JOURNAL OF CATALYSIS **106**, 378–385 (1987)

The Spillover of Hydrogen onto Silica

IV. The Use of Scanning FTIR to Follow Spillover from a Point Source

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Received November 17, 1986; revised February 16, 1987

The interphase transport of adsorbed species is referred to as spillover. A technique was developed to quantify the rate of surface diffusion across silica after spillover from platinum. The source of spillover is isolated on the accepting silica surface and the concentration of spiltover deuterium is measured as a function of time and distance from the source. The rate of surface diffusion of hydrogen across silica is rapid and is detected 1 cm from the source within a few minutes. Spillover and not surface diffusion seems the controlling rate in the combined spillover and diffusion processes. The transport seems to be facilitated by "associated" hydroxyls on the surface. Only a limited number of sites are involved and the rate of transport decreases as saturation is approached. © 1987 Academic Press, Inc.

INTRODUCTION

The transport of a species adsorbed on one surface (e.g., a metal) onto another (e.g., an oxide or carbon support) has been described as "spillover." Hydrogen spillover is a well-documented phenomenon and has been reported to occur with a variety of combinations of metals and supports. Conner *et al.* (*1*) have recently reviewed the current understanding of the phenomena associated with spillover. To determine the potential significance of spillover, it is necessary to quantify the extent and relative rate of the processes associated with spillover. In this research we studied hydrogen spillover with a novel technique that allows us to follow surface migration across an oxide surface (silica) as a function of time and distance from the metal source of spiltover hydrogen. The motivation was to develop a more direct technique to quantify the surface diffusion of spiltover species and to discern the mechanism of migration.

Most prior calculations of the diffusion coefficient for spiltover hydrogen were done by indirect volumetric adsorption studies (*2–9*). Moreover, the calculations are done assuming that the migration on the surface is the rate-determining step as contrasted with assuming that spillover was rate controlling. When data are constrained in this way the effective diffusion coefficient becomes a "lumped parameter" dependent on the system. As a result the estimated values vary from 10^{-3} to 10^{-14} cm^2/s.

An experiment was designed that takes advantage of the unique property of spillover, i.e., that the source of spillover can be the only pathway for access to a surface. By isolating the source of spillover as a single point (effectively) on a surface it might be possible to more directly measure the rate by which adsorbed species are transported across the accepting surface. A schematic of the experiment is presented in Fig. 1. Deuterium from the gas phase is adsorbed onto the platinum source of spillover present in the center of a pure silica wafer. The D_2 may be dissociatively adsorbed onto the Pt. It may then spill over onto the silica surface in contact with the Pt and subsequently migrate away from the source. Once on the surface, the spiltover deuterium exchanges readily with the surface hydroxyl groups present on the silica

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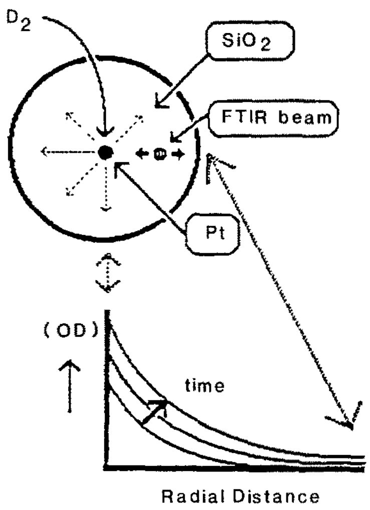

FIG. 1. Schematic of the experiment wherein a small FTIR beam is scanned across a 1-in. wafer of pressed silica containing a <1-mm "spot" of Pt. The [OD] concentration measured in the IR is recorded vs time and position.

to form deuteroxyl groups. The migration of spiltover deuterium can be followed by monitoring the appearance and growth of the IR adsorption band corresponding to surface deuteroxyl groups. The integral of the absorption of the IR band is directly proportional to concentration; thus, concentration profiles can be generated, provided that the collection time is fast when compared with the time scale of the experiment and that the radius of the IR beam is small when compared with the radius of the sample. In this paper the technique is described in detail. A second paper will discuss the implications of the results in the understanding of the mechanism of hydrogen spillover (*10*).

EXPERIMENTAL

A schematic of the experimental apparatus is shown in Fig. 2. The system can be divided into five areas: gas storage, vacuum pumps, gas circulation and purification, infrared cell, and support equipment.

The whole system can be evacuated with the help of a Duo-Seal vacuum pump to 10^{-3} Torr. Lower pressures can be achieved by using two oil diffusion pumps. The pumps were modified to operate in series and obtain pressures in the order of 10^{-7} Torr, when operated with liquid nitrogen traps. Pressure is monitored from 760 to 10^{-12} by using a pressure transducer and an ionization gauge.

The gases in the circulation area can be introduced to the infrared cell through two cold traps. This ensures that the gases are free from water and any condensables such

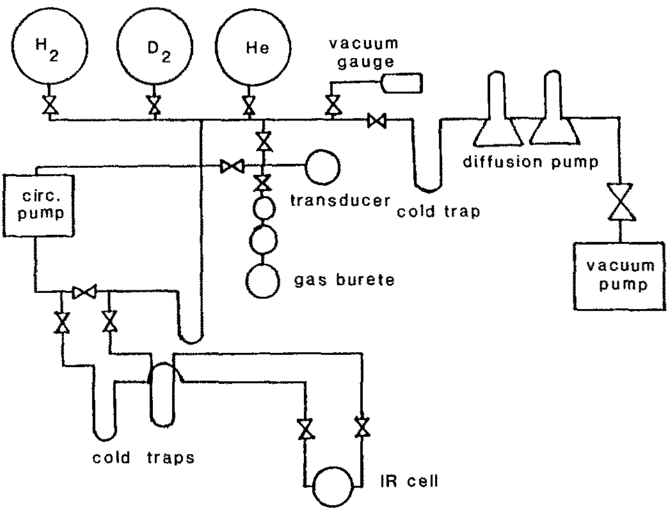

FIG. 2. Schematic of the reaction system used to pretreat and to circulate gases over the sample contained in the IR cell.

as stopcock grease. The last two valves before the IR cell are metal, high vacuum, greaseless valves.

A gas purification system can be attached to the vent valve on the gas manifold. The gases used were ultrahigh purity hydrogen, deuterium, and helium. They are passed through a liquid nitrogen trap to a heatable diffusion thimble which is connected to the manifold. The diffusion tubes were made of palladium for hydrogen and deuterium purification and of quartz for helium.

The infrared cell is the product of several attempts to design a high vacuum, high temperature, *in situ* cell of reduced dead volume and sufficiently small to fit in the IR chamber mounted on a translation stage. It was designed in collaboration with Harrick Scientific Co.

The cell is depicted in Fig. 3. It consists of a stainless steel core with space to accommodate a cylindrical metal sleeve with a sample wafer 2.5 cm in diameter. The core is heated with three cartridge heaters. Temperatures up to 500°C can be achieved on the core when the cell is under vacuum. The outer drum is equipped with two cooling rings and two vacuum ports that connect the cell to the gas handling system via stainless flexible tubing. The calcium fluoride windows have a transmission rating of better than 90%, starting at 1500 cm^{-1}. Two thermocouple wells permit measurement of temperature at the steel core and in the gas phase near the center of the wafer.

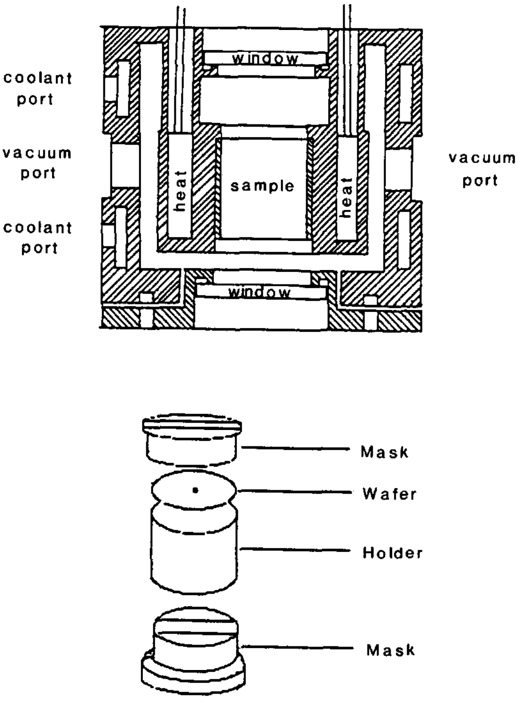

FIG. 3. Diagram of the cross section of the IR cell designed for these studies. Total dimensions of the cylindrical cell are 4.75-in. diameter and 4-in. length. The sample holder and mask are depicted in the lower portion of the figure and are slipped into the center of the cell.

The sample in the form of a wafer is placed in a stainless steel holder. It consists of a sleeve and two thermal masks. The masks provide an even distribution of heat across the sample. They are mounted around 0.5 mm from the sample surface and have a 5-mm-wide slit cut diametrically that permits the IR beam to scan the surface of the wafer.

The samples used were Degussa Aerosils pressed to form wafers 2.5 cm in diameter and less than 1 mm in thickness. In the center of the wafer a small pellet of Pt/alumina catalyst is pressed to provide the "porthole" for spillover. The catalysts were provided by UOP and were made by impregnation of gamma-alumina with chloroplatinic acid. They were prereduced and contained 0.05% Pt and 0.39% Cl.

Pretreatment was done by heating under vacuum. Typically samples were heated at 100°C overnight to remove any physically adsorbed water from the surface of silica. The temperature was then increased as high as 500°C in the core of the cell. The samples were maintained at their highest pretreatment temperature for at least 2 h.

A Nicolet 7199 Fourier transform infrared spectrometer was used to determine the transmission infrared spectra at different positions on the disk. The small infrared beam diameter, ~2 mm using a 1-mm detector element, combined with high spectral resolution and fast data collection permitted us to scan the surface of the wafer as functions of time and position.

RESULTS AND DISCUSSION

The results for a typical experiment are described in detail. The sample was a 164-mg wafer of Aerosil 300 with a 2-mg Pt/alumina catalyst pellet in the middle. It was pretreated under vacuum at 200°C for 6 h, after which the temperature was raised to 414°C for 1 h. Finally, the sample was kept under a helium atmosphere at 285°C for 5 h. The exchange experiment was conducted at 205°C for 100 min. Spectra were collected at 1-, 5-, and 9-mm distances from the platinum source.

Figure 4 depicts absorbance spectra 1 mm away from the source; these were ratioed against the background. The OH band appears at 3755 cm^{-1}, whereas the OD band appears at 2755 cm^{-1}. Examination of the spectra shows that changes as a function of time, both for OH and OD, occur not only on the sharp OD–OH bands, but on the low-frequency shoulder at the right of the sharp bands. The sharp peaks are related to the freely vibrating OH–OD groups, i.e., isolated, whereas the shoulders are related to the associated groups. In Fig. 5 the growth of the OD band is depicted as a function of time and position. The spectra are ratioed against that of silica before the beginning of the experiment. The dependence of surface exchange with radial distance is very clear. It can also be seen that the associated deuteroxyl groups change at a different rate when compared to the free deuteroxyls.

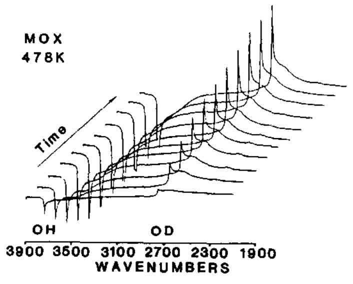

FIG. 4. Spectra depicting the increase in the OD bands, to the right, and decrease in the OH bands, to the left, as a function of increasing time, to the background. Spectra measured 1 mm from the Pt source of spiltover deuterium.

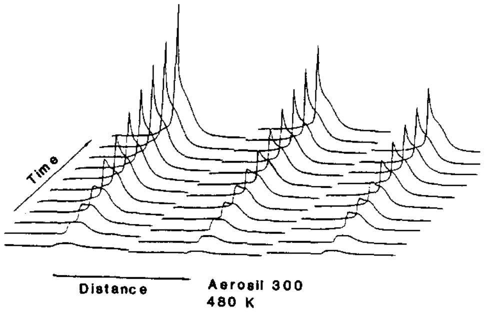

FIG. 5. Infrared spectral data showing the OD bands at distances of 1 mm (left), 5 mm (center), and 9 mm (right) from the Pt source of spiltover deuterium. As time progresses the changing spectra are shown in the background after the introduction of deuterium.

In Figs. 6 and 7 the results for this experiment are shown in a quantitative fashion. In Fig. 6 the maximum absorption of the OD band as a function of time is plotted for the three radial distances. The results show that the concentration of free OD groups increases in an almost linear fashion for this case; no saturation is evident even after 100 min. In Fig. 7 the plots show the total area under the OD bands, including the associated deuteroxyls. In this case the curves show an approach to saturation; i.e., the integrated absorption approach an asymptotic value. Most of the area under the bands corresponds to the broad shoulder; thus, the results in Figs. 6 and 7 confirm the qualitative observation that the hydrogen bonded deuteroxyls grow at a different rate than the isolated deuteroxyls.

The measured approaches to limited partial exchange of the surface hydroxyls by deuterium at first appear unusual. Why doesn't the exchange continue until all of the hydroxyls are exchanged? Two aspects of the spillover and surface diffusion phenomena may provide an explanation for these observations. There are only a limited number of surface sites able to accept spiltover hydrogen on silica or alumina sur-

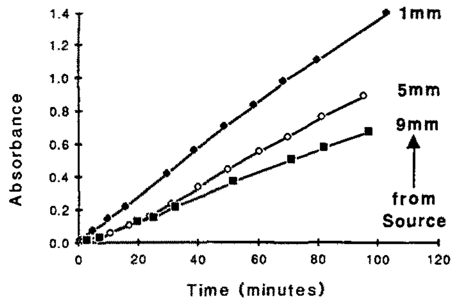

FIG. 6. Plot of the maximum absorbance (peak height) of the OD band at three positions in time after the introduction of deuterium.

faces (*1*). First, as saturation of these sites is approached, the rate of surface transport will decrease. Secondly, due to the limited number of spiltover deuteriums (on the order of $10^{12}/cm^2$) compared to the hydroxyls (10^{13}–$10^{14}/cm^2$) only a fraction of the hydroxyls exchange with the initial saturation of the surface with spiltover deuteriums; further, exchange is effectively a dilution experiment. Surface transport of the exchanged spiltover species is encumbered as the "open" sites accepting the "diffusing" species are limited. To understand this nature of the processes it is relevant to determine if the experiment is reversible.

Reexchange of the surface deuteroxyls with hydrogen was attempted for several samples. Saturation of the surface was more clearly seen with Mox-80 and Aerosil 130 silicas. Both are low surface area aerogels, with approximately 80 and 130 m^2/g, respectively. Mox-80, however, has a higher content of impurities, specifically alumina. A sample was considered saturated when absorption of the OD band has ceased to increase as a function of time. At this point D_2 can be evacuated from the gas phase, helium is then circulated through the liquid N_2 traps for a short time to assure dryness and introduced in the cell. Finally hydrogen is introduced into the system after being precirculated through the traps. Infrared spectra can be taken during the intermediate pretreatment and as a function of time after hydrogen is introduced.

The most interesting results were obtained with Mox-80. The sample was pretreated under vacuum for several hours at temperatures up to 460°C. Exchange with the surface was then carried in the usual way at 300°C. After 71 min the sample was evacuated and isolated for 15 min while helium was dried. The temperature was raised to 340°C until helium was introduced to the cell. After drying for 15 min hydrogen was circulated in the IR cell and spectra were collected for 1 h. After the reexchange was finished deuterium exchange was again attempted with the same procedure.

Figure 8 shows spectra for different times at a fixed position. The first spectra taken after saturation are under a helium atmosphere. Note that the shape of the OD band, specifically the shoulder, has already changed. After 50 min a substantial amount of the OD band has been eliminated. When H_2 is evacuated and D_2 is reintroduced, the OD band grows much like it did in the beginning of the experiment. This cyclical behavior is better illustrated in Figs. 9 and 10, where the maximum of absorption and the integral of the absorption are for the OD band are plotted as a function of time.

The results of reexchange in the Aerosils were very different from those obtained with Mox-80. A sample of Aerosil 300 was pretreated under similar conditions as the Mox-80 (above). The exchange with deuterium was performed at 285°C for 95 min,

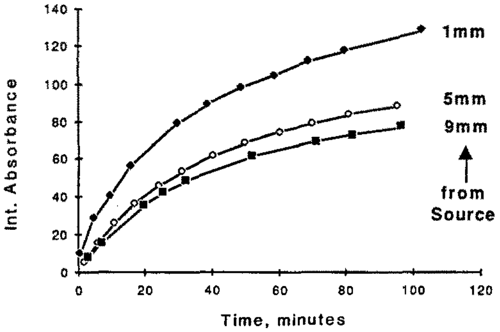

FIG. 7. Plot of the integrated absorbance of the OD band(s) at three positions as a function of time after the introduction of deuterium.

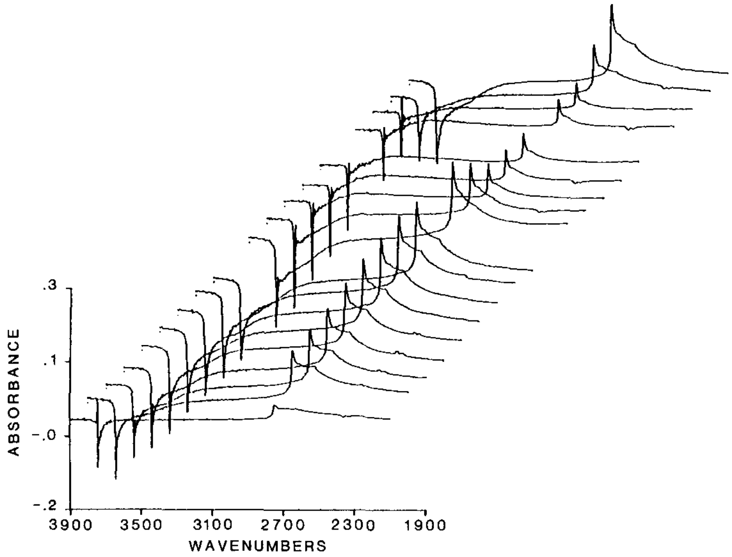

FIG. 8. Infrared spectra on MOX-80 1 mm from the source of spillover as a function of time depicting the OD (to the right) and OH (to the left) bands. During the experiment deuterium is first exchanged followed by hydrogen reexchange, and finally deuterium is reintroduced.

after evacuation the temperature rose about 40°C until dried He was introduced in the IR cell. Reexchange with H_2 was attempted for about 50 min at 160°C.

The results of this experiment appear in Fig. 11. It is apparent that the amount reexchanged in this case is comparatively small when compared to Mox-80. Moreover, the spectra taken immediately after evacuation show that the concentration of OD on the surface was still increasing even when no deuterium was present in the gas phase. It is apparent that the desorption of spiltover hydrogen/deuterium is slower on the A-series Aerosils compared to the MOX series. This may be due to the ability of alumina

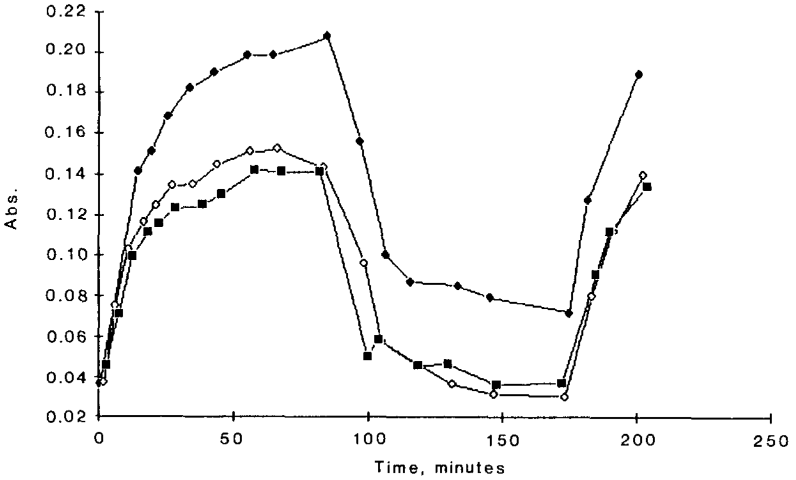

FIG. 9. Maximum absorbance of the OD bands for MOX-80 at 1, 5, and 9 mm from the source of spillover during a reexchange experiment (i.e., D_2 exchange followed by H_2 reexchange followed by D_2 reintroduction).

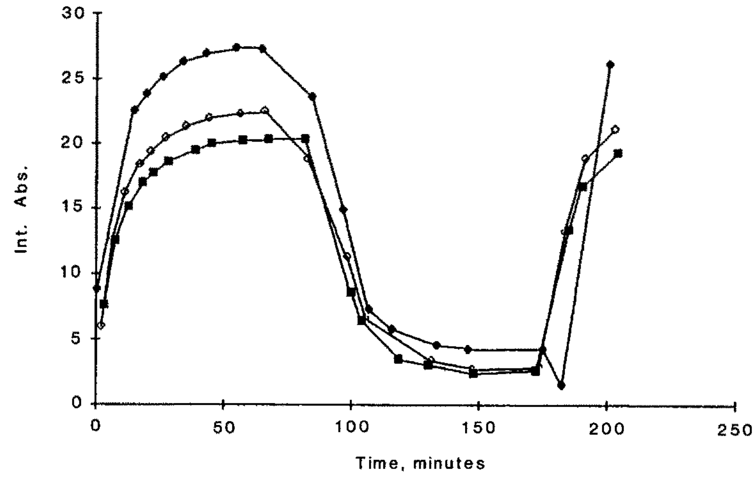

FIG. 10. Integrated absorbance of the of the OD band(s) during a reexchange experiment as in Fig. 9.

impurities (and associated surface species) on the MOX series to facilitate the atom recombination processes. Both the total area under the absorption band and the maximum absorption increased immediately after evacuation.

One of the referees has suggested that these phenomena can be accounted for by the action of trace impurities of water. In the authors' view the influence of trace water was not a factor in these studies. Indeed, in our first attempts to perform this experiment, we were plagued by the presence of trace amounts of water (or oxygen) in the system. The result was a uniform exchange across the surface as water in a known cocatalyst for the exchange reaction on oxides. Bianchi *et al.* (*13*) have directly studied the influence of water vapor on the exchange studied by FTIR and concluded that only above 10^{-5} Torr was there any direct influence of exchange via water. The rate was almost independent of the pressure of the purified hydrogen and so we concluded that it was not impurities in the hydrogen gas. As mentioned above our system employed stringent requirements (dual-staged diffusion pumps and bake-able metal valves and connections) to exclude the water and maintain pressures below 10^{-7} Torr. We see the exchange of at least 10^{18} OH's in each of these experiments. Even at 10^{-6} Torr there could be a maximum of 10^{13} water molecules in the system. The rapid exchange followed by essentially a steady state would not seem characteristic of these relative numbers. These and other calculations[1] led us to conclude that any impurity

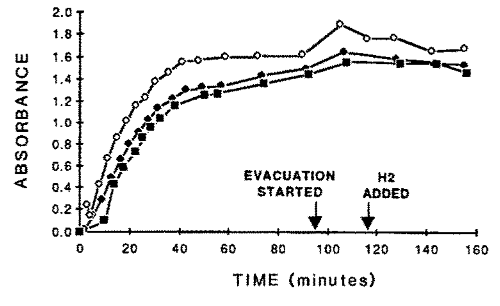

FIG. 11. Maximum absorbance of the OD bands for A-300 at 1, 5, and 9 mm from the source of spillover during a reexchange experiment as in Figs. 9 and 10. The times for evacuation of the gas phase and introduction of hydrogen are shown on the horizontal axis.

[1] Why would each water molecule be responsible for on the order of 10^5 exchanges and then stop? The turnover frequency for the exchange would be over 10^2 s^{-1} (based on the water), and with this mechanism (having to go back to the platinum) the surface diffusion coefficient would be much greater than 10^2 cm^2 s^{-1}. Note that without going back to the platinum no gradient would exist. Each of these calculations yields results that seem physically unreasonable.

present in the gas phase was not responsible for the exchange.

CONCLUSIONS

A new experimental technique to study surface migration was developed. This technique uncouples the surface migration step from the actual spillover onto the surface and produces space- and time-resolved data which can be used to study the mechanism and rate of surface migration in spillover.

The saturation of the OD curves indicates that not all of the OH groups on the surface of silica are available for exchange. It appears that the mechanism of migration is directly coupled to the presence and concentration of OH groups on the surface of silica. This relationship will be discussed elsewhere (*10*). The importance of the surface chemistry of the oxide in the migration of spiltover hydrogen is underscored by the reexchange experiments. This has been pointed out by other authors as well, most recently by Baumgarten and Denecke (*11*), who have indicated the importance of the OH groups for spillover onto alumina. Also Lenz and Conner (*12*) have observed that hydrogen spillover is not able to activate silica aerosil if the silica is dehydroxylated at high temperatures prior to the exposure to spiltover hydrogen. It seems that the hydroxyl nature and concentration are instrumental to both the transport of and induction of catalytic activity by spiltover hydrogen.

ACKNOWLEDGMENTS

The authors greatly appreciate the support of the National Science Foundation, Grant CPE 82-21800, and the Petroleum Research Fund, Grant 13703-AC7, for this research. We also wish to thank Analog Devices for their donation of computer equipment. We further thank S. Teichner, G. Pajonk, V. Haensel, S. L. Hsu, and D. H. Lenz for useful discussion on the interpretation of these results.

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