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Hydrogen Spillover on Alumina—A Study by Infrared Spectroscopy

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Infrared spectroscopy has been used to monitor the exchange of D_2 (g) with OH groups chemisorbed on Al_2O_3. It has been shown that near 300 K, the rate of the exchange process is rapid in the presence of supported Rh particles on the Al_2O_3. A qualitative model for hydrogen "spillover" is presented in which dissociative adsorption of dihydrogen by the metal is a key step. It is shown that CO chemisorption on the supported Rh leads to a marked reduction in the "spillover" rate due to site blockage on the Rh. This is consistent with recent studes of behavior of the CO and H coadsorbed on Rh (111).

I. INTRODUCTION

The hydrogen spillover phenomenon is a widely recognized property of oxide-supported transition metal catalysts. This phenomenon involves the production of a catalytically active form of hydrogen on oxides by means of a pathway involving dissociation of dihydrogen on a supported metal particle, and subsequent migration of monoatomic hydrogen species over the support and away from the metal particle (for a list of recent references to the spillover phenomenon see (*1*)).

In many of the former studies of this effect, either the enhancement of the adsorption of hydrogen or the extra hydrogenation activity arising from the "spilled-over" hydrogen species has been measured. Thus, on Al_2O_3, the ability of this hydrogen to hydrogenate ethylene has been investigated (*2*). Also, a strongly bound form of chemisorbed hydrogen produced by spillover on Al_2O_3 has been detected by thermal desorption spectroscopy. It was found that this strongly bound hydrogen could be produced by H migration from Pt or Ni particles or by direct adsorption from atomic hydrogen produced in the gas phase (*1*). The effect has been observed by electron microscopy on C and SiO thin films (*3*). For the purpose of this report, we define "spilled-over" hydrogen as surface hydrogen species which originate from H_2 (g) incident on supported metal sites, and which subsequently undergo exchange with OH species on the Al_2O_3 support.

The exchange of D_2 (g) with surface hydroxyl groups on SiO_2 via supported Pt particles was first investigated using infrared spectroscopy by Eischens and Pliskin in 1958 (*4*). Control experiments on pure SiO_2 showed that the exchange effect required the presence of the Pt particles to produce an exchangeable form of surface deuterium from D_2 (g). At that time, the ability of monoatomic hydrogen species to migrate across oxide surfaces had not been recognized, and alternate models for exchange were proposed.

In addition, Carter *et al.* (*5*) have studied the exchange of OH groups on η-Al_2O_3 in the presence of Pt particles using infrared spectroscopy. Their study was done at high temperature, and they found that the presence of Pt only slightly modified the exchange rate observed for metal-free Al_2O_3.

The H_2–D_2 exchange reaction on Al_2O_3 has been extensively studied by Hall and co-workers (*6*), as has the *ortho–para* hydrogen conversion process. It was found

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that for Al_2O_3 pretreatment temperatures (under vacuum) below 450 K, very little decrease in the hydroxyl surface coverage occurred below the saturation value. On these fully hydroxylated surfaces there was no measurable activity for *o–p* H_2 conversion. Measurable conversion does not occur until the pretreatment temperature is raised above 573 K (*7*). Similar behavior for the H_2–D_2 exchange on Al_2O_3 has been reported by Weller and Hindin (*8*). Thus it appears that one must dehydroxylate Al_2O_3 surfaces in order to induce chemical activity toward dihydrogen, presumably due to exposure of Al ions in the surface region (*6*).

In the work reported here, we have employed infrared spectroscopy to monitor the exchange of adsorbed OH on Al_2O_3 with hydrogen spillover from supported Rh particles. A method to reduce the rate of spillover has been investigated.

II. EXPERIMENTAL

Transmission infrared spectroscopy was employed in this work. Dispersed Rh on Al_2O_3 [Degussa Al_2O_3–C] was produced by hydrogen reduction in the infrared cell at 450 K of $Rh^{(III)}$ from $RhCl_3 \cdot 3H_2O$ dispersed on the Al_2O_3 using procedures described previously (*6*). The Rh weight percentage on the Al_2O_3 was 2.2%. The deposition coverage of the Al_2O_3/Rh sample was 0.016 g cm^{-2}. Chemisorption of CO by these surfaces has been well studied using volumetric adsorption methods (*9*), infrared spectroscopic methods (*9*), isotopic exchange methods (*10*), and ^{13}C–NMR methods (*11*). CO adsorption on the Rh yields ~1.2 CO/Rh at saturation, suggesting a high degree of Rh dispersion.

The reduced Rh sample was studied in a stainless-steel ir cell having CaF_2 windows. All procedures involved careful attention to elimination of hydrocarbon impurities—a grease-free bakeable stainless-steel ultrahigh-vacuum system, a liquid N_2 cooled zeolite pump, and an ion pump were employed to this end. The limiting base pressure was $<10^{-8}$ Torr.

Infrared spectra from 4000 to 1000 cm^{-1} were measured using a Perkin–Elmer Model 180 infrared spectrometer.[2] The wavenumber scale was calibrated against the CO (g) absorption spectrum above 2000 cm^{-1} (*12*).

III. RESULTS

A series of infrared spectra for 2.2% Rh/Al_2O_3 surface is shown in Fig. 1. In spectrum 1A, corresponding to the freshly prepared sample, three strong features are observed in the OH stretching region near 3600 cm^{-1}. The very broad feature with its maximum near 3550 cm^{-1} is due to surface-bound OH on the Al_2O_3. The lower wavenumber tail on this feature is thought to be due to hydrogen bonding effects. There are two shoulders at ~3720 and 3660 cm^{-1}. These are also assigned as OH stretching modes for chemisorbed OH on different Al_2O_3 sites. All of these same OH features are obtained for our Al_2O_3 surfaces prepared using the same procedure as for the supported Rh surface (*13, 14*). The spectra 1A-E correspond to continued D_2 (g) exchange with the OH species at P_{D_2} = 100 Torr and at 310 K. It can be seen that slight decreases in the intensity of the OH features are accompanied by the development of lower-wavenumber features near 2700 cm^{-1}. For the partially deuterated case, a broad feature at ~2600 cm^{-1} is assigned to hydrogen-bonded OD and the two shoulders at 2740 and 2700 cm^{-1} are assigned to OD stretching modes for chemisorbed OD groups on Al_2O_3. As shown in Table 1, these three OD species arise directly from the three observed OH species and exhibit very similar ν_{OH}/ν_{OD} ratios. Thus, it is observed that in the presence of supported Rh particles, facile isotopic ex-

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[2] The manufacturer and model of the infrared spectrometer are supplied to provide the reader with details of the experimental apparatus. No endorsement of this product by NBS is implied.

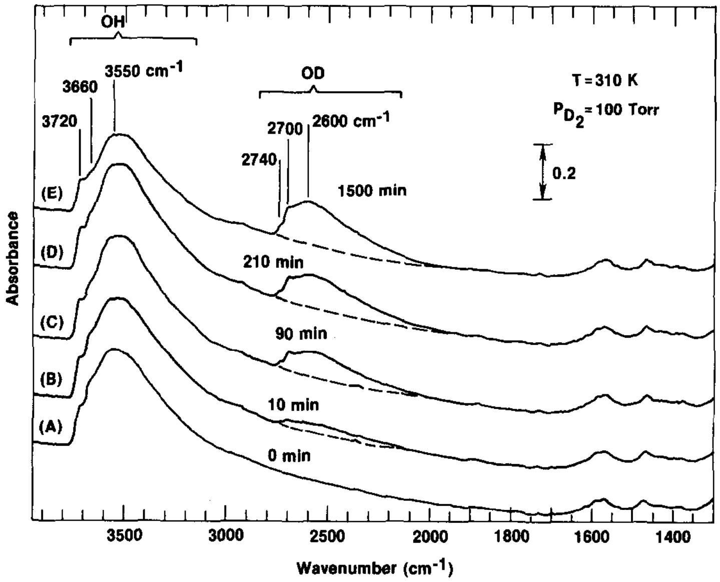

FIG. 1. Spillover of D_2 on 2.2% Rh/Al_2O_3: (A) Background spectrum prior to exposure to D_2 (g) at 100 Torr; (B) 10-min exposure; (C) 90-min exposure; (D) 210-min exposure; (E) 1500-min exposure.

change between D_2 and OH (ads) occurs at 310 K.

Following spectrum 1E, where extensive deuterium exchange has been achieved, the D_2 (g) was pumped away and CO (g) was added. This caused the CO spectra to develop in the 2000-cm^{-1} region, verifying that an active Rh surface was present throughout the exchange experiment.

A second experiment was performed on another freshly prepared Rh/Al_2O_3 surface identical to the sample above. Following H_2 reduction of the Rh and evacuation, 50 Torr of CO was added to saturate the Rh surface. Again the normal CO infrared spectra were observed in the 2000-cm^{-1} region. Following this, the CO (g) was pumped away, and D_2 (g) at 100 Torr was added. As shown in Fig. 2B, infrared spectra were recorded over a period of 19 h at 310 K. The amount of exchanged OH species is approximately 15% of that found for the CO-free sample. The D_2 (g) pressure was raised to 282 Torr for the additional exposure shown in Fig. 2C. Only 20% of the exchange found for the CO-free sample at 100 Torr was found at this higher pressure in the CO-covered sample.

TABLE 1

Frequency Comparison for Various Chemisorbed OH and OD Species on Al_2O_3

Adsorbed species	Wavenumber (cm^{-1})	Ratio ν_{OH}/ν_{OD}
OH_a/Al_2O_3	3720	1.358
OH_b/Al_2O_3	3660	1.356
$OH \cdots OH/Al_2O_3$	3550 (broad)	1.36
OD_a/Al_2O_3	2740	
OD_b/Al_2O_3	2700	
$OD \cdots OD/Al_2O_3$	2600 (broad)	

It is clear from these two experiments that clean Rh promotes D_2 dissociation followed by extensive exchange with surface hydroxyls held on the Al_2O_3 support. Blocking of the clean Rh surface by CO chemisorption prevents extensive exchange. Blank experiments with *pure* Al_2O_3 (subjected to identical preparation treatment as the Rh samples) exposed to D_2 at 300 Torr and at 310 K showed that no measurable isotopic exchange with surface hydroxyl groups occurred.

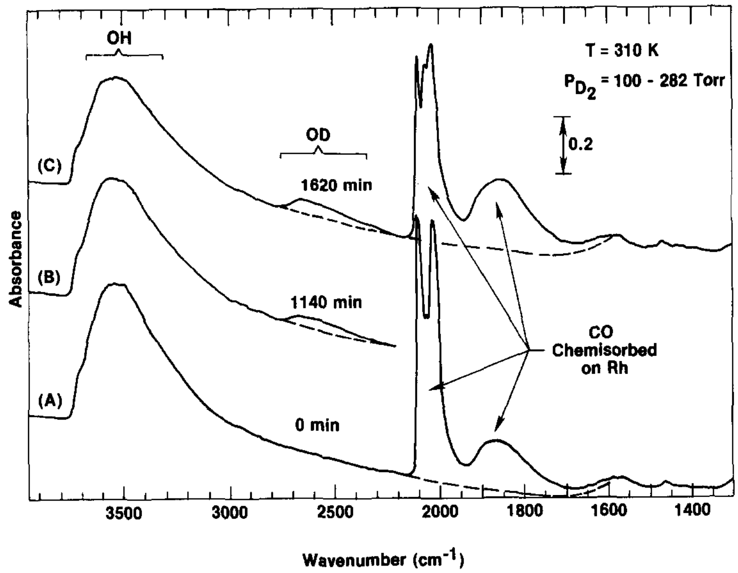

FIG. 2. Spillover of D_2 on CO-saturated 2.2% Rh/Al_2O_3: (A) CO-saturated sample following evacuation to 10^{-6} Torr; (B) following 1140-min exposure to 100 Torr of D_2 (g); (C) following an additional 480-min exposure at 282 Torr of D_2 (g). Broken line indicates background level.

IV. DISCUSSION

The observed infrared features for the OH (ads) species are tabulated in Table 1 along with their deuterated counterparts. Examination of the infrared spectra near 1650 cm^{-1} indicates that little or no adsorbed H_2O is present on these surfaces, since the bending mode of H_2O (ads) is absent. Both Peri and Hannan (*13*) and Pliskin and Eischens (*15*) report a strong infrared bending feature at 1650 cm^{-1} for H_2O (ads) on Al_2O_3. On our Rh/Al_2O_3 surfaces, D_2 exchange was found to cause no effects in the 1650-cm^{-1} region of the spectrum in agreement with the absence of the H_2O (ads) on these surfaces.

It is of interest to plot the integrated absorbance of all the OD species as a function of (diffusion time)$^{1/2}t^{1/2}$. This plot should be linear if a model involving *isolated* deuterium sources (Rh sites) feeding the Al_2O_3 surface is correct. It is seen in Fig. 3 that the plot exhibits curvature early in its development. This may be due to interference between the neighboring H-atom concentration profiles, producing a net drop in the rate of diffusion away from the localized H-atom sources. Kramer and Andre (*1*) have suggested that the surface concentration of diffusing hydrogen or deu-

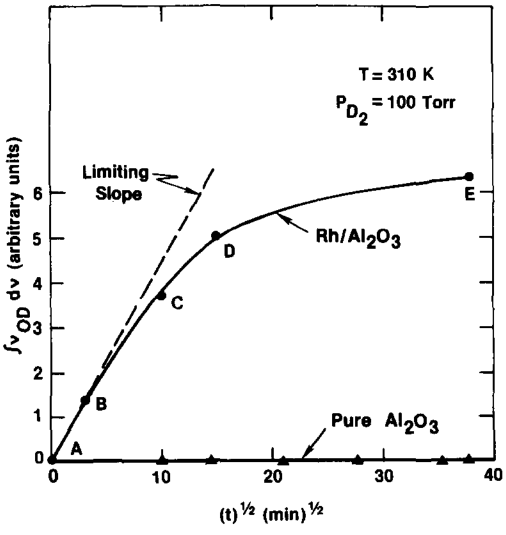

FIG. 3. Kinetics of growth of OD absorbance. Integrated absorbance versus (time)$^{1/2}$ for total OD adsorption shown in Fig. 1. The results of a blank experiment on pure Al_2O_3 exposed to D_2 (300 Torr) are shown by the triangles.

terium species is much lower than the maximum possible surface concentration of chemisorbed OH species, the ratio being about 10^{-3}. They measured a high activation energy 7 ($\sim$121 kJ $mole^{-1}$) for diffusing hydrogen species.

In summary we envision the spillover process to consist of fast dihydrogen dissociation on Rh sites, fast transfer to Al_2O_3, slow migration of chemisorbed hydrogen atoms across the Al_2O_3 substrate, and fast exchange with surface hydroxyls. The process will be retarded by poisoning of the Rh sites, recombination of hydrogen on the Al_2O_3 substrate by collision, and recombination of hydrogen at Rh sites. The latter two processes were not considered in a model proposed by Kramer and Andre (*1*).

According to the above model, the preferential adsorption of CO by Rh with subsequent blocking of dissociative H_2 adsorption and retardation of the spillover effect is expected. Recent studies of H_2/CO chemisorption on Rh (111) have shown that CO effectively blocks subsequent hydrogen adsorption and that in coadsorbed layers, repulsive H–CO interactions are observed (*16*). The activation energy for CO desorption from Rh (111) is 132 kJ $mole^{-1}$ in the limit of zero coverage (*17*). At full coverage, two CO binding states exist together on Rh (111) crystals (*17,18*) and also on the Rh crystallites supported on Al_2O_3 in this work (*9*). These data, taken together, suggest that CO should strongly bind to Rh surfaces, and at full coverage should exclude the chemisorption of hydrogen.

In summary we have shown that supported Rh on Al_2O_3 induces slow deuterium exchange at 310 K with surface hydroxyl groups. Blocking of the Rh sites by CO chemisorption is effective in preventing this process from occurring. A spillover of atomic hydrogen from Rh sites is suggested to explain these results. In addition, unambiguous spectroscopic evidence of this exchange is provided by these infrared transmission measurements.

ACKNOWLEDGMENTS

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