A REACTION BETWEEN CO-ADSORBED SULFUR AND BUTADIENE ON THE Pt(111) SURFACE

EVIDENCE FOR ALKYLTHIOL FORMATION IN PRESENCE OF HYDROGEN

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The desorption of methylthiol and propylthiol has been observed, induced by the co-adsorption of hydrogen, butadiene and sulfur on Pt(111). This phenomenon goes with increase of the total amount of sulfur adsorbed on the surface by a factor of 20%.

Sulfur is one of the most efficient poisons of platinum for hydrogenation reactions. Precise data on the adsorption of sulfur on single crystals of this metal have been obtained by Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Thermal Desorption Spectroscopy (TDS) on single crystals [1,2], and from uptake isotherms on polycrystalline [3] and supported platinum [4]. In a recent comparison of the effects of sulfur on the H_2-D_2 equilibration reaction and on butadiene hydrogenation, sulfur was observed to desorb from platinum at much lower temperature in the presence of the butadiene-hydrogen gas mixture than in presence of pure hydrogen [5,6]. This effect has been interpreted by a displacement of sulfur atoms by butadiene molecules from highly energetic to less energetic adsorption sites.

In this paper we discuss the possible formation of a surface compound between sulfur and butadiene from results obtained by AES and TDS. The experiments were carried out in an ultra high vacuum device: the preparation of the sample by standard procedure has already been described [5]. The amounts of sulfur and carbon on the surface were measured by AES and evaluated using the calibration made by Berthier and Oudar [1] for sulfur and by Biberian and Somorjai [7] for carbon. Temperature programmed desorption was performed at 20 K s^{-1}, and desorption signals were monitored by quadrupole mass spectrometry. In a first series of experiments, butadiene was adsorbed on a surface precovered by various amounts of sulfur ($0 \leqslant \theta_s < 0.4$). Sulfur was adsorbed on the initially clean surface using H_2S and subsequent moderate heating of the surface in order to desorb hydrogen, C_4H_6 was then introduced into the chamber under the following

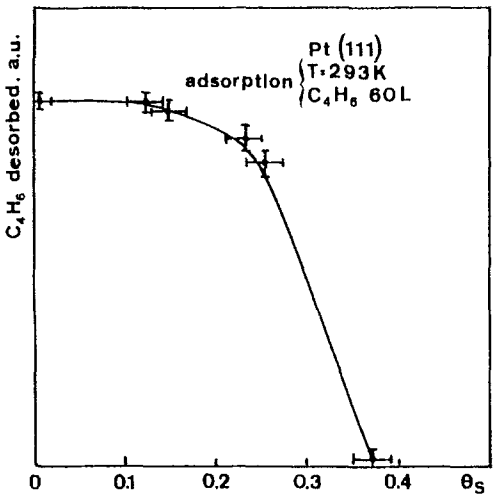


Fig. 1. Desorption of butadiene as a function of sulfur coverage on Pt(111).

conditions: $T = 293$ K, $P_{C_4H_6} = 1.3 \cdot 10^{-5}$ Pa for 10 minutes. These conditions had been previously determined as leading, in the absence of sulfur, to a reproducible saturation state which corresponds to an AES peak-to-peak ratio $I_{C_{272}}/I_{Pt_{237}} = 2$ equivalent to 1 butadiene molecule per two surface platinum atoms. Below $\theta_s = 0.2$, nearly the same carbon saturation state was obtained under these conditions.

The amount of desorbed C_4H_6 was measured by flash desorption as a function of the sulfur coverage. As shown in fig. 1, the amount of desorbed C_4H_6 does not vary linearly with θ_s. It initially remains nearly constant, then, from $\theta_s = 0.2$, it suddenly decreases. For $\theta_s > 0.3$, the butadiene desorption is negligible: the latter result is consistent with the fact that, when θ_s is above 0.3, before thermal desorption no carbon could be detected by AES indicating a totally poisoned surface for butadiene adsorption. During butadiene desorption the sulfur coverage measured by AES remained constant. These first results indicate that, *in the absence of hydrogen, sulfur and butadiene coadsorbed on Pt(111) do not react to form a surface compound.*

In another series of experiments the kinetics of sulfur adsorption from a H_2S-H_2 mixture and from a H_2S-H_2 mixture containing butadiene were studied. Experiments were performed at $T = 373$ K under the following pressure conditions:

a) $P_{H_2} = 1.3 \cdot 10^{-5}$ Pa, $P_{H_2S} = 6.5 \cdot 10^{-6}$ Pa

b) $P_{H_2} = 1.3 \cdot 10^{-5}$ Pa, $P_{H_2S} = 6.5 \cdot 10^{-6}$ Pa, $P_{C_4H_6} = 6.5 \cdot 10^{-6}$ Pa

Figure 2 shows the variations of the Auger ratio $I_{S_{152}}/I_{Pt_{168}}$ as a function of time for both experiments. The two curves (a), (b) are very similar but the amount of adsorbed sulfur is higher when butadiene is present in the gas phase. This feature

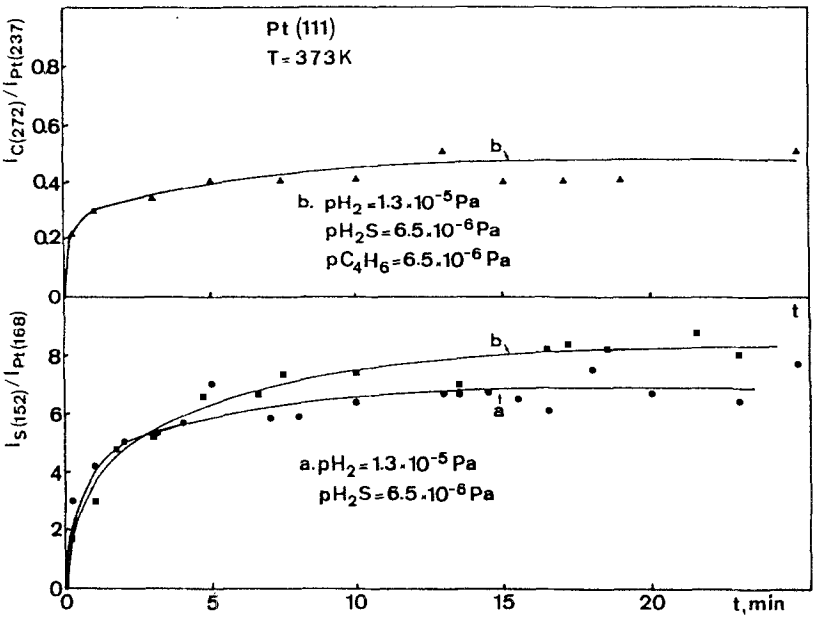


Fig. 2. Auger C/Pt and S/Pt signal ratio on Pt(111) as a function of time in the presence of: - a: H_2-H_2S mixture - b: H_2-H_2S-C_4H_6 mixture.

cannot be due to the screening of the platinum peak due to carbon; the latter is negligible in the submonolayer range. When the plateau is reached the coverage is about $\theta_s = 0.4$ for the H_2S-H_2 gas mixture and $\theta_s = 0.5$ for the H_2-H_2S-C_4H_6 gas mixture. When θ_s was equal or above 0.2, the amount of carbon fixed on the surface from the gas mixture containing butadiene (experiment b) was measured by AES. It increases as a function of time i.e. as a function of the sulfur coverage. At saturation ($\theta_s = 0.5$) the amount of carbon evaluated from the Auger ratio $I_{C_{272}}/I_{Pt_{232}} \sim 0.45$ corresponds to a $\theta_c = 0.55$ coverage i.e. 0.14 C_4H_6 molecules per platinum atom. The simultaneous increase of the carbon coverage and of the excess in sulfur coverage observed in the b experiment strongly suggests the formation of a surface compound between sulfur, butadiene and hydrogen. Note that the excess in sulfur coverage, $\Delta\theta_s$ (saturation) = 0.1, is of the same order of magnitude as the equivalent total number of butadiene molecules present on the surface: 0.14 C_4H_6 molecules per Pt atom. In order to check this asumption, thermal desorption has been performed using the same conditions as previously.

Desorption of S_2, H_2 and of only the two following mercaptans CH_3SH and C_3H_7SH were observed; the maxima of the four desorption peaks are at roughly the same temperature, $T = 900$ K, which corresponds to the desorption peak of sulfur adsorbed on Pt(111) without butadiene. We did not make a precise calibration of the mercaptan desorption peaks but, from the experimental spectra presented in fig. 3 and assuming that the ionization probability is roughly proportional to the number of carbon atoms, we evaluated the number of desorbed CH_3SH and C_3H_7SH molecules to be equal with a possible 20% error.

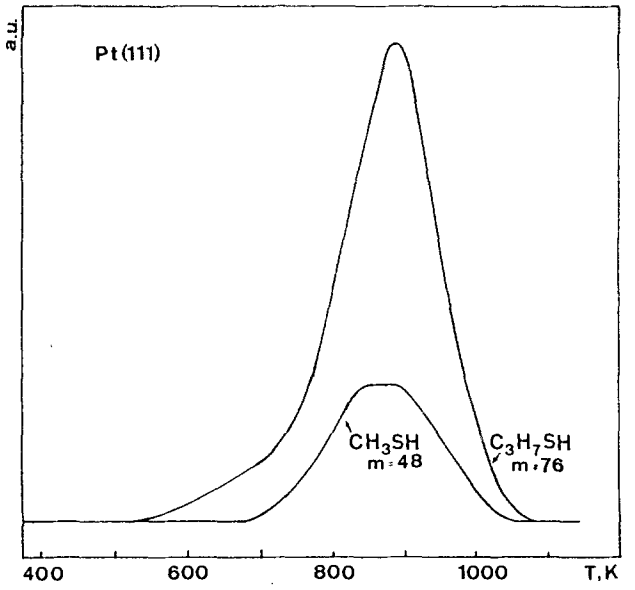
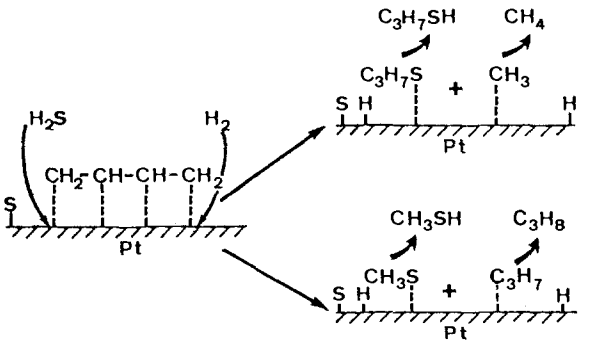


Fig. 3. Desorption of CH_3SH and C_3H_7SH from Pt(111).

After desorption at $T = 900$ K the amount of carbon remaining on the surface was negligible and the sulfur coverage decreased from $\theta_S = 0.5$ to $\theta_S = 0.25$. The identification of *alkylthiols in the desorption spectrum reflects the formation on the surface of hydrogenated compounds containing both sulfur and carbon.*

The formation of these compounds only occurs when the three ingredients H_2S, H_2 and C_4H_6 are present in the gas phase. We propose that the methylthiolate CH_3S and the propylthiolate C_3H_7S are present on the surface before desorption. The fact that the butylthiol does not form, but only alkylthiols with 1 or 3 carbon atoms, indicates that sulfur induces a preferential carbon-carbon bond breaking in the hydrocarbon from which alkylthiols are derived. We propose the following pathway: addition of H_2S on the double bond of the 1 butene with subsequent breaking of this bond and hydrogenation of the intermediate. The reaction mechanism can be schematically represented by:



Scheme 1.

In this scheme, C_4H_6 is supposed to be tetra-σ-adsorbed to the surface as suggested by the work of Avery and Sheppard [8]. A close examination of the desorption spectra revealed that propane, but not butane, desorbs with the alkylthiols in agreement with the proposed mechanism. No special attention has been put forward on the methane desorption. Formation of surface methylthiolate has already been characterized on Pt(111) by means of EELS. It has been shown that this species reacts at 340 K by competitive hydrogenolysis to gaseous methane and dehydrogenation into chemisorbed thioformaldehyde [9]. In our experiments such a decomposition reaction seems inhibited by the presence of adsorbed sulfur. There is much evidence that, on transition metals, sulfur inhibits the decomposition of sulfur-containing species, for example the decomposition of thiophene on molybdenum or rhenium [10,11].

Referring to the mechanism proposed above, the desorption of one sulfur atom involved in an alkylthiol molecule corresponds to the desorption of four carbon atoms. At saturation, we saw that θ_c varies from 0.55 to 0 when θ_s varies from 0.5 to 0.25. We deduce that, from the total amount of sulfur desorbed i.e. 0.25 S atoms per Pt atoms, only 0.14 (number of C_4H_6 desorbed molecules) sulfur atoms are desorbed as alkylthiols; the residual sulfur atoms are desorbed as S_2 molecules, in agreement with the existence of an S_2 desorption peak. The fact that all sulfur containing species desorb at the same temperature as the desorption temperature of sulfur from clean Pt(111) seems to indicate that the desorption of alkylthiols requires, as a preliminary step, the desorption of S_2: this step would provide a pathway for the hydrogenation of thiolate intermediates and for the desorption of hydrogen in excess. Additional work is now in progress in order to try to identify the formation of thiols during the butadiene hydrogenation reaction at high hydrogen pressure.

This study clearly shows the possible formation of surface compounds between sulfur and hydrocarbons. This feature suggests that, in heterogeneous catalytic hydrogenations, complex interactions between sulfur, reactants and metal atoms have to be considered to explain the poisoning phenomena.

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