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NMR, ESR, and TPD Study of H_2 Adsorption on Rh/TiO_2 Catalyst

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The adsorption of H_2 on a Rh/TiO_2 catalyst results in spectroscopic properties which depend on the method of pretreatment. An explanation consistent with the results is proposed, which invokes the presence of at least two distinct hydrogenic species.

INTRODUCTION

There has been interest recently in the Fischer–Tropsch reaction, i.e., production of hydrocarbons from H_2 and CO. This interest has spurred investigation of the mechanisms of adsorption of CO and H_2 on catalysts used in this reaction. Several methods have been employed to study adsorption processes including infrared spectroscopy (*1–4*), inelastic electron tunneling spectroscopy (*5, 6*), electron spin resonance spectroscopy (ESR) (*7, 8*), and nuclear magnetic resonance (NMR) spectroscopy (*9–11*).

The nondissociative adsorption of H_2 on catalytic surfaces is not amenable to study by infrared spectroscopy, and very little spectroscopic evidence exists on the adsorption of H_2 on supported metals. Most studies of H_2 on supported metal catalysts by techniques such as temperature-programmed desorption (TPD) and hydrogen uptake (*11–13*) have led workers in the field to propose the existence of at least two types of hydrogen on the surface, reversibly and irreversibly adsorbed. There is currently not enough experimental evidence to elucidate either the state of hydrogen on the catalyst or the mechanism of its adsorption. As a result, the role of these species in catalysis is still not completely understood.

NMR is an excellent technique for the study of adsorbed hydrogen due to the sensitive dependence of the resonance position on both environment and state of molecular motion. A great deal of NMR work done to date has been concerned with low-resolution broadline studies or the determination of molecular correlation times by study of the NMR relaxation times (*9*). Cirillo *et al.* have studied the hydrogen held by solids such as Al_2O_3 and Mo/Al_2O_3 by a combination of wide-line NMR and adsorption–desorption techniques (*10*). We have used ^1H nuclear magnetic resonance spectroscopy to study the adsorption of H_2 on a supported metal catalyst, Rh/TiO_2. With this technique combined with ESR and TPD studies, we have been able to demonstrate that there are at least two hydrogenic species on the surface of this catalyst when placed under a H_2 atmosphere. One of these is strongly adsorbed and is associated with Rh atoms, and the other is weakly adsorbed on the support.

METHODS

NMR spectra were taken on a home-built spectrometer similar to that described by Vaughan *et al.* (*14*), but with gating and phase shifting of the sort used by Gerstein *et al.* (*15*). The spectrometer operates at a frequency of 56.405 MHz for the proton resonance ($H_0 = 1.325$ T). Observation of a NMR signal above the noise in a single experiment requires at least 10^{19} spins in

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this apparatus. Since the magnet has no active lock, our ability to improve S/N is limited by the stability of the magnet system. Typical runs of 2–4 h were possible. The proton spectra were recorded by coaddition of from 250 to 1000 transients, followed by Fourier transformation in a PDP-11/10 computer. Sample temperature regulation is accomplished by a conventional gas flow cryostat. ESR spectra of the same samples were recorded with a Varian E-109 ESR spectrometer operating at a frequency of 9.41 GHz. Minimum detectable signals for our ESR spectrometer, based on the observed linewidth, is about 10^{15} spins. All experiments were performed on samples in a specially designed flow reactor, which allowed the NMR and ESR spectra to be taken without removing the sample from its environment, thus eliminating the chance of contamination of the surface. Moreover, this reactor can be attached to a volumetric system for measurement of H_2 adsorption and TPD.

The TiO_2 was prepared by hydrolysis of titanium isopropoxide (Tyzor) by adding dropwise to Tyzor a water–isopropanol solution. The resultant precipitate was washed, dried, and calcined at 400°C under 1 atm of O_2 to remove any organic impurities. X-Ray analysis indicated that the TiO_2 formed was primarily anatase, although traces of brookite were observed. The BET surface area (N_2) was 103 m^2/g. Impregnation of Rh on the support was accomplished by the "wet" method from a solution of $Rh(NO_3)_3$. The pH of the solution was deliberately kept high by addition of ammonium hydroxide to prevent modification of the support during treatment and to form rhodium ammonia complexes. This technique results in catalysts of high dispersion. The catalyst was washed, dried, and calcined at 350°C under O_2 flow. The final catalyst was analyzed by atomic absorption spectroscopy and was found to contain 3.8 wt% rhodium. The H_{irr}/Rh atomic ratio, as determined by hydrogen chemisorption, was 0.6 at an equilibrium H_2 pressure of 50–120 Torr.

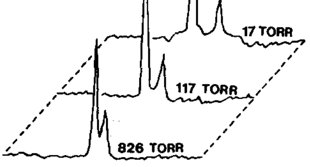

FIG. 1. ^1H NMR spectra of H_2 on Rh/TiO_2 pretreated at 300°C at a number of equilibrium pressures.

The samples were pretreated at one of two temperatures, 300 or 400°C, under hydrogen flow (1 atm, 40 cm/min). The reduced sample was then outgassed at the reduction temperature and, after cooling, was equilibrated with a desired pressure of H_2. The NMR spectra were recorded at either 25, −15, or 100°C. ESR spectra were recorded at 25°C.

RESULTS AND DISCUSSION

The proton NMR spectra of the catalyst samples pretreated at 300°C are shown in Fig. 1. Each spectrum consists of two distinct resonances at all pressures of H_2 studied. The position of the resonance at low field is independent of hydrogen pressure and falls within a few parts per million of the resonance of an external TMS sample. The resonance at higher field shifts toward lower field and increases slightly in intensity relative to the low-field resonances, as the H_2 pressure is increased. After vacuum degassing at room temperature, the proton NMR spectrum of the catalyst shows only one resonance, as in Fig. 2, the peak position corresponding to the low-field resonance observed on the previous samples. It is clear that the upfield resonance corresponds to a rather weakly adsorbed hydrogenic species. The extremely large (several kHz) isotropic shift associated with this species is assigned to a species interacting with paramagnetic centers. The ESR spectrum of TiO_2 (Fig. 3) shows a strong signal near $g = 2.0$, indicating the presence of

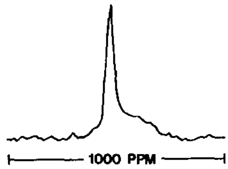

FIG. 2. ^{1}H NMR spectrum of H_2 on Rh/TiO$_2$ after pretreatment at 300°C followed by outgassing.

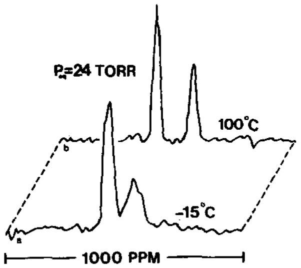

FIG. 4. ^{1}H NMR spectra of H_2 on Rh/TiO$_2$ pretreated at 300°C, at (a) −15°C; (b) 100°C. P_{eq} = 24 Torr.

paramagnetism in the support. The loosely held species is therefore adsorbed on the support. The downfield resonance does not experience a paramagnetic shift and corresponds to a more strongly bound surface species adsorbed on the rhodium.

Spectra taken at two different temperatures are shown in Figs. 4 and 5 at hydrogen pressures of 24 and 117 Torr (1 Torr = 133.3 Nm^{-2}), respectively. At the lower temperature for both pressures, the upfield resonance is broadened and experiences a *smaller* upfield shift than at room temperature. The downfield peak is unshifted from its position at room temperature. At the higher temperature the resonances are somewhat sharper and the paramagnetically shifted resonance is shifted farther upfield than it is at room temperature. The position of the downfield resonance is again unaffected by changes in temperature. The paramagnetic or pseudocontact shift is in itself temperature independent; however, if the shifted species is mobile its contact time with the paramagnetic center and, therefore, its shift may change with temperature in the fast exchange limit. At higher temperatures the mobility of the support-associated species is increased, and it will come in contact with more paramagnetic Ti^{3+} sites. The reverse effect is seen at low temperatures. The smaller upfield shift of this species indicates that its mobility is decreased at lower temperatures and fewer Ti^{3+} sites are contacted on average.

The pressure dependence of the paramagnetic shift of the mobile species may be explained by similar arguments. As the equilibrium pressure of H_2 is increased, the number of mobile hydrogens on the support is increased. Since the number of Ti^{3+} sites is fixed, there is a greater competititon for these sites as more hydrogens are adsorbed. Thus, at higher pressures the mobile hydrogens will contact fewer Ti^{3+} sites on average and their upfield shift will be decreased.

The NMR spectra of the hydrogen on the Rh/TiO$_2$ catalyst, which has been pretreated at 400°C, are shown as a function of hydrogen pressure in Fig. 6. A comparison of these spectra with those of Fig. 1 shows marked spectral differences for the adsorbed hydrogen depending upon the cata-

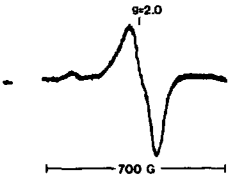

FIG. 3. ESR spectrum of TiO$_2$ catalyst after reduction at 300°C.

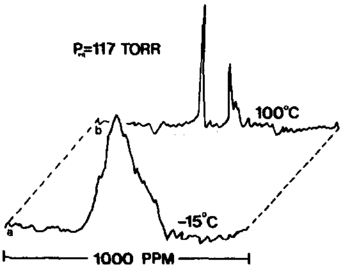

FIG. 5. ^{1}H NMR spectra of H_2 on Rh/TiO$_2$ pretreated at 300°C, at (a) −15°C; (b) 100°C. P_{eq} = 117 Torr.

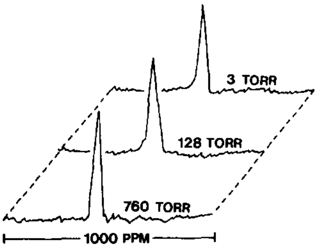

FIG. 6. ^1H NMR spectra of H_2 on Rh/TiO_2 pretreated at 400°C at a number of equilibrium pressures.

lyst pretreatment temperature. At all equilibrium pressures of hydrogen, a single resonance is observed. This resonance is coincident with the position of the downfield stationary resonance observed on the catalyst pretreated at 300°C. In no spectra is a paramagnetically shifted resonance observed at this reduction temperature. No ESR signal is obtained from TiO_2 pretreated at 400°C. This must result from a decrease in the number of paramagnetic centers. The decrease in paramagnetic species removes the mechanism for distinguishing metal-associated hydrogen from support-associated hydrogen.

The adsorption of hydrogen by pure TiO_2 is extremely small, being only one-tenth that of Rh/TiO_2. Figure 7 shows the proton NMR spectrum of H_2 equilibrated with TiO_2 pretreated under H_2 flow at 300°C exactly as the Rh/TiO_2 catalyst was. There is very little change in the spectrum as the pressure is changed. The resonance is broad and is present when the hydrogen is removed by outgassing under vacuum. ESR spectra of this sample show the presence of paramagnetic species, but nowhere in the NMR spectrum is there evidence of a paramagnetically shifted resonance from a mobile species similar to that seen with Rh on the surface. The weak resonance is attributed to surface hydroxyls and is broadened, either by the nuclear dipolar interaction or, perhaps, by interaction with paramagnetic species.

The TPD spectrum of the catalyst is shown in Fig. 8. This TPD experiment was performed on samples pretreated under H_2 flow (30 cm^3/min) for 4 h at 300°C then cooled to room temperature still under H_2 flow. From Fig. 8 it is clear that there are at least three forms of hydrogen species on the catalyst, giving maxima at 80, 240, and 540°C, respectively. To correlate NMR results with the TPD results, an interrupted TPD was carried out. NMR spectra were recorded at various points in the TPD using the same NMR reactor attached to the vacuum manifold used in TPD experiments. This procedure allowed determination of which species remain on the surface at each stage. At point A only argon has been passed over the catalyst at room temperature. The NMR spectrum at this stage already shows the removal of the weakly adsorbed species. At points B and C, the nonparamagnetically shifted resonance is the only one observed, and the intensity of the NMR signal decreases as the desorptions occur. All the desorption peaks therefore correspond to rhodium-bound species, which are not paramagnetically shifted in the NMR experiment. At point D, where all hydrogen has been desorbed, no NMR signal is observed.

It is clear from the NMR results that there are at least two distinct species on the

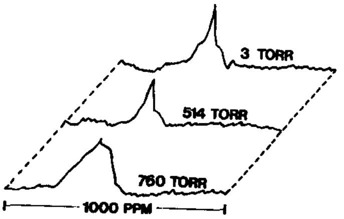

FIG. 7. ^1H NMR spectra of H_2 on TiO_2 pretreated at 300°C at a number of equilibrium pressures.

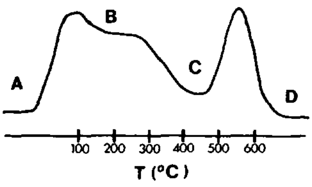

FIG. 8. TPD spectrum of Rh/TiO_2 showing points where NMR spectra were taken.

surface, one of which is relatively weakly bound and one which is strongly bound. It is clear from the studies of pure TiO_2 samples that the adsorption of all of these species requires the presence of the metal on the surface; i.e., the rhodium promotes the adsorption of weakly, as well as strongly, adsorbed hydrogen. Although only one resonance is observed for the catalyst samples pretreated at 400°C, this does not necessarily imply that a mobile species is not present on these samples. One, in fact, would infer that the resonances are overlapping and unresolvable without the extremely large shift due to paramagnetism. This argument is consistent with the ESR observation that paramagnetic centers are not present on TiO_2 pretreated at 400°C. The presence of various forms of adsorbed hydrogen, as indicated by the TPD results, shows that the downfield NMR resonance is composed of several chemically distinct forms of hydrogen. It may be that in experiments such as the CRAMPS experiments of Gerstein *et al.* (*16*), one may be able to improve resolution sufficiently so that the rather small differences in the chemical shift of these species will be resolvable.

A model of the Rh/TiO_2 surface consistent with our observations is shown in Fig. 9. H_2 is primarily adsorbed on the rhodium, some retaining its molecular character and some being dissociatively adsorbed into atoms (species a). The hydrogen species interacting with the metal are rather strongly held. Species b is relatively free to move about on the support. In the course of its motion it may encounter paramagnetic sites (Ti^{3+}). Its NMR shift will depend on the number of paramagnetic sites and the likelihood of accessing them. These paramagnetic sites may be formed during either the reduction of the catalyst with H_2 or the subsequent outgassing. "Spillover" hydrogen atoms formed during the reduction may scavenge hydroxyl groups during outgassing, leaving the surface as water. This process leaves an anion vacancy on the titania which is in the +3 oxidation state after loss of the hydroxyl. This type of behavior has been observed on other supported metal catalysts (*17*). Subsequent treatment with hydrogen may lead to the heterolytic adsorption of H_2 directly on the support (*18*), the mobile H^- species stabilizing the Ti^{3+} and the H^+ species interacting with oxygenic species known to exist on reduced anatase (*19*). However, one cannot rule out the possibility that the mobile species is an atomic species which is formed at the rhodium metal and "spills over" onto the TiO_2 surface. Other studies indicate that this "spillover" hydrogen desorbs at high temperature on catalysts exhibiting this behavior (*12*), whereas the mobile species observed here desorbs by simply passing argon over the sample at room temperature.

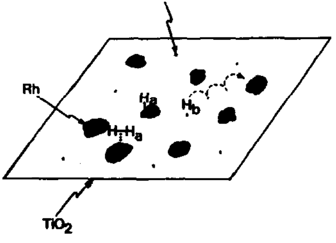

FIG. 9. Model of hydrogen adsorption on Rh/TiO_2.

The reduction of the pure anatase is probably of a different form. Without the metal to activate the hydrogen, reduction may only occur by reductive adsorption by formation of surface hydroxyls (*18*). The electron donated by the hydrogen can reduce the titanium from the +4 to the +3 oxidation state; however, the titanium maintains its coordination sphere and no anion vacancies are formed. Heterolytic adsorption, therefore, cannot take place and no mobile species is formed.

CONCLUSIONS

Nuclear magnetic resonance has been used in conjunction with ESR spectroscopy and temperature-programmed desorption to study the states of H_2 adsorbed on

Rh/TiO_2 and TiO_2 catalysts. The paramagnetism of the support under certain pretreatment conditions allows distinguishability by NMR of two species of hydrogen on Rh/TiO_2, reversibly adsorbed support-associated hydrogen, and irreversibly bound metal-associated hydrogen. Study of the spectra at various stages of desorption indicate that the nonparamagnetically shifted resonance is actually a superposition of resonances from several distinct species. None of these types of adsorbed hydrogen are observed on the pure TiO_2, indicating that the metal is necessary in activating the hydrogen and leading to formation of both reversibly and irreversibly formed hydrogen.

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