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Model Experiments on the Poisoning of Pt Catalysts by Sulfur

T. E. FISCHER AND S. R. KELEMEN

Exxon Research and Engineering Company, P. O. Box 45, Linden, New Jersey 07036

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Surface reactions have been studied in high vacuum on the (100) surface of platinum that was clean or covered with various amounts of sulfur. This system was chosen for its simplicity in order to observe the mechanisms by which sulfur poisons catalytic activity. Three different poisoning mechanisms were identified: (i) When the surface is covered with one S atom per two surface Pt atoms, it is chemically inert. (ii) At lower coverages, the strong chemical bond to sulfur modifies the chemical properties of the platinum surface and weakens its interaction with adsorbates. (iii) When the sulfur coverage is one S per four Pt, a regular sulfur overlayer is established; molecules can adsorb on the surface but are prevented by the sulfur structure from participating in Langmuir–Hinshelwood reactions. The reactions on which these observations were made are the dissociation of H_2S, the adsorption and desorption of CO, the reduction of NO by CO, the dissociation and desorption of NO, and the adsorption and dehydrogenation of benzene and acetylene.

It is well known that the catalytic activity of platinum and of most transition metals is drastically reduced when the reagents contain even very small quantities of sulfur. This poisoning of the catalyst is an important industrial problem because it prevents the catalytic conversion of many feeds that cannot be readily desulfurized. On the other hand, the controlled, partial poisoning of catalysts has been found useful in industrial processes and in scientific investigations (*1*, *2*). Thus, a knowledge of the diverse mechanisms by which sulfur prevents or slows down chemical reactions on a platinum surface is desirable. The most detailed information about these poisoning mechanisms can be obtained in a system that is so simple that it represents the repetition of only one configuration of the platinum atoms, on the surface, one position of the sulfur with respect to the platinum atoms and the encounter of single molecules of the reaction under study. This ideal situation is well approximated by the clean, low-index, surface of a single crystal and very low pressures of the reagent gases. The study of catalyst poisoning mechanisms is thus well suited for the methods of surface physics (*3*). Hopefully, such an investigation will allow the quantitative observation of fundamental processes of poisoning already known to, or surmised by, the catalytic chemists on the basis of their measurements on dispersed catalysts under reaction conditions close to those of industrial processes, and perhaps, it will uncover some mechanisms that could not be observed under the much more difficult, realistic, conditions.

Bonzel and Ku (*4*) have investigated the effect of sulfur on the oxidation of CO on the (110) surface of platinum. They found that the rate of CO_2 formation [$r(CO_2)$]

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is affected by the presence of sulfur on the surface in a manner expressed by the relation,

$$r(CO_2) = (1 - K[S_{ad}])^2. \quad (1)$$

In this equation, $[S_{ad}]$ represents the concentration of sulfur atoms on the surface and the value of the parameter K is such that the oxidation rate $r(CO_2)$ is zero when the number of sulfur atoms on the surface is 28% or more of the number of Pt atoms. Bonzel and Ku (*4*) concluded from their observations that "the sulfur poisoning effect on Pt in the low coverage range can be directly related to the rate of dissociative adsorption of oxygen."

The present investigation was conducted on the (100) surface of platinum which presents an attractively simple situation because the sulfur is adsorbed in the two well-defined structures (*5*, *6*) shown in Fig. 1. When the platinum is covered with a half-monolayer[1] of sulfur, the latter is ordered and forms the structure shown in Fig. 1a. We label this structure centered (2 × 2) or c(2 × 2). When the sulfur layer contains one-quarter monolayer, it forms the primitive or p(2 × 2) superlattice of Fig. 1b. These sulfur layers are very stable, desorption from the c(2 × 2) layer does not start below $T = 800°C$, and the p(2×2) layer is stable up to 950°C in an ultrahigh vacuum (*6*). Bonzel and Ku (*4*) have shown that the removal of sulfur by oxidation is a slow process that must be nucleated and proceeds in expanding patches of clean surface. The bonding of sulfur to the platinum is covalent (*7*) and the c(2 × 2) overlayer in Fig. 1a represents the highest concentration that is compatible with the van der Waals radius of sulfur and with a well-defined position of the sulfur atoms with respect to the platinum atoms. While the structure of the sulfur overlayers is known from low-energy electron diffraction (LEED) measurement, the exact position of the sulfur atoms with respect to the platinum substrate has not been determined experimentally (i.e., the sulfur atoms could in principle be sitting atop the Pt atoms or in bridge positions between two neighboring Pt atoms). The fourfold coordination sites shown in Fig. 1 have been

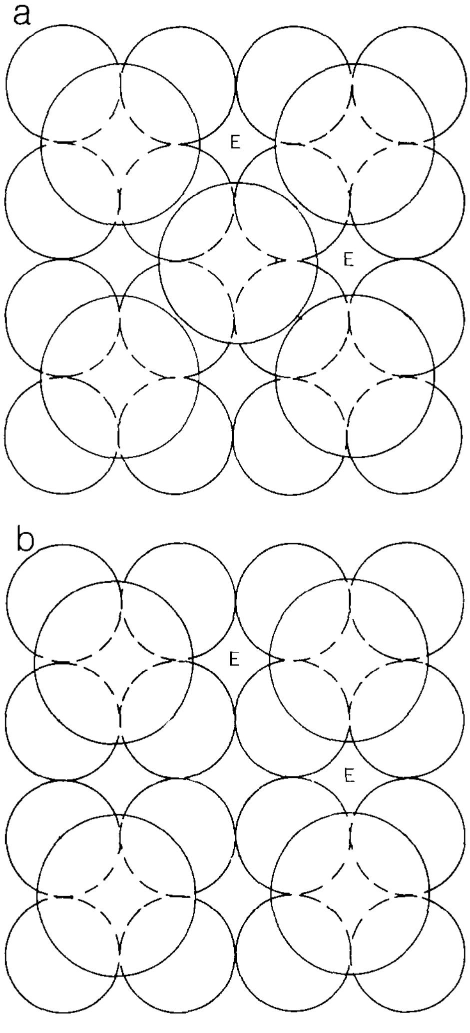

FIG. 1. Structure of the sulfur overlayers on the Pt(100) surface. (a) c(2 × 2) Structure of a sulfur-saturated surface containing 6.5×10^{-14} sulfur atoms cm^{-2} or one S atom for two surface Pt atoms. (b) p(2 × 2) Structure of a sulfur overlayer consisting of 3.25×10^{14} atoms cm^{-2} or one S atom for four surface Pt atoms.

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[1] We define a monolayer ($\theta = 1$) as a layer of adsorbate that contains exactly as many atoms or molecules per unit area as does the platinum substrate, namely, $1.35 \cdot 10^{15}/cm^2$.

chosen to be the most probable because they have been established by LEED for sulfur on nickel (*8*) and are analogous to the relative positions of Pt and S atoms in the compounds PtS and PtS_2.

Our measurements were performed in a stainless steel ultrahigh vacuum chamber equipped with ion and titanium sublimation pumps. The surface was cleaned *in situ* by argon ion bombardment followed by heating in 10^{-7} Torr of oxygen at 800°C. The chemical composition was determined by Auger electron spectroscopy with primary electron currents (10^{-8} A) low enough to avoid a measurable effect of the electrons on surface species of reactions. The surface structures were monitored by LEED and the composition of the gas phase was measured with a quadrupole mass spectrometer. Photoemission (UPS) measurements served to determine the nature of the adsorbed species. All chemical reactions were performed at very low pressure, $P \leq 10^{-6}$ Torr (1.3×10^{-4} N m^{-2}). We studied the effect of the two sulfur layers shown in Fig. 1 on the decomposition of H_2S, the adsorption and desorption of CO, the reaction $2\ CO + 2\ NO \rightarrow CO_2 + N_2$, the adsorption and decomposition of NO, the adsorption and dehydrogenation of benzene, and the adsorption and dehydrogenation of acetylene. We will demonstrate that sulfur can modify a surface chemical reaction in three different ways, depending on the amount of sulfur present and on the reaction.

EXPERIMENTAL

1. Decomposition of H_2S and Sulfur Saturation

When the clean Pt(100) surface is exposed to H_2S gas at a pressure of 10^{-8} Torr ($\sim 1.3 \times 10^{-6}$ N m^{-2}), the gas molecules colliding with the surface decompose with high probability and deposit sulfur (*4–6*). As the sulfur coverage increases, the decomposition rate r varies (*7*) as

$$r = d\theta/d\epsilon = S(\theta_0 - \theta), \qquad (2)$$

where ϵ is the exposure to the gas, θ is the surface coverage, and θ_0 is the maximum coverage obtained.[2] This maximum coverage θ_0 corresponds to the $c(2 \times 2)$ sulfur layer of Fig. 1. Thus adsorbed sulfur poisons the decomposition of H_2S, the rate of which is proportional to the fraction of sulfur-free surface. The deposition of additional sulfur is possible by raising (*5*) the H_2S pressure to 1 Torr; thus the decomposition probability of H_2S on the $c(2 \times 2)$ sulfur overlayer is smaller than 10^{-8}. In addition, this surface will not adsorb, nor allow the surface reaction of any gas we experimented with, namely, O_2, H_2, N_2, NO, CO, NH_3, C_2H_2, C_2H_4, and benzene at any temperature below 400°C.

This observation presents the first mechanism of catalyst poisoning: The Pt surface that is covered with a saturation layer of sulfur is chemically inert.

2. The Adsorption and Desorption of CO

We have not performed a detailed study of CO adsorption and desorption as a function of the amount of sulfur present on the Pt surface as Bonzel and Ku have done on the (110) surface (*4*). Our results are qualitatively similar to theirs: The amount of CO adsorbed and the desorption temperature of CO are decreased by the presence of sulfur.

One particular feature is worth mentioning in view of the results to be described below: In the presence of the $p(2 \times 2)$ layer (Fig. 1b), saturation coverage with CO produces a $c(2 \times 2)$ LEED pattern; the total amount as measured by thermal desorption approaches but never exceeds one-half the amount that is necessary to

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[2] Equation (2) is written in this form to make it independent of the choice of definition for a monolayer. With the definition in Footnote 1, $\theta_0 = 0.5$.

produce a c(2 × 2) pattern when CO alone is adsorbed on a clean Pt(100) surface (*9*). In other words, one CO molecule can be adsorbed in the middle of the sulfur square of Fig. 1b in a position similar to that of the center sulfur atom of Fig. 1a. The theoretical saturation CO coverage in the presence of the p(2 × 2) sulfur layer is 3.25×10^{14} CO/cm^2. Whether this coverage is actually achieved depends on the substrate temperature because the desorption energy of CO from p(2 × 2) sulfur-covered Pt decreases rapidly with increasing CO coverage (*10*).

3. The Adsorption and Dissociation of NO

It has been established that NO is adsorbed on the Pt(100) surface in molecular form (*11*) and a fraction of it dissociates at about 180°C and desorbs as N_2 and O_2 at elevated temperature (*12, 13*). When NO is adsorbed on top of a p(2 × 2) sulfur layer ultraviolet photoemission measurements yield a difference spectrum which is similar to the one obtained from NO on the clean Pt(100) surface (*11*), showing that no measurable amount of the adsorbate is dissociated at room temperature. Figure 2a shows the desorption and dissociation behavior of NO on the clean Pt(100) surface in a temperature-programmed desorption experiment. The abscissa represents the temperature, which increases linearly in time at a rate of 25°K sec^{-1}, and the ordinate shows the partial pressures of NO (mass 30), O_2 (mass 32), and N_2 (mass 28) which result from the desorption of NO and its decomposition products. Figure 2b displays the results of the same experiment when NO is adsorbed on, and desorbed from, a surface previously covered with a p(2 × 2) sulfur layer. No signal due to the evolution of N_2 and O_2 is obtained with the gas analyzer, which shows that the decomposition of NO on the platinum surface is prevented by the presence of sulfur. The shape of the NO desorption spectrum (Fig. 2b) shows that the bonding of the molecules to the surface is weakened by the presence of sulfur in a manner that is similar to the case of CO.

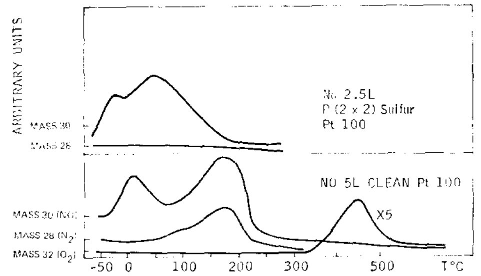

FIG. 2. Mass spectrometric measurement of the evolution of NO, N_2, and O_2 after a Pt surface had been exposed to NO gas and its temperature was raised linearly with time. a, Bottom: Gas evolution from the sulfur free surface. b, Top: Evolution from a surface that had been covered with a p(2 × 2) sulfur layer prior to NO adsorption.

The poisoning of NO dissociation by sulfur can be rationalized by a modification of the electronic and chemical properties of the Pt substrate as in the case of CO adsorption. This modification of the "bare" Pt is easily understood by looking at Fig. 1b: The four Pt atoms onto which the NO can adsorb are also nearest neighbors to, and most probably form a bond with, the sulfur atoms. Since this bond is strong (*7*), it most certainly weakens the bond the Pt atoms can form with NO. This, in turn, diminishes the effect of adsorption on the intramolecular N–O bond. Thus one would expect the sulfur layer to decrease the desorption temperature and increase the dissociation temperature of NO so that the latter is higher than the former and dissociation does not take place.

4. The Reaction of CO and NO

On a platinum surface, CO and NO react to produce mainly CO_2 and N_2 and minor amounts of O_2 and N_2O (*12*). On the clean Pt(100) surface this reaction occurs with peculiar kinetics (*14*) that indicate an autocatalytic reaction, or "surface ex-

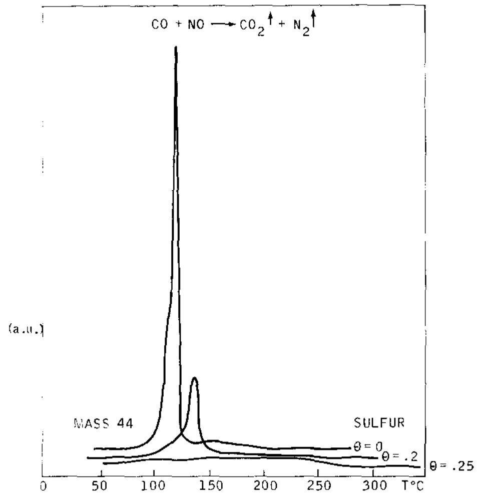

Fig. 3. Mass spectrometric measurement of the evolution of CO_2 during the surface-reaction $CO + NO \rightarrow CO_2 + N_2$ on platinum. Abscissa: Temperature of the surface during heating at a constant rate of 50°K sec^{-1}. Ordinate: Partial pressure of CO_2. θ denotes the ratio of the number of preadsorbed sulfur atoms to the surface density of Pt atoms. $\theta = 0.25$ corresponds to the p(2 × 2) overlayer.

plosion" (*15*). As shown in Fig. 3 for $\theta = 0$ (sulfur-free surface), when equal amounts of CO and NO are adsorbed on a clean Pt(100) surface and the system is heated at the constant rate of 50°K sec^{-1}, one observes the sudden evolution of CO_2 (mass 44). Bonzel and co-workers have observed that N_2 is evolved simultaneously with CO_2 in a pressure peak which is very similar to the one shown in Fig. 3. Evolution of O_2 or N_2O is below the limits of detectability with the Pt(100) surface (*14*).

Figure 3 also shows the effect of a sulfur overlayer on this reaction. The mass spectrometer trace labeled $\theta = 0.25$ shows that formation of CO_2 is completely suppressed by the presence of a p(2 × 2) sulfur layer (Fig. 1b). CO and NO, which have been adsorbed at room temperature, are simply desorbed again, unreacted, when the surface is heated.

The poisoning of the NO–CO reaction can be rationalized again in terms of a weaker interaction of the platinum substrate with the reagent molecules, as we did for the dissociation of NO. A second mechanism for poisoning can be equally valid. At least four reagent molecules must participate in the reaction,

$$2\,CO + 2\,NO \rightarrow CO_2 + N_2. \qquad (3)$$

We have seen that the p(2 × 2) sulfur layer allows the adsorption of one CO or one NO molecule in the center of each sulfur square. Since neither CO nor NO dissociates (*11*), these molecules must be able to come into contact with each other to react. CO or NO cannot be adsorbed on the sites marked E in Fig. 1b, either because there is no space to fit them or because their heat of adsorption on these sites is too small. For the same reasons, a molecule adsorbed inside one square cannot migrate through the site E without being desorbed. Thus the CO and NO molecules are contained in their sulfur cages and cannot migrate toward each other to react.

We have explored how the amount of CO_2 produced in the CO–NO reaction depends on the amount of sulfur on the surface if inhibition of surface migration of reagents by sulfur cages is indeed responsible for poisoning the reaction. We have considered a (100) surface with a p(2 × 2) overlayer of sulfur and CO and NO adsorbed at random in the middle of the sulfur squares. We then removed sulfur atoms at random and replaced them with NO or CO molecules. Every sulfur vacancy then forms and island of five molecules in contact. The probability of having at least two of each reagent in the island is 5/8 so that 5/8 the number of single sulfur vacancies represents the number of CO_2 molecules formed. With $\theta \leq 0.22$, we observed a number of contiguous sulfur vacancies which formed larger domains in which the probability of having approximately equal numbers of CO and NO molecules is quite large. In these large domains we simply took one-fourth the

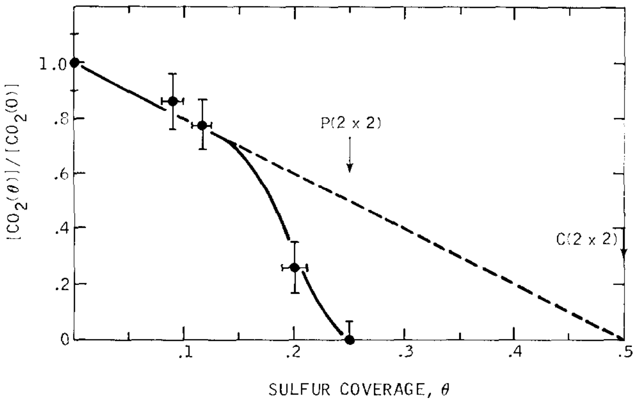

FIG. 4. Poisoning of the reaction $CO + NO \rightarrow CO_2 + N_2$ by preadsorbed sulfur on the Pt(100) surface. The ordinate represents the amount of CO_2 formed. The abscissa is the sulfur coverage θ. The dashed line represents the amount formed if all the molecules adsorbed on the presulfided surface can react. The solid line shows the prediction of the cage model for poisoning. Data points were obtained from curves similar to those in Fig. 3.

number of adsorbed molecules as the amount of CO_2 formed. The result of the Monte Carlo simulation is shown in Fig. 4. The straight dotted line between 1 at $\theta = 0$ and 0 at $\theta = 0.5$ [c(2 × 2) layer] represents the fraction of platinum surface that is not occupied by sulfur and is available for CO and NO adsorption. The full line represents the amount of CO_2 produced (normalized to the CO_2 production on the clean surface). $\theta = 0.25$ corresponds to a fully developed p(2 × 2) layer. For any sulfur coverage $\theta \geq 0.25$, the cage model predicts total poisoning. As sulfur coverage decreases from $\theta = 0.25$, we obtain a rapid increase in the fraction of adsorbates that react; at $\theta < 0.15$ virtually all the CO and NO that can be adsorbed react to form CO_2 and N_2. Also shown in Fig. 4 are the results of experiments in which the amounts of CO_2 were estimated from desorption curves as shown in Fig. 3. The experimental data are certainly compatible with the cage poisoning model.

Figure 4 cannot be considered as proof that this mechanism is alone or even principally responsible for the poisoning. Electronic (i.e., ligand) effects certainly play a role; their presence is evident in Fig. 3 in which the reaction occurs at a higher temperature for $\theta = 0.2$ than on the clean surface. Our quantitative knowledge of the consequences of the electronic poisoning effect on the CO_2 evolution is not sufficient to claim that the latter is incompatible with the experimental data shown in Fig. 4. An unequivocal observation of the cage mechanism of poisoning would require a reaction in which the reagent molecules desorb at temperatures much higher than those required for reaction and product desorption.

5. Adsorption and Dehydrogenation of Benzene

Benzene and acetylene are two interesting adsorbates to compare (*16*). Both are bonded to the platinum via their π orbitals, both are adsorbed strongly enough on the clean surface to dehydrogenate at elevated temperatures rather than to desorb (*16*). Because of their differing sizes, however, the steric aspects of their adsorption are different. Acetylene is a small molecule and forms small domains of c(2 × 2) structure; saturation coverage is 6.5×10^{14}

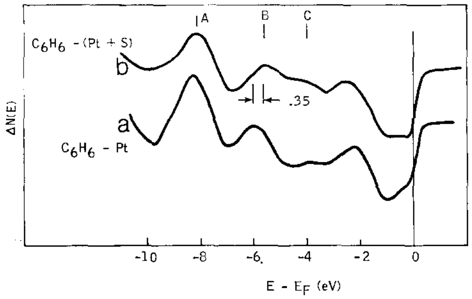

FIG. 5. Photoemission difference spectra at hν = 21.2 eV for (a) benzene adsorbed on clean Pt(100) and for (b) benzene adsorbed on Pt(100) previously covered with $3.25 \cdot 10^{14}$ sulfur atoms cm^{-2} in a p(2 × 2) overlayer. The curves represent the differences in energy distributions of electrons from the benzene-covered and the benzene-free surface. The abscissa represents the energy levels from which the electrons were excited; the origin is at the Fermi level.

molecules cm^{-2} or one molecule per two Pt atoms. Benzene is much larger, its van der Waals area is 35.2 Å, which corresponds to an average radius of 3.36 Å. The π orbitals responsible for its bonding to the platinum overlap with several platinum atoms and, therefore, sample the average properties of the platinum surface. It is logical that the maximum density N of benzene molecules adsorbed on the Pt(100) surface is not related to the density of platinum atoms, but is determined by the van der Waals area A; $N \approx 1/A$, as shown by Auger measurements (*16*). Considering the similarities and differences between these two molecules, we thought it interesting to compare the way their adsorption and dehydrogenation is affected by the presence of sulfur on the surface.

Figure 5 compares the photoemission difference spectrum due to benzene adsorbed on a clean Pt(100) surface [curve a form Ref. (*16*) and on the Pt(100)] surface with a p(2 × 2) layer of sulfur (curve b). These curves represent the changes in the energy distributions of photoelectrons excited by HeI radiation (hν = 21.2 eV) that are caused by the adsorption of benzene. The peaks A and B represent photoemission from molecular orbitals of adsorbed benzene. Similar measurements (not shown) with HeII radiation (hν = 40.8 eV) show the presence of peaks due to benzene orbitals at 8.2, 10.7, and 13.7 eV below the Fermi level for both cases [benzene on clean Pt(100) and on Pt(100) + p(2 × 2)S]. From the similarity of the spectra we conclude that benzene is not dissociated, dehydrogenated, or otherwise transformed upon adsorption on the clean or the sulfided surface. There are differences between the spectra a and b in Fig. 5 that need clarification. Peak B has a lower binding energy by 0.35 eV and peak C is more pronounced on the sulfided (curve a) than on the clean surface (curve b). While it is possible to rationalize the shift of peak B in terms of changes in the molecular orbitals of adsorbed benzene, the following will show that these differences can equally be attributed to the presence of sulfur. We are studying the coadsorption of benzene, acetylene (*17*), and CO (*10*) with S on Pt. In the case of acetylene, for instance, the photoemission measurements clearly show a modification of the electronic spectrum of the platinum–sulfur system by adsorption of the hydrocarbon. Specifically, when C_2H_2 is adsorbed the electronic spectrum of sulfur-covered platinum changes from one characteristic of a p(2 × 2) overlayer to one normally observed with the c(2 × 2) saturation sulfur layer (*7*). Such an electronic transformation would lead to peak at $E - E_f = 4$ eV similar to C and to a depression at $E - E_f = -6.2$ eV that could account for an apparent shift of peak B as observed. Thus, we shall not interpret our photoemission measurements beyond stating that benzene, at room temperature, is not dissociated on the clean or the sulfided Pt surface.

Figure 6 shows how the adsorption and dehydrogenation of benzene on the Pt(100)

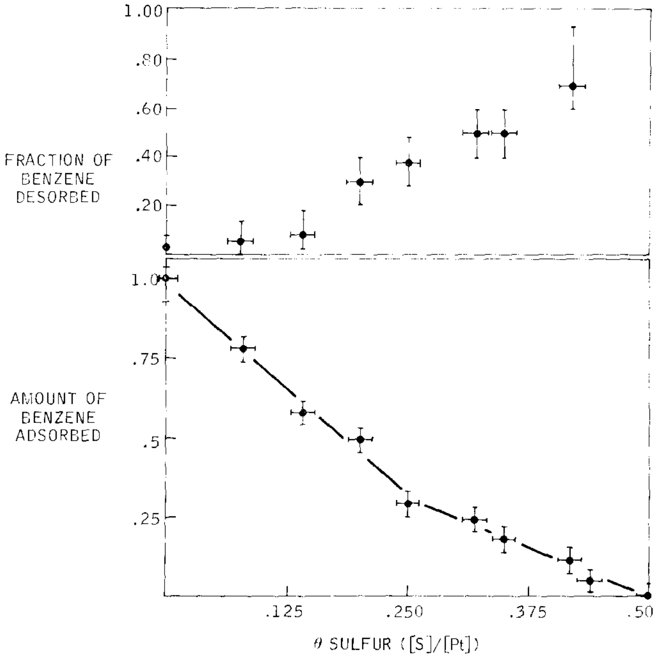

FIG. 6. Adsorption and dehydrogenation of benzene on the Pt(100) surface as a function of preadsorbed sulfur. The abscissa shows the sulfur concentration in number of sulfur atoms per surface platinum atoms. Bottom: Amount of benzene adsorbed; $\theta = 1$ corresponds to 2.8×10^{14} molecules cm^{-2}. Top: Fraction of adsorbed benzene that desorbs upon heating (the remainder is dehydrogenated.)

surface are influenced by various amounts of preadsorbed sulfur. The abscissa in the figure shows the sulfur coverage varying between the clean surface and sulfur saturation with the c(2 × 2) layer at $\theta = 0.5$. The ordinate of the bottom figure shows the amount of benzene that can be adsorbed. This amount was measured with the amplitude of the carbon Auger signal. The amount adsorbed decreases in two linear segments which intersect at $\theta = 0.25$ where the structure is p(2 × 2). It is quite logical that the effect of sulfur should be different for $0 < \theta < 0.25$ than for higher coverages because of the different structures formed in the two domains. Earlier we found (*7*) that the S atoms on the Pt surface are adsorbed at mutual distances of at least 5.54 Å. The sulfur structure is random at low coverages. As coverage is near $\theta = 0.25$, the p(2 × 2) structure forms quite suddenly. Further coverage to $\theta = 0.5$ simply proceeds by occupation of the center sites of the sulfur squares as shown in Fig. 1a. The local configuration of sulfur atoms interfering with benzene adsorption is different in the two coverage ranges, $0 < \theta < 0.25$ and $0.25 < \theta < 0.5$. It is interesting that benzene can be adsorbed despite the presence of the p(2 × 2) overlayer and no new order structure was observed. When one considers that $\theta = 0.25$ corresponds to an area of 31 Å^2/sulfur atom and that the van der Waals area of the benzene molecule is 35.2 Å, it is impossible for benzene to be adsorbed on the surface without coming into contact with a sulfur atom. The density of benzene molecules coadsorbed with the p(2 × 2) sulfur is 30% of the amount adsorbed on the clean surface. This corresponds to 1 benzene molecule per 4 S atoms or 1 benzene per 16 Pt

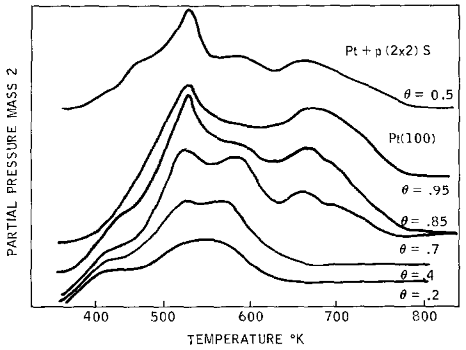

FIG. 7. Dehydrogenation of acetylene on Pt(100). Abscissa: Temperature of the surface during heating at constant rate. Ordinate: Hydrogen partial pressure. The top curve corresponds to maximum C_2H_2 adsorption on a surface with preadsorbed p(2 × 2) sulfur layer. The lower curves show the dehydrogenation of various fractions θ of a monolayer of C_2H_2 on sulfur-free Pt.

atoms on the surface. We do not have enough information to be able to propose a structure of the surface covered with one-fourth monolayer of sulfur and one-sixteenth monolayer of benzene.

The top of Fig. 6 shows that the bonding of benzene is sufficiently modified by the presence of sulfur to allow an increasing fraction of the adsorbed benzene molecules to desorb at elevated temperatures rather than to dehydrogenate. These data were obtained by means of the Auger measurements when benzene was adsorbed on the clean Pt surface; subsequent heating causes the evolution of hydrogen and no decrease in the carbon Auger peak: Benzene dehydrogenates and does not desorb. With preadsorbed sulfur, heating after adsorption of benzene causes a decrease in the carbon Auger peak. The upper part of Fig. 6 shows the fractional decrease of this Auger peak as a function of the amount of preadsorbed sulfur. Since acetylene does not desorb, even in the presence of sulfur (see next section), the simplest explanation of these measurements is in terms of desorption of benzene rather than hydrocarbon fragments thereof.

6. The Adsorption and Dehydrogenation of Acetylene

On clean Pt(100) surface (*16*), adsorption of acetylene follows Langmuir kinetics with an initial sticking probability of 50±5% at the two surface temperatures of 330 and 180°K. Maximum surface coverage is 6.5×10^{14} molecules/cm^2 or one molecule for two surface Pt atoms; low-energy electron diffraction patterns show relatively small domains of c(2 × 2) order.

When the Pt surface with the p(2 × 2) sulfur layer was exposed to acetylene gas, adsorption kinetics still followed the Langmuir equation with an initial sticking probability of 0.5 at room temperature. Maximum surface coverage was 40 to 50% of the coverage for the clean surface. Adsorption of acetylene transforms the p(2 × 2) LEED pattern of the sulfur overlayer into a sharp c(2 × 2) pattern, which shows that the acetylene molecules adsorb in the center of the sulfur squares, producing a structure like Fig. 1a and that they scatter electrons in a manner quite similar to that of sulfur atoms.

Auger measurements showed no decrease in the amount of carbon when the surface was heated: In contrast to benzene, acetylene is dehydrogenated, but not desorbed at elevated temperatures, even in the presence of a p(2 × 2) sulfur layer. Figure 7 shows the evolution of hydrogen as the temperature of the acetylene-covered surface is raised linearly with time at the rate of 50°K sec^{-1}. The top trace in Fig. 7 shows the hydrogen evolution from the surface with the p(2 × 2) sulfur layer and saturated with acetylene. The lower curves show the evolution of hydrogen from the sulfur-free Pt surface previously covered with various fractions θ of a monolayer of acetylene. (A full monolayer, $\theta = 1$, corresponds to 6.5×10^{14} molecules cm^{-2}). The amount of acetylene on the p(2 × 2) sulfur-covered surface corresponds to $\theta = 0.45 \pm 0.05$. The shape of this dehydrogenation curve, however, is very similar to that corresponding to $\theta = 0.85$ on the clean surface. The effect of the p(2 × 2) sulfur layer on the adsorption and dehydrogenation of acetylene is small: A sulfur atom influences an adsorbing and dehydrogenating acetylene molecule as another acetylene molecule would. The fact that the dehydrogenation curve on the sulfided curve has the shape of the $\theta = 0.85$ curve for the free surface provides interesting information on the coverage dependence of the dehydrogenation of acetylene on the sulfur-free surface. One could think that complete dehydrogenation at high coverages requires higher temperatures because the surface hydrocarbons interact with each other and possibly polymerize at high temperatures. But we have said that the molecule in one sulfur square cannot interact with those of a neighboring square. The data of Figure 7 suggest the alternate interpretation that dehydrogenation at low coverages on a clean surface is completed at lower temperatures because a larger fraction of free platinum surface is available of interaction with the hydrogen from the acetylene and formation of H_2. Conversely, it is possible that the strength of interaction of platinum with the acetylene decreases with increasing coverage (a fact that has been observed with a large number of gases). In that case, the weakening of the C–H bond at the surface because of bonding to the surface would be decreased and the dehydrogenation temperature would be increased at higher coverages.

CONCLUSIONS

The experimental observations we have described have suggested three different mechanisms by which sulfur poisons the catalytic activity of platinum.

(i) Where the platinum surface is covered with a saturation sulfur layer [which has the c(2 × 2) structure of Fig. 1a on the (100) surface], the catalyst is chemically inert; it does not chemisorb any further molecules.

(ii) When the sulfur coverage is at least half as large as the saturation coverage, the sulfur overlayer will assume the p(2 × 2) structure of Fig. 1b; additional sulfur atoms and gas molecules can be adsorbed in the middle of the sulfur squares. These molecules are inhibited from reacting with each other.

(iii) At all sulfur coverages below saturation, the strong chemical bond formed with the sulfur weakens the interaction of the platinum with other adsorbates. This last effect is utilized in industry when a "cooling" of the catalyst is desired. This interaction of sulfur with other adsorbates can be direct, but more likely occurs through a modification of the electronic properties of platinum in the vicinity of the sulfur atom. Such modifications have repeatedly been described qualitatively in the catalytic literature (*18*) and have also been treated from a solid-state physics viewpoint by Einstein and Schrieffer (*19*).

An important feature of sulfur as a catalyst poison is the fact that it is strongly bonded to the Pt surface (*7*) and forms a stable, nondesorbing, adsorbate at temperatures considerably higher (*6*) than most catalyzed chemical processes.

As we have already stated in the Introduction, one does not expect all the conclusions of such an investigation to be novel; in fact one hopes that some of the findings agree with the knowledge that was previously acquired by others with the dispersed catalysts under higher pressures. This is the case at least with our conclusions i and iii. The possible usefulness of the present investigation lies in the fact that we were able to observe directly and quantify the poisoning mechanisms under particularly simple conditions. Strictly speaking, the mechanisms observed and the conclusions drawn apply only to the flat

(100) single crystal surface subjected to very low pressures. It is quite possible that other poisoning mechanisms exist in industrial catalysis.

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