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Hydrogen Spillover on Silica

III. Detection of Spillover by Proton NMR

Two aspects of the hydrogen spillover phenomenon still under debate are the nature of the spiltover species and the nature of the active site created on oxide surfaces (*1*), e.g., on silica. The answers require an analytical technique capable of determining the structure and/or electronic properties of adsorbed, mobile hydrogen as well as of the surface. Also, as spillover is a dynamic phenomenon, this technique should be amenable to *in situ* studies. NMR spectroscopy can address each of these concerns. To this end, a novel *in situ* NMR experimental setup will be described. We report preliminary studies using proton NMR to gain insight into the nature of the spiltover species and of the active sites for spillover onto silica.

Prior studies have employed NMR to investigate the adsorption and spillover of hydrogen. Bonardet *et al.* (*2*) first investigated the use of NMR to study the adsorption of hydrogen on silica-supported platinum. Apple *et al.* (*3*) applied NMR as well as TPD techniques to study hydrogen adsorption on Rh/TiO_2 catalysts. NMR showed two species of hydrogen on the supported metal catalyst not found for hydrogen adsorption on the support alone. They concluded that one type of hydrogen is reversibly adsorbed and is associated with the support whereas the second type is irreversibly bound and is associated with the metal. The upfield resonance line of the reversibly adsorbed hydrogen is presumed to be due to the spiltover hydrogen species (H_{sp}). Sheng and Gay (*4*) also utilized NMR to identify and study adsorption and spillover of hydrogen on various supported platinum catalysts. Confirming the initial results of Fraissard and co-workers (*2, 5*), they reported that adsorbed hydrogen on platinum is evident with a 50 ppm upfield shift from TMS due to covalent bonding of the H on Pt. Sheng and Gay also invoke spillover to explain the decrease in the relaxation time of the support hydroxyls, SiOH. They suggest that paramagnetic H atoms can be effective relaxation agents for the SiOH protons. This could propagate their influence over the whole surface in a sufficiently short time. This requires that the hydrogen atoms have chemical diffusion coefficients larger than the spin diffusion coefficients; numerous NMR studies determining the surface diffusion coefficient of hydrogen spillover (*6–8*) suggest that this requirement is reasonable.

It appears that spiltover hydrogen may exist in a variety of states (charged, radical, or bound) depending on the catalytic system and cosorbing species. Several investigators (*9–16*) identify the spiltover hydrogen species as protonic hydrogen, H^+. Other investigators (*17–20*) conclude that the active species for hydrogen spillover is a hydrogen radical, $H^\cdot$. Bianchi *et al.* (*21*), in their study of hydrogen spillover from Pt/Al_2O_3 catalysts onto methoxylated silica Aerogel, even postulated an H_3^+ species on the basis of kinetic arguments. Most of these experiments have involved spillover onto oxides.

Spiltover species can be involved in the activation of the support as well as in surface diffusion and reaction. Teichner *et al.* (*22*) have devised a system to study support activation and report that silica, alumina, and magnesia acquire new catalytic properties when activated by hydrogen spillover

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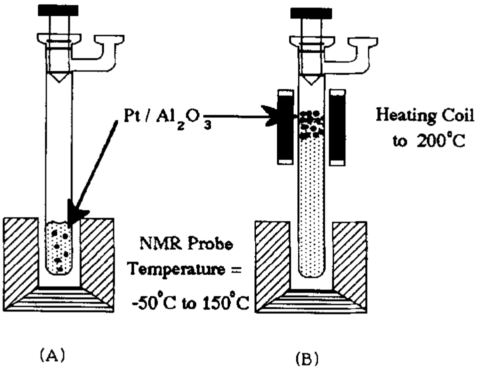

FIG. 1. Schematic of the two experimental configurations employed in these studies. The source of spillover (Pt/Al_2O_3) was mixed with the silica in the NMR cavity in configuration A but was not present in the NMR cavity in configuration B.

at 700° K. On activated silica, the creation of one to three types of sites has been postulated. For example, according to Dmitriev *et al.* (*23*), the spiltover hydrogen could remove oxygen ions from the silica surface leaving unscreened silicon ions which would react as Lewis-type acids and be poisoned by ammonia and oxygen. On titania, Apple *et al.* (*3*) reported that the spiltover hydrogen scavenges OH groups from titania. This action would leave an anion vacancy ($Ti^{4+} \rightarrow Ti^{3+}$ as H_{sp} donates an electron) creating a paramagnetic center capable of adsorbing hydrogen heterolytically. They report increases in the upfield shift associated with these centers at increasing temperatures or decreasing pressures.

EXPERIMENTAL

Since spillover is a dynamic phenomenon, it was important to utilize an *in situ* NMR technique without perturbing the system being studied. Figure 1 depicts the two types of *in situ* experiments employed. The experimental apparatus was adapted from a typical NMR experiment with modified 10-mm Pyrex and quartz NMR sample tubes containing the samples. Teflon vacuum stopcocks were used to seal the sample tubes. A heating coil was attached to the probe in place of the spinner. The heating coil was capable of producing temperatures to 200°C without affecting the sample cavity. The probe temperature could be varied from −90 to 150°C using dry N_2 that was heated or passed through liquid nitrogen. The exact temperature was regulated by adjusting the N_2 flow rate.

Two different types of experiments were performed. In one the source of spillover (UOP 0.4% platinum-on-alumina catalyst) was present within the NMR cavity, and in the other the source of spiltover hydrogen was outside the cavity. Degussa Aerosil 200 was the acceptor of the spiltover hydrogen. The NMR spectra were recorded on a Brucker CXP FT spectrometer at 90 MHz. Tetramethylsilane (TMS) gas was used as the reference for the chemical shifts. The Fourier-transformed spectra were deconvoluted using the method of Nogier (*24*).

For each of the experiments the NMR spectrometer operating parameters were held constant except for DLO, i.e., the time period between the sequential pulses. DLO was varied to selectively suppress the spectra for the hydroxyls. The relaxation time for adsorbed hydrogen is very fast compared to the relaxation time for surface hydroxyls. For Aerosil 200 without H_2 present, the resonance line for adsorbed hydrogen was detected using a DLO of 0.2 s with an accumulation time of 20 min. To observe the resonance line for the SiOH protons, a DLO of 2.0 s was necessary (employing an accumulation time of 90 min).

The standard experimental procedure consists of pretreatment followed by *in situ* NMR measurements. Each of these stages will be described in detail. The creation of active sites involves an additional activation procedure which will also be discussed. Common to each pretreatment was an evacuation to $<10^{-5}$ Torr at either 430 or 650°C. It is important to note, from MacBain balance studies (*25*) and the literature (*26*), the effects on the Aerosil surface due to the different pretreatments. At 430°C, the surface contains both associated and isolated hydroxyls which could influence the proton spectra. Infrared studies of silica surface hydroxyls, as reviewed by Kiselev and Lygin (*26*), first demonstrated that the population of isolated hydroxyls would not be affected by the different pretreatment conditions of these studies. However, at 650°C, the associated (vicinal and geminal) hydroxyls are reduced leaving predominantly isolated hydroxyls.

After pretreatment at 430 or 650°C, hydrogen was admitted to the sample at 430°C for a period of time. In every case, the samples were then evacuated before fresh hydrogen was admitted for the start of the dynamic studies. For example, a sample was evacuated at 650°C and 10^{-5} Torr for 7 h, then reduced in 490 Torr of hydrogen at 430°C for 3 h (which does not create active sites (*27*)). The sample tube was then evacuated at room temperature overnight and then a reference spectrum was collected. Following this, 480 Torr of hydrogen was introduced for the start of a dynamic experiment as shown in Fig. 1.

The first type of *in situ* experiment involved physically admixing the spillover source (Pt/Al_2O_3) with the silica so that both were within the NMR cavity during the measurement (Fig. 1a). The sample was placed in the probe as soon as fresh hydrogen was admitted over the sample. Hydrogen adsorbs and dissociates on the metal. It then spills over across the alumina onto and across the silica at a constant temperature of 130°C. The NMR chemical shift due to the accumulating concentration of spiltover hydrogen on the silica was measured with time.

Aerosil 200 was used as the silica for these samples. It is a very high-purity silica (impurities <5 ppm) with ~ 200 m^2/g surface area. The equilibrium concentration of the spiltover species on the silica surface present in the cavity was $\sim 10^{18}$ atoms, within the sensitivity range of the NMR spectrometer. In contrast, the concentration of hydrogen adsorbed on platinum ($<10^{17}$ atoms) was below the sensitivity limits of the spectrometer. Thus the chemical shift of metal-bound hydrogen species should not be detected even if the Pt were present in the probe.

To ensure that spiltover hydrogen does not enhance the signal of hydrogen adsorbed on platinum, the second type of *in situ* experiment was performed. In this case, the spillover source was removed from the probe area, although it was still within the sample tube (Fig. 1b). The tube was placed through the heating coil and into the NMR probe as soon as fresh hydrogen was admitted. The dynamic situation now was slightly different. The hydrogen adsorbs, dissociates, and is spilt over from the source onto the silica at a constant temperature of 200°C. The spiltover hydrogen then migrates and/or diffuses across the continuous powdered silica surface for a distance of approximately 12 cm into the probe area. The probe temperature was 130–150°C, so a slight temperature gradient existed. Infrared studies by Conner *et al.* (*28*) have shown that spillover occurs under these conditions and would be able to diffuse across this distance within a reasonable time period.

Following typical evacuation and reduction steps as described, active sites were then created on fresh silica Aerosil using standard activation procedures (*22*). High-temperature (430°C) evacuation for 21 h was followed by spillover and activation in 515 Torr of hydrogen at the same temperature for >12 h. The spectra were accumulated at a DLO of 0.2 s for 20 min prior to any evacuation of the gaseous, adsorbed, or spiltover hydrogen on the silica and the newly created sites.

RESULTS AND ANALYSIS

In order to observe the effect of the spiltover hydrogen on the proton NMR spectrum, initial characterizations (i.e., chemical shifts, relative peak intensities) of adsorbed hydrogen, the surface hydroxyls, and their interaction with each other on the silica were performed for each pretreatment condition. The results are summarized below.

Adsorbed hydrogen. It should be noted that a sample that comprised only silica (no source of spillover) was pretreated for 8 h *in vacuo* at 430°C and 500 Torr of H_2 was then admitted. A single line at ~6 ppm downfield from TMS was seen with a DLO of 0.2 s. There was no change in the NMR spectra after 3 days at room temperature. Recall that at this DLO no spectra are evident without H_2 present.

Adsorbed hydrogen on Degussa Aerosil, at a DLO of 0.2 s, shows a chemical shift around 6 ppm downfield from TMS regardless of pretreatment temperature or the proximity of the supported platinum catalyst. There was no apparent effect of pretreatment temperature on the NMR spectra at a DLO of 2 s with or without gaseous hydrogen present at a probe temperature of 130°C. Only after hydrogen spillover had been allowed to occur was there a change.

Hydroxyls. The chemical shift for the SiOH proton is ~4 ppm downfield (seen for a DLO of 2 s), with similar relative areas for all samples even after evacuation of 650°C. Again, as the population of isolated hydroxyls is also independent of the pretreatment conditions used during these studies but the associated hydroxyls change substantially, we deduce that only free or isolated hydroxyls are involved in the measured NMR spectra under these conditions.

Hydrogen and hydroxyls. However, obtaining the characteristics for the hydrogen–hydroxyl resonance peak could be complicated by the fact that spillover can occur from the reduced metal source present as soon as hydrogen is admitted into the sample tube. It appears, though, that the resultant spectrum was not influenced by spiltover hydrogen. It is presumed that the concentration of spillover species able to migrate into the probe area within the time period of the scan (to 90 min) was less than 10^{17} "molecules" and therefore would have little, if any, effect on the initial spectrum. There was no difference either in the initial or, with enough time, in the final spectra if the spillover source was within the probe or 12 cm distant.

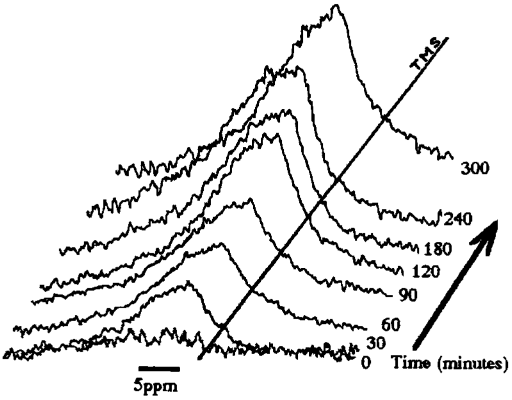

FIG. 2. Proton NMR spectra of a silica sample as a function of time after exposure of the sample to hydrogen with a source of spillover in contact with the sample.

Spiltover hydrogen. Care has been taken in these studies that once hydrogen was admitted into the sample tube containing the silica and the source of spillover, the tube was sealed. Any changes in the NMR spectra from the initial conditions may be attributed to the presence of the spiltover species.

A typical example of the resonance peak's changing with time for a DLO of 0.2 is shown in Fig. 2. In this case the silica had been pretreated at 430°C and the spillover source was present within the NMR tube. As spillover proceeds, a resonance peak grows and becomes increasingly broad. Further, the maximum resonance peak height shifts upfield of the initial hydrogen spectrum. In each case the resonance peak exhibits an increasing upfield shift with time. After 180 min a shoulder begins to appear downfield and is readily distinguishable after 300 min.

It is important to ascertain whether or not the resonance peaks of the final and initial spectra are independent. For each spectra, the initial free induction decay (FID) curve was subtracted from the final FID curve before Fourier transformation. The result indicates that *at least two* independent peaks always exist under the adsorption curve. This suggest that the NMR spectra reflect both adsorbed and spiltover hydrogen as well as the free hydroxyls, and that exchange or surface complex formation among these species may be occurring. Initially, the final spectra were deconvoluted into two peaks, assuming a Lorentzian fit for the curves. Although good matches between the calculated and the experimental curves could be obtained for some of the spectra, there were no consistent patterns of change with time and pressure. The deconvolution of the NMR spectra into three peaks yielded the highest correlation coefficient (>0.995) and the lowest average deviation in every case compared to the corresponding two-peak deconvolution. In general, the three-peak pattern involves a central peak around 5 ppm downfield from TMS and two "wing" peaks of approximately equal relative areas and shifts (ppm + and −) from the central peak.

Pressure changes also have a noticeable effect on the spectra. Decreasing the hydrogen gas pressure tends to decrease the relative peak area and broaden the resonance peak so that two shoulders become apparent. One shoulder is upfield of the initial hydrogen chemical shift and the other is downfield. As the hydrogen gas pressure is reduced to zero, the resultant resonance peak matches that of the original hydroxyl spectra for a DLO of 2.0 s.

Characteristic examples of the final NMR spectra taken at a DLO of 0.2 s and of their deconvolutions are shown in Fig. 3. Each spectrum corresponds to >2000 accumulated–averaged scans. This figure actually shows the deconvolution for the final smoothed spectra of Fig. 2 in 3A. Spectra taken for either 0.2 or 2.0 DLOs are quite

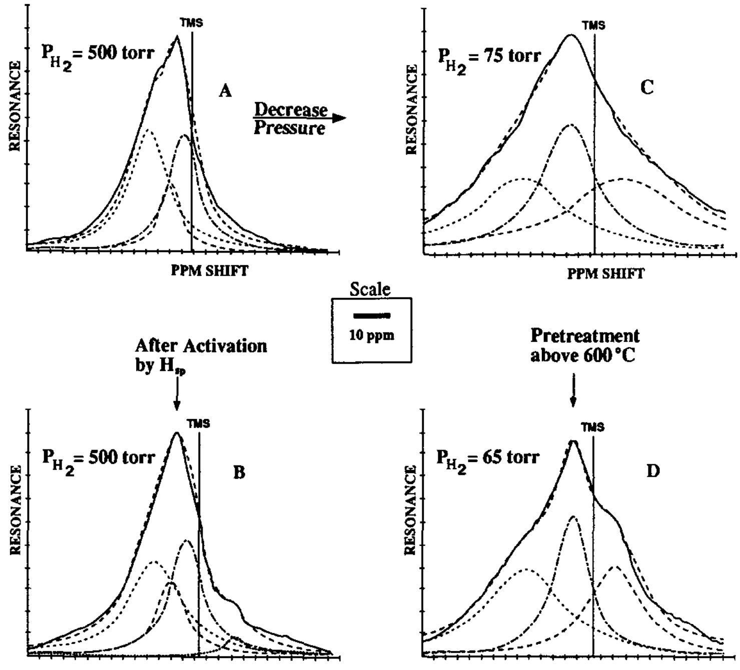

FIG. 3. Final proton NMR spectra of silica samples as a function of the hydrogen pressure or the pretreatment of the silica prior to the exposure to spiltover hydrogen.

similar as the center peak is approximately the same and the wing peaks are slightly more shifted from the central peak for the higher DLO. Both isolated and associated hydroxyls were present for each of the spectra except the one depicted in 3D which contains essentially only isolated hydroxyls (i.e., after 650°C evacuation).

The effect of pressure on the deconvoluted NMR spectra can be seen in Fig. 3C. There was little change in the chemical shift of the central peak. However, the chemical shift of the two "wing" peaks increased significantly more downfield and upfield respectively from the central peak and the relative intensities of these peaks decreases. There was also an overall broadening of all the peaks and indeed of the whole resonance spectrum.

After activation by H_{sp}. The presence of active sites changes the resonance spectra, all other conditions constant. The sample which has been shown in Fig. 3A was activated as previously described and the resultant spectra are shown in 3B. The three peaks already observed are still present in the deconvoluted spectra and are practically unchanged; however, a fourth resonance peak is clearly present upfield ~12 ppm from TMS.

DISCUSSION

These initial *in situ* studies demonstrate changes in the NMR spectra due to spiltover hydrogen interacting with a silica surface and with active sites created on the surface. The interpretation of the three peaks associated with the spillover of hydrogen will be discussed. Since at least three types of spiltover species have been suggested (trihydrogen, protonic, and radical), each will be considered in light of the NMR evidence. Finally, insights into the active sites created will be discussed.

It is essential to understand the phenomenon occurring while the series of spectra are being collected in order to assign identities to the peaks being observed simultaneously. Recall that during these *in situ* studies adsorbed hydrogen was dissociating on the spillover source, followed by spillover, migration, and a concentration buildup of the spiltover species on the silica surface.

The central peak can be identified as H_2. With hydrogen being spilled over onto the silica, the central peak decreases with time as two "wing" peaks increase. The rate of decrease of the intensity of the central peak was faster if the spillover source was closer to the probe. The two "wing" peaks can both probably be associated with the spiltover hydrogen species. They increase with time as does the population of spiltover species on the silica surface. The increasing shift in the two wing peaks with decreasing pressure was unexpected, but may be explained by a decreasing average strength of interaction with increased pressure and sorption. Note that care was taken to eliminate any other species (water, oxygen, etc.) from the samples during preparation and pretreatment.

Nature of the Spiltover Species

Trihydrogen species. A trihydrogen species had been suggested by Bianchi *et al.* (*21*). It is possible to estimate the NMR spectra for each of the various trihydrogen species and compare these to the observed spectra. Only the thermodynamically favored configuration will be discussed. The stable structure is linear for the trihydrogen anion and radical, but triangular for the cation. The accuracy of these calculations was verified independently, at least for the cationic molecule, by Gaillard *et al.* (*29*). Theoretical calculations were performed of the chemical structure and magnetic properties of various forms of a trihydrogen anion, cation, and radical. Recall the deconvolution results which indicate that two peaks of approximately 1 : 1 relative area ratio are associated with the appearance of spiltover hydrogen on silica.

For the triangular cation, H_3^+, the electron charge density is positive and equally shared on all the hydrogen atoms. Therefore, only one resonance peak will occur shifted downfield from TMS.

For the linear anion, H_3^-, the central atom has a small positive charge density and the two end atoms have large, equal negative charge densities. This will produce two resonance peaks, a large one upfield and a smaller one downfield of TMS. The relative area ratios would be approximately 2 : 1.

For the linear trihydrogen radical, spin density is more important than charge density. There are a small negative spin density for the central atom and larger positive spin densities for the other two. This effect will also give two peaks, although now the larger one will be shifted downfield and the smaller one upfield from TMS. However, the ratio of relative areas is about 2 : 1.

As the deconvoluted spectra represent two peaks of approximately equal area shifted up and down from the central peak, we reject any form of a trihydrogen species giving rise to the observed spectra.

Charged atomic hydrogen species. It has also been suggested that the hydrogen is heterolytically split resulting in both a proton and a hydride anion as the spiltover species. A proton on the silica surface should produce a resonance peak ~30 ppm downfield from TMS, whereas a hydride will give a resonance peak 1–2 ppm upfield from TMS. Low-temperature studies were conducted to determine whether the spiltover species was charged, H^+ and H^-. The probe temperature was lowered to inhibit any exchange reactions, since both charged species could be involved in either exchange interaction or surface complex formation with the hydrogen or the hydroxyls. The *in situ* studies allowed spillover to occur at −90°C over 24 h. These studies yielded a small peak appearing as a shoulder of the H_2–OH (at ~3.5 ppm from TMS) peak for a DLO of 2.0 s about 1–2 ppm upfield from TMS. This peak would disappear upon an increase in the probe temperature but reappear upon a decrease back to −90°C. Also, for a DLO of 0.2 s, a single dominant peak was evident at ~4.5 ppm from TMS. However, no simultaneous peak was observed ~30 ppm downfield. Since only one peak was observed at low temperature, we conclude that there is one spiltover species. Also, it seems, again, that the resonance peaks from spiltover hydrogen are due to some type of exchange interaction, since the typical spectra associated with the presence of spiltover hydrogen returned upon reheating the sample.

Hydrogen radical. Since the spiltover species does not seem to be either a trihydrogen molecule or a pair of charged atoms, a final possibility is the radical hydrogen atom. Our results are consistent with a radical, spiltover hydrogen species interacting with the surface hydroxyls. A single radical hydrogen atom can generate two resonance peaks from the interaction or exchange with surface hydroxyls. The interaction of spiltover hydrogen with the hydroxyls (probably through the oxygen) gives rise to a change of both the spin and charge densities of the two hydrogen species. The result is a concomitant but opposite chemical shift for the two species, the spiltover hydrogen and the hydrogen of the hydroxyl. This is in agreement with the experimental results.

The interaction of spiltover hydrogen with the free hydroxyls seems to allow them to be observed at a shorter DLO. Recall that there was very little difference in the spectra at a DLO of 2.0 or 0.2 s with spiltover hydrogen present. From the reference studies, the DLO should determine whether or not the hydroxyl resonance is observed. However, paramagnetic hydrogen atoms can decrease the relaxation time of surface hydroxyls and permit them to be observed at shorter DLO.

The fourth resonance peak which appeared upfield from TMS in the deconvoluted spectra after activation of the silica was probably due to spiltover hydrogen adsorbed on the active sites. The gas phase had not been evacuated after activation and it is known that spiltover hydrogen will remain on the active site under these conditons (*22*). Therefore, especially if the spiltover species is a hydrogen radical, the active site appears to have a high electron density creating an upfield shift. It seems to be "metallic." Recall that hydrogen adsorbed on platinum resonates upfield (about 50 ppm) from TMS due to covalent bonding of H on Pt. Alternately, the upfield shift could be attributed to hydrogen interacting with a paramagnetic center as suggested by Apple *et al.* (*3*) or perhaps be an F defect center, either (Si–O)– or Si–.

CONCLUSIONS

These novel proton NMR *in situ* studies have successfully demonstrated that spiltover hydrogen has a noticeable effect on the resonance spectra. Three peaks are present, one upfield and one downfield from a central H_2–OH resonance peak. Although ongoing low-temperature studies seek to identify the spiltover species directly by eliminating all exchange interactions, the experimental results in this note can be explained most simply by the existence of a radical hydrogen as the spillover species as contrasted with charged or trihydrogen species. Finally, adsorption peaks associated with spillover-induced active sites are observed, yielding clues as to the nature of both active sites and active species. If the active species is radical-like, then the active site appears to have a high electron density and thus is metallic, anionic, or basic in nature.

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