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# Reduction of Silver Sulfide by Hydrogen Spillover

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The catalytic activity of platinum in the reduction of silver sulfide by hydrogen was investigated at 100, 160 and 200°C. Silver sulfide was used in the form of evaporated thin films, which were in contact with an evaporated platinum layer, either directly or indirectly through a common support. The results show that adsorbed hydrogen atoms formed on platinum are able to spill over onto a support surface and diffuse over distances of more than 1000 Å. There they may react chemically with a suitable substrate as shown by the increased reduction rate of silver sulfide as compared to that of molecular hydrogen from the gas phase.

## INTRODUCTION

Hydrogen atoms formed by dissociative adsorption of molecular hydrogen on the surface of a metal such as platinum may diffuse from that surface to a substrate on which the direct dissociative adsorption of hydrogen does not occur (*1*). This diffusion of hydrogen atoms may lead to an increased adsorption of hydrogen on carbon supported platinum (*2*) as well as to a higher rate of reduction of $WO_3$ in a tungsten oxide–platinum mixture (*3, 4*). It has also been proposed that various catalytic reactions on supported noble metal catalysts are influenced by the migration of atomic hydrogen.

In a previous study (*5*) we have investigated the reduction of $Ag_2S$ by hydrogen catalyzed by platinum and compared the results with those obtained in the noncatalyzed reduction. It has been concluded that the enhancement of the reaction rate is due to the surface diffusion of hydrogen atoms from the Pt catalyst to the $Ag_2S$ (spillover effect), where they react to form Ag and $H_2S$. If no direct contact is provided between $Ag_2S$ and Pt it should be possible to investigate the migration of hydrogen atoms on different carrier surfaces, on which dissociative adsorption does not occur. Under experimental conditions where the noncatalyzed reaction does not take place, the reduction of $Ag_2S$ would then serve as an indication of hydrogen atom migration. In this paper results concerning the reduction of evaporated layers of $Ag_2S$ by spillover of hydrogen from platinum will be reported.

## EXPERIMENTAL

In all the experiments a thin film of carbon (mean thickness 50 Å) was used as a carrier. The films were prepared by evaporating carbon in high vacuum ($5 \times 10^{-6}$ Torr) onto NaCl cleavage planes. Carbon films of 50 Å medium thickness evaporated at room temperature are continuous and exhibit a small degree of surface roughness (6). Without exposing the substrate to air, $Ag_2S$ was evaporated from a molybdenum crucible onto the carrier, yielding films approximately 90 Å thick. These films contain an excess amount of silver which forms whiskers on the surface. If a thin film of platinum (15 Å medium thickness) is now evaporated at an oblique angle of incidence (60° to the surface normal) these whiskers will cast shadows on the surface, so that certain parts of the surface will not be covered by the Pt film. This is shown schematically in Fig. 1a,b. The mean thickness of the evaporated films was determined by a quartz crystal microbalance. Unlike carbon and silver sulfide platinum cannot

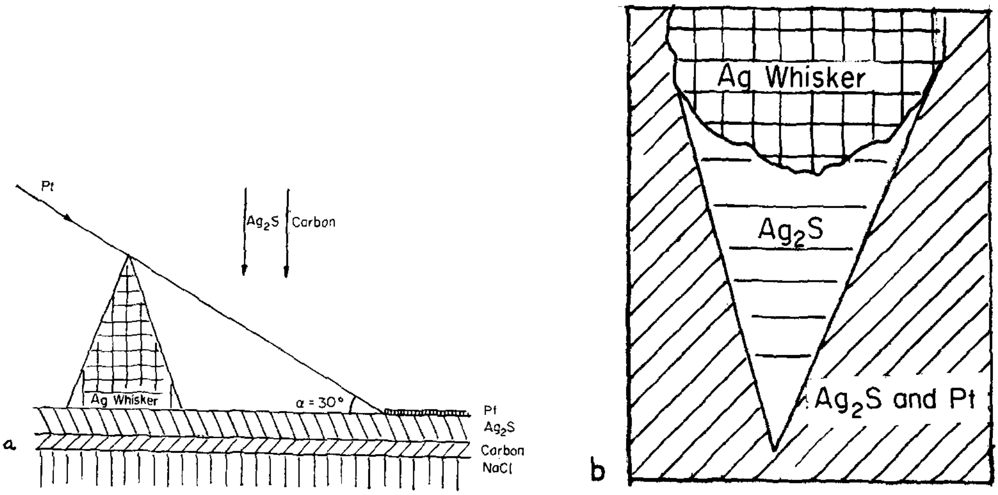


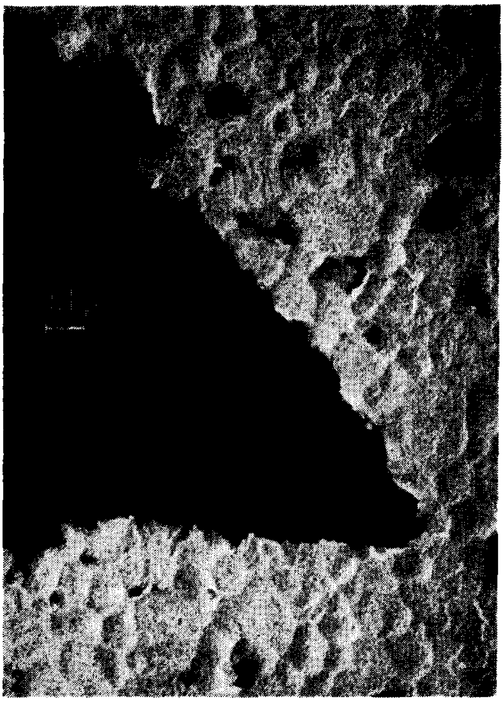
FIG. 1. a. Schematic cross section through the sample → directions of incidence. b. Schematic view of an unreduced sample (corresponding to a magnification of about 60,000).

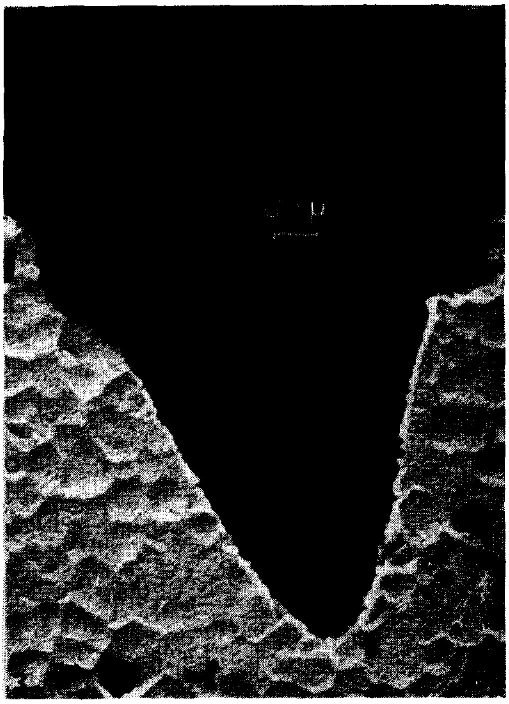
be evaporated easily by resistance heating and hence an electron bombardment method (*7*) was used. The samples were then transferred to a flow apparatus where the reduction was carried out. Hydrogen and nitrogen were both purified by passage over copper catalysts and through nitrogen traps. Different samples were reduced at different temperatures (100, 160, 200°C) and for varying periods of time, but all at the same pressure of 1 atm $H_2$. Eventually the sodium chloride was dissolved in water and the resulting films were transferred to the electron microscope.

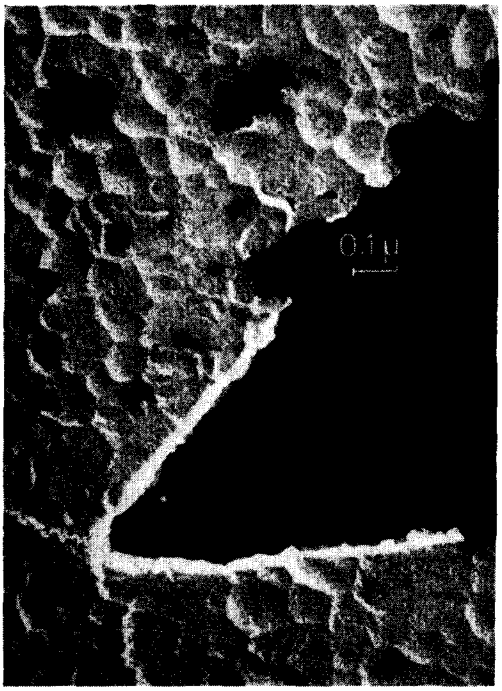
## RESULTS AND DISCUSSION

The parts of the $Ag_2S$ covered by Pt are reduced very rapidly as compared to the uncovered regions. At 200°C and 1 atm $H_2$ the reduction of the Pt covered $Ag_2S$ layer is completed after a period of 2 min. At 100°C about 20 min are needed. After the same period of time the platinum-free layer as shown in Fig. 2 is still unaffected (*5*). [The noncatalyzed reduction would be completed within 10 hr at 200°C and within 2000 hr at 100°C (*5*).] With increasing reduction time a gap forms between the boundary of the Pt film and that of the remaining $Ag_2S$ layer. This gap is found to increase with increasing reduction time (Figs. 2–4). It can be shown by tantalum/tungsten shadowing (*8*) that the Pt film originally present on the top of the $Ag_2S$ layer is now adhering to the substrate surface. As seen in Figs. 3–5 the boundary of the $Ag_2S$ layer at which the reaction takes place remains relatively sharp. Hence, the increase of the gap with reduction time is a measure of the rate of reduction. Within the accuracy of our measurements the width of this gap was found to be proportional to the square root of the reduction time. The reaction must proceed through the sequence of the following elementary steps (*5*): Adsorption of hydrogen on platinum; migration over the platinum surface to the Pt/carrier boundary; transfer from platinum to the carrier; diffusion over the carrier surface including side reactions such as recombination and reaction with the carrier; transfer to the silver sulfide; diffusion on and reaction with $Ag_2S$. Of these elementary steps the only one whose rate can be considered dependent upon the gap width (distance Pt/$Ag_2S$) is the mass transport. Thus it can be assumed that the rate is determined by mass transport. Based on these results, we would propose in agreement with others (*1–4, 9*) that the diffusing reactive intermediates are H atoms which are formed on the platinum by dissociative adsorption.

In other experiments the Pt layer was replaced by a film of Pd or Au. On Pd, like on Pt, H is adsorbed dissociatively and







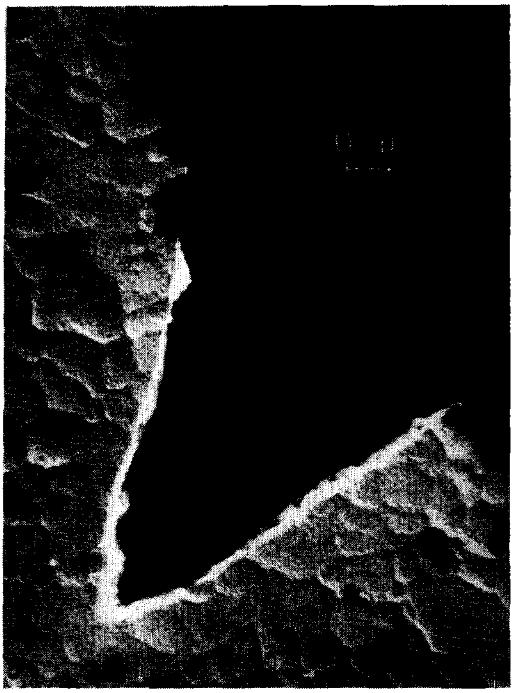


FIG. 2. Sample reduced 30 min at 100°C in 1 atm $H_2$ Magnification 60,000.
FIG. 3. Sample reduced 4 hr at 100°C in 1 atm $H_2$ Magnification 60,000.
FIG. 4. Sample reduced 14 hr at 100°C in 1 atm $H_2$ Magnification 60,000.
FIG. 5. Sample reduced 12 min at 160°C in 1 atm $H_2$ Magnification 60,000.

hence similar results were obtained. Au films, however, did not show any measurable catalytic activity, which is to be expected in view of the fact that molecular hydrogen is not adsorbed dissociatively in significant amounts on gold at temperatures below 200°C (*10*).

The specimens shown in Figs. 2–5 were first dried in purified nitrogen at 200°C for 10 min and subsequently reduced with $H_2$. The results obtained were not affected by longer drying times. However, the specimens are certainly not free of water since it is well known that chemisorbed water can not be desorbed completely from NaCl and from the substrate at 200°C.

The electron micrographs of Figs. 3–5 show that the substrate between the boundaries of the Pt and $Ag_2S$ consists of the carbon film only and that neither Ag nor $Ag_2S$ are present between the boundaries. However, they do not tell about the presence of adsorbed impurity layers and perhaps of very small clusters of Ag which can not be resolved in the microscope. The low mass thickness observed after the reduction also raises the question as to what happened to the silver formed during the reaction. It must be concluded that due to its high mobility in $Ag_2S$ (*11*) most of the silver has accumulated in the whiskers.

From the reduction rate a lower limit of the diffusion coefficient of adsorbed hydrogen atoms on the carrier can be determined. In order to calculate the diffusion coefficient the following assumptions must be made:

(1) H atoms do not recombine on, nor react with the carrier;
(2) the influence of surface roughness is neglected;
(3) the difference between the concentrations of adsorbed hydrogen atoms at the Pt boundary and at the $Ag_2S$ boundary, respectively, is constant.

Introducing a steady state approximation we obtained for the diffusion coefficient

$$D = \frac{x^2 d\rho}{tM(c_H{}^0 - c_H)}$$

where

| | |
|---|---|
| $D$ | diffusion coefficient of H atoms |
| $d$ | mean thickness of $Ag_2S$ film |
| $\rho$ | density of $Ag_2S$ |
| $M$ | molecular weight of $Ag_2S$ |
| $x$ | gap width (distance Pt–$Ag_2S$) |
| $t$ | reduction time |
| $c_H$ | concentration of H atoms on the carrier at the $Ag_2S$ boundary |
| $c_H{}^0$ | concentration of hydrogen atoms on the carrier at the platinum boundary. |

An upper limit of $(c_H{}^0 - c_H)$ is given by monolayer coverage at the Pt boundary $(c_H{}^0)$ and by the assumption that $c_H = 0$. For this case the following values of $D$ can be calculated:

| | |
|---|---|
| 200 (°C) | $4 \times 10^{-12}$ (cm$^2$ sec$^{-1}$) |
| 160 | $6 \times 10^{-13}$ |
| 100 | $8 \times 10^{-15}$ |

According to the assumptions stated above those values are to be interpreted as lower limits; their accuracy is ±20%. The temperature dependence of $D$ yields an apparent energy of activation of approximately 21 kcal/mole.

In conclusion, the results presented here show that adsorbed hydrogen atoms formed on platinum are able to spill over onto a support surface and diffuse over distances of more than 1000 Å. There they may react chemically with a suitable substrate as shown by the increased reduction rate of silver sulfide as compared to that of molecular hydrogen from the gas phase.

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