addition on 2-butene, followed by hydrogenolysis. Since this mercaptan is no more detected in the gas phase at point (B) on fig 1, we must consider that it readsorbs on the surface through C-S bond breaking. The resulting adsorbed species can then reticulate and yield diethylsulfide, which appears at point (C) on fig. 1, leaving sulfur adsorbed on the surface. A study on sulfur-butadiene coadsorption in the presence of hydrogen on Pt(111) has already shown evidence for alkylthiol formation, ie methyl- and propylmercaptans [4], with a $\Delta\theta s = 0.1$ sulfur coverage excess. On the polycrystalline sample, the mercaptans are different; this could be due to experimental conditions. On the one hand, high hydrogen pressure favors the isomeric change of the diolefine, which can explain the presence of a 2-butene precursor for ethylmercaptan formation. On the other hand, [4] a 1-butene precursor was responsible for the alkylthiol formation pathway under ultra high vacuum conditions. As far as the

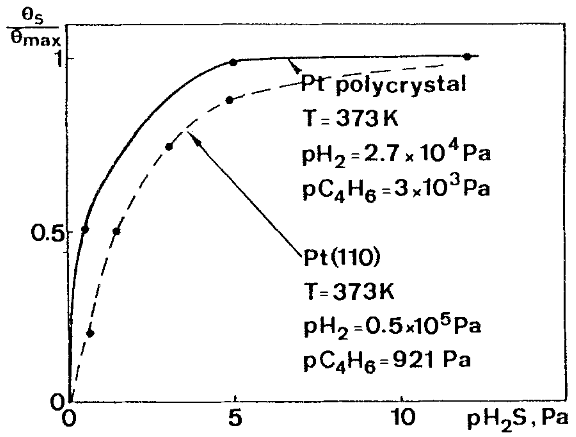

Fig. 3. Sulfur adsorption isotherms on platinum during butadiene hydrogenation [polycrystal and Pt(110)].

polycrystalline sample is concerned, the various orientations that compose the surface can also direct preferential mercaptan formation. If now we consider only the "(110)" planes, the relation between the S_{rev} coverage and the H_2S partial pressure in the reactive gas at 373 K gives the adsorption isotherm of sulfur. This adsorption isotherm is in the same range of H_2S partial pressure as that previously obtained at the same temperature on Pt(110) (fig. 3). The slight displacement to higher H_2S pressure for the Pt(110) isotherm may be partially due to the higher hydrogen pressure in the experiments performed on this plane. In any case, "(110)" means similar to Pt(110) but not identical, if we consider that on a polycrystalline sample $S_{rev}/S_{irr} = 2$, instead of 1.25–1.33, as it was observed on Pt(110) [14].

5. Conclusion

In summary, the understanding of the complex results obtained in this study on polycrystalline platinum has greatly benefited from the previous studies on single crystals. These new data confirm the synergic destabilizing effect of the diolefine on adsorbed sulfur and the structure sensitivity of this effect. These observations may contribute to clarify in some extent, the strange behavior of sulfur in reforming reactions [15]. From a pactical viewpoint, the possibility of partially reactivating a surface totally poisoned by sulfur at a temperature as low as 373 K seems to be very promising. Work is in progress to investigate a larger domain of temperatures and the effect of other unsaturated hydrocarbons.

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