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On the Reduction of Ag_2S Films by Hydrogen Spillover under Ultra High Vacuum Conditions

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The diffusion of reactive hydrogen from Pt to an Ag_2S phase boundary has been studied by following the reduction of a thin Ag_2S film which was either in direct contact with a Pt film or separated from the Pt by carbon or SiO. Electron microscopic observation of the specimens showed that the hydrogen diffuses over distances of the order of 2000 Å with a diffusion coefficient $D = 7 \times 10^{-5} \exp(-15{,}500/RT)$. The reduction of the thin-film specimens evaporated under UHV conditions was carried out either directly in the UHV system right after the evaporation of the thin-film system or after transfer of the specimens into a flow apparatus. From the fact that the results of both reduction experiments were essentially identical it is concluded that the hydrogen spillover in the system investigated is not dependent on the presence of water and that the migrating species are indeed hydrogen atoms.

1. INTRODUCTION

Considerable effort has been devoted recently to investigations of the surface diffusion of a reactive hydrogen species which is formed on a dissociatively adsorbing metal and which then may migrate over a phase where dissociative adsorption does not occur (i.e., supporting material such as SiO_2, Al_2O_3, carbon zeolite, etc.) to a "sink," where the migrating species finally may be used up in a chemical reaction. The term "hydrogen spillover" (*1*) is used to describe this process, and a number of laboratories have presented experimental support for the existence of this phenomenon (*2–4*). A first electron microscopic investigation of this hydrogen spillover effect was carried out in this laboratory by Bechtold and Schwabe (*5, 6*). These authors used a thin-film specimen to obtain an indication of this effect. In contrast to regular supported metal catalysts such thin-film systems in principle offer more defined experimental conditions and in particular the possibility of direct observation of specimen details in the electron microscope. In their experiments Bechtold and Schwabe produced thin Ag_2S films by flash evaporation under high vacuum conditions. Furthermore the Ag_2S films were exposed to air before the evaporation of the Pt catalyst and during the transfer of the specimen into the reduction apparatus. Thus the presence of adsorption layers (i.e., H_2O) in their thin-film system could not be excluded and may have affected the rate of the diffusion of the reactive hydrogen species. The main objective of the work reported here was a more extensive and detailed investigation of the spillover system proposed by Bechtold and Schwabe under carefully controlled ultra high vacuum conditions, including *in situ* reductions, to find out whether the absence or presence of water has any noticeable effect on the rate of the hydrogen spillover in the Ag_2S/Pt system.

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2. EXPERIMENTAL

The experiments were carried out at background pressures of 2×10^{-10} Torr in a stainless steel UHV system (Balzers PST 170 UHV). During the different evaporations a mean pressure of 5×10^{-8} Torr was registered. Figure 1 shows a schematic diagram of the vacuum system. The heatable and rotatable specimen holder is positioned in the center of the vacuum chamber. Onto a freshly cleaved mica sheet MgO crystals were deposited for a reason discussed in Section 3. This mica sheet was used as the specimen support and was clamped onto the specimen holder. After bakeout of the vacuum system, a fresh substrate was deposited from the carbon or SiO evaporator to establish clean and defined surface conditions. The SiO (Balzers No. 261516) was evaporated by resistance heating (see Fig. 1), while the carbon (Carbopur S + E) was deposited from an electron beam evaporator (*7*, *8*), which then replaced the SiO source. The thickness of the respective films was determined by a quartz crystal oscillator (Balzers QSG 201) and was between 40 and 50 Å. Immediately thereafter, the Ag_2S layer was deposited from two separate sources as described earlier (*9*). Ag (Ögussa 99.99%) was again evaporated from a resistance-heated source with a quartz crystal microbalance controlling the evaporation rate. The sulfur was produced from an electrochemical cell $Pt/Ag_2S/AgI/Ag$ (*10*, *11*). The total amount of sulfur produced can be calculated by Faraday's law from the cell current, and the part reacting with Ag on the specimen surface was determined in a separate calibration experiment. This method allows the evaporation of Ag_2S films with a well-defined silver:sulfur ratio. The Ag_2S layers were deposited at a rate of 0.5 to 1 Å/sec. After completion of the Ag_2S evaporation, the Pt catalyst was deposited at an angle of 30° with respect to the specimen plane from the electron beam evaporator shown in Fig. 1. A third quartz crystal oscillator monitored the thickness of the Pt film, which was deposited at a rate of 1–2 Å/sec with thicknesses between 5 and 70 Å.

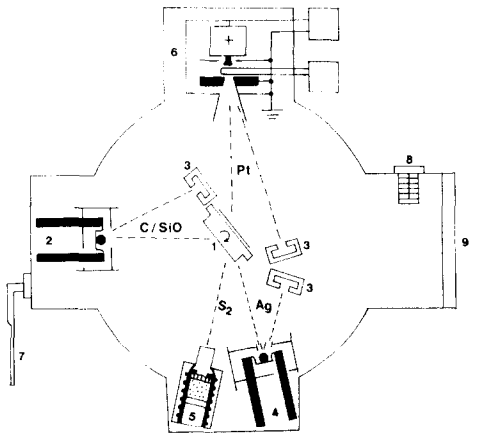

FIG. 1. Ultra high vacuum apparatus: (1) heatable specimen holder; (2) carbon or SiO evaporator; (3) quartz crystal oscillators; (4) Ag evaporator; (5) electrochemical cell, $Pt/Ag_2S/AgI/Ag$ as sulfur source; (6) electron beam evaporator for Pt; (7) Pd permeation cell; (8) Bayard–Alpert ionization gauge; (9) window.

The specimens were reduced at temperatures between 100 and 200°C. The reduction was carried out in a steady flow of hydrogen either directly in the vacuum system or in a flow apparatus. In the ultra high vacuum system the high H_2 pressure (>400 Torr) necessary to complete the reduction within a reasonable time was established by diffusing H_2 through a heated Pd tube and throttling the main valve to the pumping unit. During the reduction the temperature of the specimen was kept at the desired value by heating the specimen holder. The reduction experiments in the flow apparatus were performed at an H_2 pressure of 1 atm. The gases used in this system, namely, N_2 and H_2, were both purified by passage over copper catalysts and through liquid nitrogen traps.

For the electron microscopic observation, the reduced specimens were stripped

from the mica substrate onto distilled water and mounted on 400-mesh copper grids. Electron micrographs were taken at a magnification of 8000 to 100,000× with a Siemens Elmiscope IA microscope with a 100-μm objective aperture and 80-kV accelerating voltage.

3. RESULTS

Figure 2 shows a schematic diagram of the specimen evaporated onto a thin mica support sheet (not shown here) at characteristic stages of the reduction. Figure 2a shows a cross section of the specimen after completion of the evaporation. A carbon or SiO layer was evaporated just prior to the formation of the 300-Å-thick Ag_2S layer to eliminate the possible influence of various impurities in the mica sheet. Both the carbon or SiO as well as the Ag_2S film were evaporated at right angles to the specimen surface. As described earlier, MgO crystals were deposited on the mica surface before the pumpdown. Since the Pt layer on top of the Ag_2S film was evaporated at an angle to the specimen plane, a Pt-free area on one side of the MgO crystal is produced. This Pt-free area is indicated in the center of Fig. 2a. The reduction of this specimen starts where the Ag_2S film is covered with Pt. Because of the high mobility of the Ag in Ag_2S (*12*), most of the silver produced during the reduction moves into larger aggregates (up to several thousand angstroms in diameter) distributed over the specimen surface and therefore does not hinder the electron microscopic investigation of such reduced specimens. The H_2S which is formed simultaneously is transported away by the H_2 stream. When the reduction of the Ag_2S underneath the Pt film is completed, the Pt layer is in contact with the carbon or SiO film (Fig. 2c). At this time the platinum-free Ag_2S layer is still unaffected, since the noncatalyzed reduction in the temperature range of 100–200°C is still negligibly slow. This specimen is now used to investigate the hydrogen spillover effect, since the Pt film as "source" and the Ag_2S layer as "sink" for the reactive hydrogen species are not in direct contact with each other anymore, but are separated by some distance by the common support film. The Ag_2S film is now further reduced

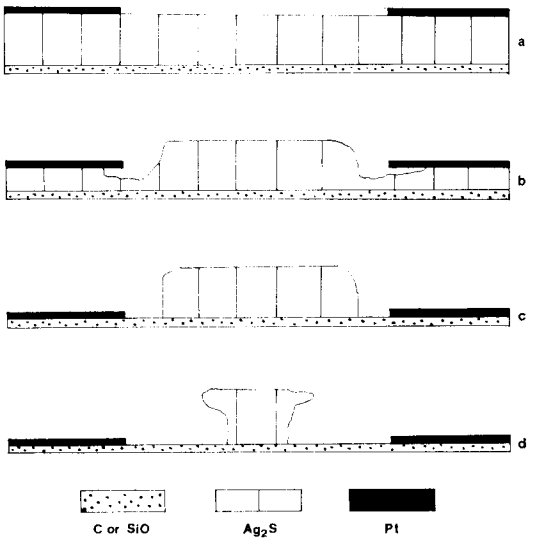

FIG. 2. Schematic cross section through the specimen at characteristic moments of the reduction: (a) unreduced sample; (b) start of the reduction of the sample; (c) start of the spillover measurement; (d) widening of spillover gap after further reduction of the Ag_2S in the Pt shadow area.

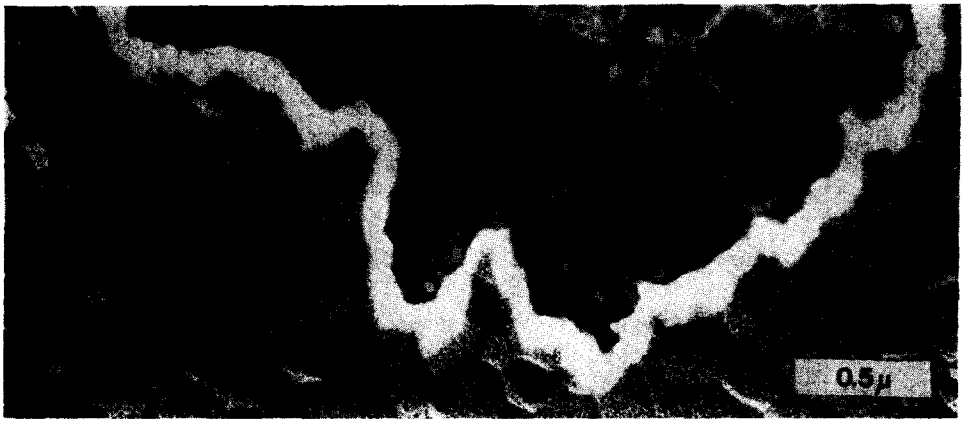

FIG. 3. Electron micrograph of a thin-film specimen reduced for 67 hr at 100°C and 1 atm H_2. Note the excellent parallelism of the Ag_2S and Pt phase boundaries. Magnification, 36,000×.

by hydrogen dissociatively adsorbed on the Pt film and spilled over the carbon or SiO film to the Ag_2S. Hence the gap between the Ag_2S and the Pt film widens (Fig. 2d). The dependence of the width of this gap on reduction time and temperature can be determined from electron micrographs.

For a correlation of hydrogen spillover and widening of the gap, clear-cut Pt shadows and highly stable Ag_2S films are essential. Because of the shadowing geometry used (source size to source specimen distance <1:80), the fringe region of variable Pt thickness at the shadow edge is smaller than 120 Å for a shadow length of 1 μm and is thus within the accuracy of this experiment. For very long distances from the shadow-casting MgO crystal, however, this fringe region can be considerable. In Figure 7 the widening of this fringe is the reason for the gradual increase of the gap width with increasing distance from the MgO crystal. In Fig. 3, however, the Pt phase boundary runs at more or less constant distance from the MgO crystal. That in turn results in a constant gap width. Gap widths were therefore determined for distances between 0.1 and 2 μm from the MgO crystal and corrected for this fringe region. Furthermore, we found that the shape of the Pt phase boundary itself was not affected by the prolonged heating of the specimen necessary to facilitate the reduction. Of similar importance was the stability of the edge of the Ag_2S film in the Pt shadow. The thermal stability of the Ag_2S films produced by evaporation of the components from two separate sources was investigated in separate experiments (*9*) and found to be adequate when film thicknesses above 200 Å were used. The almost ideal parallelism of the Pt and Ag_2S phase boundaries (Fig. 3) further proves that this assumption is justified.

As mentioned earlier, the Ag_2S layer covered by Pt is reduced first. However, our experiments have shown that the permeability of the Pt film for H_2S becomes rate-determining as long as the activity of the Pt catalyst is unaltered. On the other hand, in places where the H_2S can escape through a hole in the Pt film, the reduction can proceed uninhibited (see Fig. 2b). This effect is also indicated in Fig. 4. The reduction is faster at the edge of the Pt shadow and can thus be registered there first (Fig. 4a), since the H_2S can escape into the H_2 stream. Similarly in an area where small shadow-casting particles produced holes in the Pt film, the escape of the H_2S is made easier and the result is a faster reduction of the Ag_2S in the vicinity of the hole (see Fig. 4b). During this phase of the reduction, the Pt film in

fact remains in the suspended position indicated in Fig. 2b. This can be shown on specimens shadowed again after partial reduction. Simultaneously the Ag_2S layer covered with Pt is reduced, and the Pt film is eventually sitting on the carbon substrate (Fig. 2c). Therefore at the start of the actual spillover measurement, a small gap already exists between the edge of the Pt shadow and the Ag_2S. The size of the gap corresponds roughly to the thickness of the Ag_2S film (200–300 Å), but varies with reduction temperature. Up to this stage of the reduction, the geometric conditions for the actual spillover experiment are not clearly defined, since the contact between the Pt catalyst and the carbon or SiO substrate is not yet established. From this moment on, however, the geometry of the specimen is such that the diffusion of hydrogen over the substrate can be measured from the widening of the gap between the Pt and the Ag_2S phase boundary (Fig. 2d), which in turn is determined from the electron micrographs. The uncertainty about the actual start of the reduction by the spilled over hydrogen is the reason for the fact that the curves in Figs. 5 and 6 do not pass through the origin.

While trying to improve the permeability of the Pt film for the H_2S produced during the reduction, by lowering the thickness of the Pt film, we found that the activity of the Pt catalyst was not constant during a sufficiently long time. As has been demonstrated earlier (*13*), the Pt catalyst is deactivated by the Ag produced during the reduction of the Ag_2S. As is evident from Fig. 5a, using 10-Å-thick Pt films, no widening of the gap between the Pt and Ag_2S edge is found, indicating that the Pt film is already deactivated by the time the contact between the Pt film and the substrate is established. This deactivation was considerably delayed when the direct contact between the Ag_2S layer and the Pt catalyst was prevented by a thin SiO or carbon film. Since this intermediate layer has to be permeable for hydrogen and H_2S, the thickness could not be raised to values much higher than 7–10 Å in the case of SiO and less than 7 Å for carbon. These thin films therefore are not thick enough

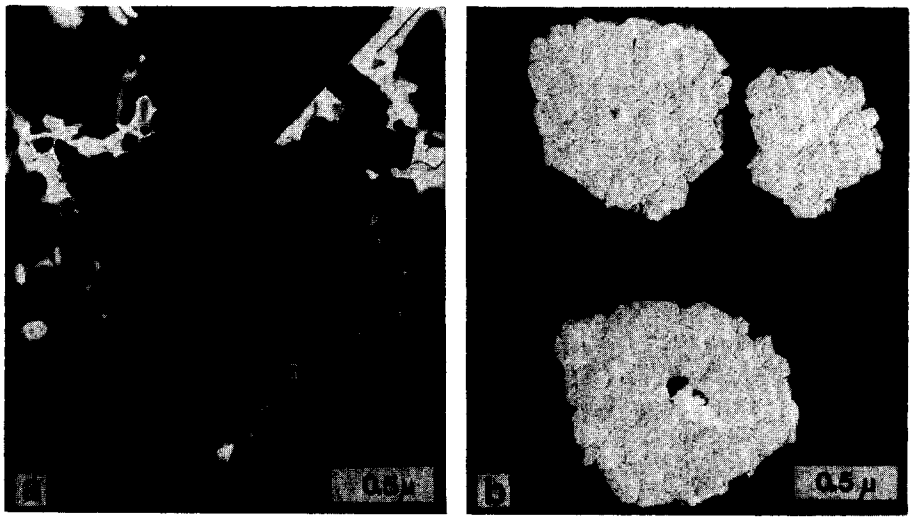

FIG. 4. Electron micrographs of a specimen (a) after a 15-min reduction at 100°C (note that the reduction started at the Pt shadow edge.); (b) after a 2-hr reduction at 100°C. Magnification, 27,000×.

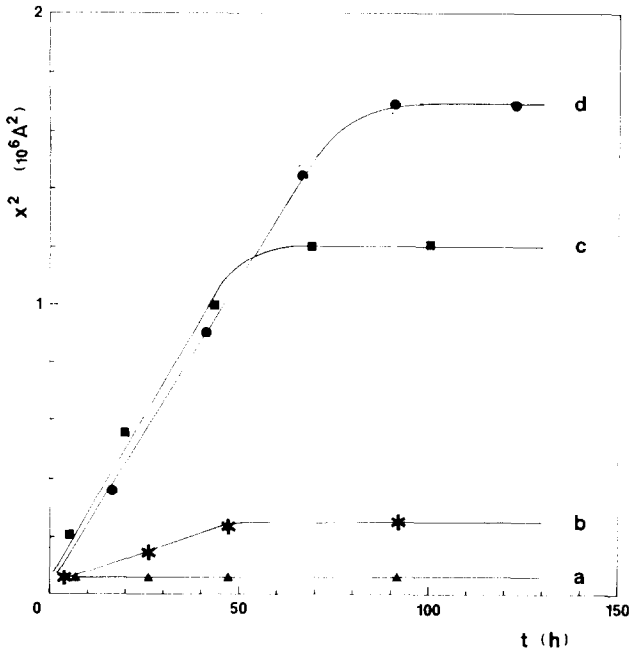

FIG. 5. Dependence of spillover gap width on reduction time and specimen parameters for a reduction of a 300-Å-thick Ag_2S film at 100°C. No SiO film between Ag_2S and Pt in (a), 7-Å SiO film between Ag_2S and Pt in (b), (c), and (d). Pt film thickness in (a) and (b), 10 Å; (c), 40 Å; and (d) 70 Å.

to preserve the activity of this 10-Å Pt film for extended times, although the maximum gap width is increased by a factor of 2 using a 7-Å SiO intermediate layer (Fig. 5b). Only after increasing the mean thickness of the Pt film from 10 to 40 (Fig. 5c)

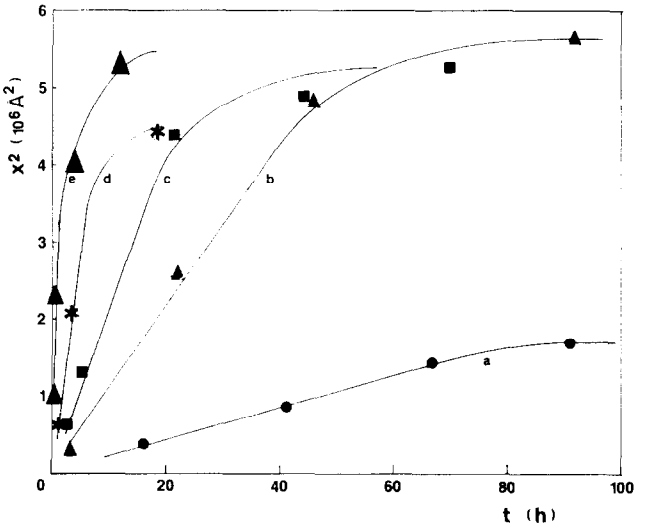

FIG. 6. Dependence of spillover gap width on reduction time and temperature. The thin-film specimen consisted of a 300-Å Ag_2S film, a 7-Å SiO intermediate layer, and a 70-Å Pt film. Reduction temperature in (a), 100°C; (b), 130°C; (c), 150°C; (d), 170°C; and (e) 200°C.

or 70 Å (Fig. 5d) was this deactivation delayed sufficiently in the early stages of the reduction. For both Pt film thicknesses the square of the gap width is now linearly dependent on the reduction time, indicating the diffusion of the reactive hydrogen from the Pt surface over the substrate to the Ag_2S phase boundary as a rate-determining step. For very long reduction times, however, the curves again flatten out. Although

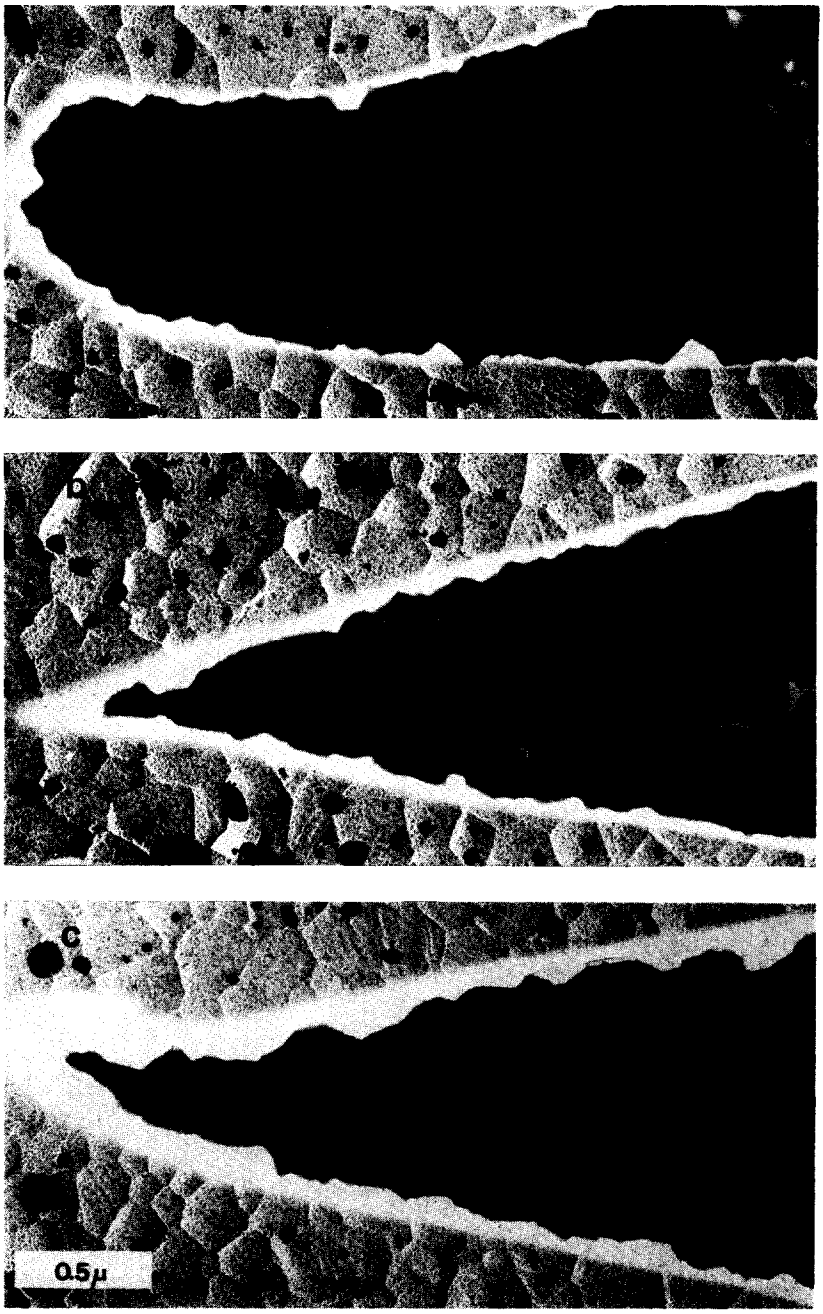

FIG. 7. Electron micrographs representative of curve shown in Fig. 6a: after (a) 2 hr, (b) 6 hr and (c) 70 hr of reduction. Magnification, 36,000×.

this constant width of the gap with further reduction could be caused by effects such as recombination of the reactive hydrogen species, reaction with the substrate, or desorption, we believe that the deactivation is again responsible for this result. To check whether or not this conclusion is justified, a specimen with a 7-Å SiO intermediate layer and 40-Å Pt layer was heated in a separate experiment in a nitrogen atmosphere for 80 hr at 100°C. The reduction of this specimen then showed that the activity of the Pt catalyst was drastically reduced but not completely lost. In the normal reduction experiment the catalyst is inactive after this time (see Fig. 5c). This difference is most likely due to the difference in availability of metallic Ag in the two specimens. While in the heating experiment only the excess Ag built into the Ag_2S film is available for the deactivation, fresh Ag is produced continually during the reduction.

Figure 6 shows the dependence of the square of the gap width on the reduction time and reduction temperature. Characteristic electron micrographs for the reduction experiments at 100°C (Fig. 6a) are shown in Fig. 7. The specimens used consisted of 300-Å Ag_2S and an intermediate layer of 7-Å SiO, and the mean thickness of the Pt film was 70 Å. For the reduction at 100°C, the maximum gap width between the Ag_2S and Pt boundary was found to be about 1300 Å. At 130°C this maximum gap width was roughly 1000 Å wider. A further increase of the reduction temperature only accelerated the rate of widening of the gaps because of the faster diffusion of the reactive hydrogen species over the substrate. An increase in the maximum gap width, however, could not be observed. For temperatures above 130°C this maximum for the gap width was found to be between 2000 and 2300 Å. As already mentioned, we consider the deactivation of the Pt catalyst by the Ag produced during the reduction mainly responsible for this result.

TABLE 1

Hydrogen Diffusion Coefficients

T (°K)	D ($cm^2\ s^{-1}$)
373	5.3×10^{-14}
403	2.7×10^{-13}
423	5.4×10^{-13}
443	1.5×10^{-12}
473	1.5×10^{-11}

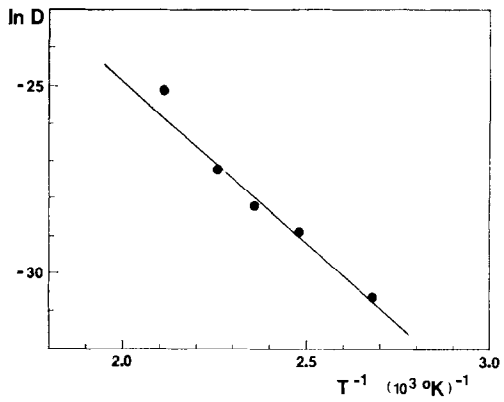

FIG. 8. Arrhenius plot of diffusion coefficient D. The activation energy is 15.5 kcal/mole and the preexponential factor is 7×10^{-5} $cm^2\ sec^{-1}$.

Using the steady-state approximation suggested by Schwabe and Bechtold (*6*), we calculated lower limits for the diffusion coefficients according to the assumptions made in this approximation. In Table 1 results of this calculation are summarized. From the temperature dependence of the diffusion coefficient in Fig. 8 an apparent activation energy for the diffusion of the reactive hydrogen species over the substrate was calculated to be 15.5 kcal/mole with a preexponential factor of 7×10^{-5} $cm^2\ sec^{-1}$. At the reduction temperature of 200°C the values of the square of the gap width are not linearly dependent on the reduction time over a sufficiently long period. This is due to the fact that the well-defined geometrical arrangement of Fig. 3c was not obtained within the time the catalyst remained active. An approxi-

mate evaluation yielded the value in Table 1 for the diffusion coefficient, which differs from the value extrapolated on the basis of the four values obtained at lower temperatures via the Arrhenius equation by a factor of 2. However, the assumption made in the calculation of the diffusion coefficient, that the difference between the concentrations of adsorbed hydrogen atoms at the Pt phase boundary and at the Ag_2S boundary is temperature-independent, may not be completely justified. We therefore eliminated the value for the diffusion coefficient at 200°C in the calculation of the activation energy.

4. DISCUSSION

With the experimental setup described, a thin-film specimen can be prepared under well-defined UHV conditions allowing the qualitative and quantitative investigation of the diffusion of a reactive hydrogen species from the dissociatively adsorbing Pt film over the carbon or SiO film to a Ag_2S layer which is then reduced. The suitability of this thin-film specimen was first discussed by Bechtold and Schwabe (*5*, *6*). As mentioned earlier, these authors prepared their thin Ag_2S film specimens under high vacuum conditions by flash evaporation, and for experimental reasons the Ag_2S film was exposed to air before the Pt film could be evaporated. Therefore the experimental conditions were not as well-defined as would be desired, and thus the presence of adsorption layers that could act as co-catalysts could not be ruled out.

The results reported here are in qualitative agreement with the results of Bechtold and Schwabe; however, due to the fact that these authors investigated the reduction of their specimens to gap widths up to only 1000 Å, the deactivation of the Pt catalyst by the Ag produced during the reduction was overlooked. The fact that their much thinner platinum films (<15 Å) stayed active during the reduction time used is another striking difference in comparison with our experimental results. These differences could be due to (i) the different evaporation method used to prepare the Ag_2S film, and (ii) the formation of an adsorption layer on the Ag_2S film while the Ag_2S films were in air prior to the Pt film evaporation. To verify this latter assumption, we exposed to air an Ag_2S film, prepared by the method described in this paper, for 24 hr and found the deactivation of the Pt catalyst to be delayed considerably (*13*), but still about twice as fast as in the case of a 7-Å SiO intermediate layer. Thus a gradual increase of the deactivation of the catalyst, the fact that Schwabe and Bechtold determined diffusion coefficients only for three different temperatures, and finally the fact that they included the value obtained for 200°C in the calculation of the activation energy (see results) could account for the deviations of their values from the values reported in this paper.

The principal goal of this paper, however, was to investigate whether or not the presence of water has any noticeable effect on the rate of the hydrogen spillover in the thin-film system investigated here, as was found for the WO_3/Pt system (*1*, *3*, *14*). For this purpose, the spillover experiments were carried out under clean UHV, i.e., water-free conditions. For comparison, identical experiments were performed in a high vacuum system, where adsorption layers of H_2O and possibly hydrocarbons could have been present and acted as co-catalysts for the hydrogen spillover. In some cases the thin-film specimens were reduced directly in the vacuum system immediately after the specimen formation, and the results were compared with those obtained from reduction experiments performed in a flow apparatus where the specimens had to be exposed to air prior to the reduction.

On the basis of our results, we could not find differences concerning rate and extent

of the hydrogen spillover regardless of whether the experiments were performed under UHV or HV conditions or whether the specimens were reduced in the flow apparatus. Furthermore, in a control experiment a specimen was reduced in the flow apparatus at a water vapor pressure of about 10 Torr and again no drastic effect on the spillover was detected. We therefore conclude that in the thin-film specimen used, the hydrogen spillover is not influenced by the presence of H_2O vapor.

However, it is also possible that H_2S formed during the reduction could act as co-catalyst in a manner similar to that proposed for water, enabling proton diffusion to occur via hydrogen bonds as discussed by Levy and Boudart (*14*). However, for this to occur a monolayer of H_2S has to be formed on the carbon or SiO film. In view of the work of DeRosset (*17*) this is very unlikely at the H_2S partial pressures which may possibly be reached during the reduction ($<10^{-6}$ Torr). If at all, adsorption will occur with the formation of SH groups (*15*, *16*), which again could not allow hydrogen migration as a proton as proposed in the model by Levy and Boudart (*14*). Furthermore, in contrast to other co-catalysts such as water, H_2S is a very weak base. An H_3S^+ ion is known only in very strong acids. Therefore the H_2S is not likely to perform the decisive step in the model of Levy and Boudart, namely, the exothermic breaking of the bond between the Pt catalyst and the chemisorbed hydrogen with the simultaneous formation of an H_3S^+ ion and loss of the electron to the conduction band of the metal.

In agreement with Bechtold and Schwabe we could not find a surface specificity of the hydrogen spillover. The rate and the extent of spillover were similar on carbon and SiO substrates. This result could be due to the fact that the influence of the surface properties of the two substrates is so small that it was within experimental error and was therefore not detected. On the other hand, differences in surface properties could have been compensated by adsorption of H_2S and formation of SH groups or by Ag left over from the reduction. Although the specimens were viewed under high magnification in the electron microscope, no indications of leftover Ag could be detected; nevertheless the possibility of atomically dispersed Ag cannot be definitely ruled out at the moment.

In summary then, for all the reasons discussed above, it is highly unlikely that in the system described in this paper the reactive hydrogen species migrates as a proton via a co-catalyst. We believe that the chemisorbed hydrogen diffuses directly from the Pt film to the substrate, as has been postulated already for carbon-supported Pt catalysts (*18–20*) and for the system Pt/Al_2O_3 (*21*). The diffusion coefficient and the preexponential factor calculated from these experiments are physically reasonable and in fair agreement with values reported previously. Thus this study demonstrates that the combined use of UHV thin-film techniques and electron microscopy is a powerful technique which may prove to be applicable to a number of systems in heterogeneous catalysis.

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