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Electron Spin Resonance and Nuclear Magnetic Resonance Study of the Reduction of Rh/TiO_2 Systems at 298 K

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The reduction of Rh/TiO_2 catalysts is monitored with ESR and NMR spectroscopies. Reduction is observed to occur readily at 298 K on Rh/TiO_2, whereas it does not occur on TiO_2 to any appreciable extent. The hydrogenation of benzene over the Rh/TiO_2 catalyst at 298 K is observed. The results can be interpreted in terms of spillover-hydrogen production.

Introduction

The spillover phenomenon plays a significant role in certain heterogeneous catalytic reactions,[1] such as hydrogenation, the Fischer–Tropsch synthesis of oxyalkanes, and hydrogen–deuterium exchange among support hydroxyls. Several spectroscopic techniques have been used to monitor the production and effects of such spillover on catalysts.[2-6] In particular, proton nuclear magnetic resonance (NMR) spectroscopy can be used to observe the interaction of hydrogen with supported metal catalysts.[3-6] Electron spin resonance (ESR) spectroscopy is particularly informative of the state of paramagnetic species formed in these processes, as has been demonstrated in investigations of the reduction of Pt/TiO_2[7,8] and Rh/TiO_2[9] catalysts at high temperatures. Homolytic cleavage of hydrogen at the metal has been proposed to occur during these reductions, after which spillover to the support surface causes the production of paramagnetic Ti^{3+} observable by ESR spectroscopy.

The previous studies of reduction, both on Rh/TiO_2 and on Pt/TiO_2, have been directed at (1) determining the relationship between catalyst reducibility and the induction of the strong metal–support interaction (SMSI), and (2) elucidating the differences between the reductive processes occurring on TiO_2 and Rh/TiO_2 at high temperatures. The proposed induction of SMSI, of course, requires high temperatures. In both systems (Pt/TiO_2 and Rh/TiO_2), the reversibility of hydrogen adsorption was illustrated, provided that the SMSI had not been induced. In this paper, we examine the reducibility of Rh/TiO_2 catalysts at 298 K by ESR and NMR spectroscopies and the effect of spillover hydrogen on the hydrogenation of benzene at 298 K.

Experimental Section

TiO_2 was prepared by the hydrolysis of titanium isopropoxide (Du Pont Tyzor organic titanate). The Rh/TiO_2 catalysts were prepared by the wet impregnation method from a solution of $Rh(NO_3)_3$ containing a small amount of NH_4OH. The TiO_2 was primarily anatase. The two Rh/TiO_2 samples were 3.8 and 0.7 wt % rhodium. These samples have been described previously.[9]

ESR spectra were recorded at room temperature (298 K) and low temperature (150–200 K) with a Varian E-109 spectrometer. Sample treatments were performed in a Pyrex reactor, equipped with high-vacuum Teflon stopcocks, which could be directly connected to volumetric adsorption equipment. After treatment, the samples could be transferred to the reactor's quartz side arm, which could be inserted directly into the ESR cavity.

^1H NMR spectra were obtained on a home-built spectrometer operating at 56.4 MHz (1.32 T) for protons. Spectra were obtained by the accumulation of transients, followed by Fourier transformation in a PDP-11 minicomputer. During NMR studies, catalyst samples were contained in a Pyrex reactor similar to the one described above, except the one used in NMR experiments had a 5-mm NMR tube attached as a side arm, for insertion into the NMR probe.

All gases were of the highest purity obtainable. H_2 was obtained from Air Products and CO from Matheson. The benzene used was obtained from Fisher (Certified ACS Spectranalyzed).

Results and Discussion

After calcination at 673 K under flowing oxygen and outgassing to 1.0×10^{-3} torr (1 torr = 133.3 N m^{-2}) at 298 K, the ESR spectra of TiO_2 and Rh/TiO_2 exhibit only weak resonances near $g = 2.00$ (Figure 1A), due to oxygen radicals present at lattice defects.[10] The exposure of each of these samples to 500 torr of H_2 at 298 K has profoundly different results for Rh/TiO_2 than for TiO_2. For TiO_2, this process results in no additional detectable ESR signals.

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[⊥] Contribution No. 3326.

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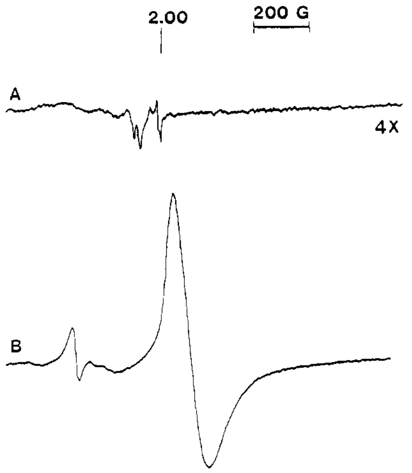

Figure 1. ESR spectra of 0.7 wt % Rh/TiO_2 obtained at 298 K: (A) sample after calcination at 673 K in flowing O_2; (B) sample after exposure to 500 torr of H_2 at 298 K.

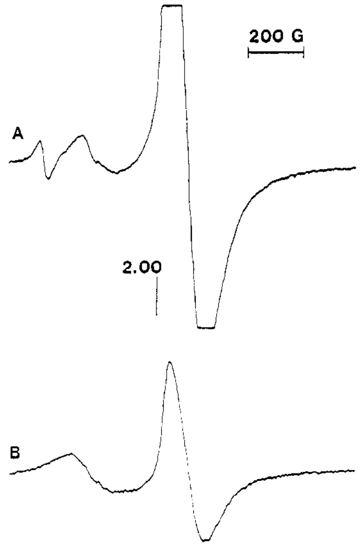

Figure 2. ESR spectra of 0.7 wt % Rh/TiO_2 obtained at 160 K: (A) after exposure to 500 torr of H_2 at 298 K; (B) after subsequent outgassing to 25 × 10^{-3} torr at 298 K.

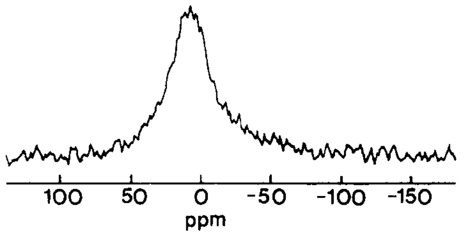

Figure 3. ^1H NMR spectrum of 0.7 wt % Rh/TiO_2 after exposure to 500 torr of hydrogen at ambient temperatures.

It is well-known that such a process carried out at 573 K or higher produces Ti^{3+} radicals in TiO_2.[7,9,10] However, exposure of the Rh/TiO_2 catalyst to 500 torr of H_2 at 298 K results in the appearance of a resonance at $g = 1.94$ (Figure 1B), characteristic of Ti^{3+} ions in octahedral environments.[10] Thus, the reduction of the support is a facile process, even at 298 K, if rhodium is present. Furthermore, the resonance observed is identical in line shape and position to resonances observed under reducing conditions at 573 K,[7,9] where the results have been interpreted by assuming that homolytic cleavage of hydrogen occurs at the metal, followed by spillover to the support:

$$^1/_2H_2 \overset{Rh}{\rightleftharpoons} H\cdot \rightleftharpoons H\cdot_{spillover} \tag{1}$$

$$Ti^{4+}O^{2-} + H\cdot_{spillover} \rightleftharpoons Ti^{3+}OH^- \tag{2}$$

Outgassing of these samples, at 298 K, leads to a decrease in the number of Ti^{3+} species observed by ESR. Thus, the reactions in eq 1 and 2 must be, at least partially, reversible (Figure 2).[7,9,11]

In addition to the resonance attributable to Ti^{3+}, there are two additional resonances (Figures 1B and 2) in the ESR spectrum of the reduced Rh/TiO_2. These resonances occur at $g = 2.29$ ($\Delta H_{pp} = 30$ G) and at $g = 2.16$. Upon slight outgassing at 298 K (25 × 10^{-3} torr), the resonance at $g = 2.29$ disappears (Figure 2). The resonance at $g = 2.16$ remains unchanged upon outgassing at 298 K. These two resonances may be attributed to the presence of Rh^{2+} in the sample upon reduction at 298 K. Typical g values for low-spin d^7 ions, like Rh^{2+}, have been reported to occur in the range from $g = 2.1$ to $g = 2.3$.[12] The resonance at $g = 2.29$ may be associated with $Rh^{2+}OH^-$, which formed during spillover. The results of the outgassing experiment indicate that the decrease in this signal parallels the decrease of the Ti^{3+} signal, presumably because the production of these Rh^{2+} species is also reversible:

$$Rh^{3+}O^{2-} + H_2 \underset{\text{outgassing}}{\overset{\text{reduction}}{\rightleftharpoons}} Rh^{2+}OH^- + H\cdot_{spillover} \tag{3}$$

In our previous study,[9] Rh^{2+} species were never observed after reduction in H_2 at 573 K. Presumably, under such stringent conditions of reduction, the concentrations of Rh^{2+}, if they remain at all, are too low to be detected. On the other hand, if reduction is carried out under milder conditions as was done in this study, the production of rhodium in several oxidation states, including Rh^{2+}, is likely.[13]

A further indication of the nature of these species can be gained from the effects of adsorption of carbon monoxide on the resonances due to Rh^{2+}. The ESR spectrum of a catalyst which had been exposed to carbon monoxide at 298 K, subsequent to H_2 reduction described above, has much weaker resonances due to Rh^{2+} than the sample before adsorption of CO. This result is consistent with the formation of carbonyl species when CO interacts with the noble metal.[14] In a further experiment, when a freshly calcined sample of Rh/TiO_2 is first exposed to 200 torr of CO at 298 K, followed by exposure to 500 torr of H_2, also at 298 K, *no* ESR-detectable amounts of Ti^{3+} are produced. Thus, "poisoning" of the rhodium surface, probably through formation of rhodium carbonyl species,[2f] occurs at room temperature, which is a further indication that the spillover processes of eq 1–3 are occurring on the surface.

Proton NMR spectra of the calcined Rh/TiO_2 samples show only a single resonance centered at δ 5 ppm relative to external tetramethylsilane (TMS), attributable to hydroxyl groups on the TiO_2 support.[4,15,16] After reduction with H_2 at 298 K, either statically at 500 torr or in a hydrogen flow, the surface is reduced, indicated by a color

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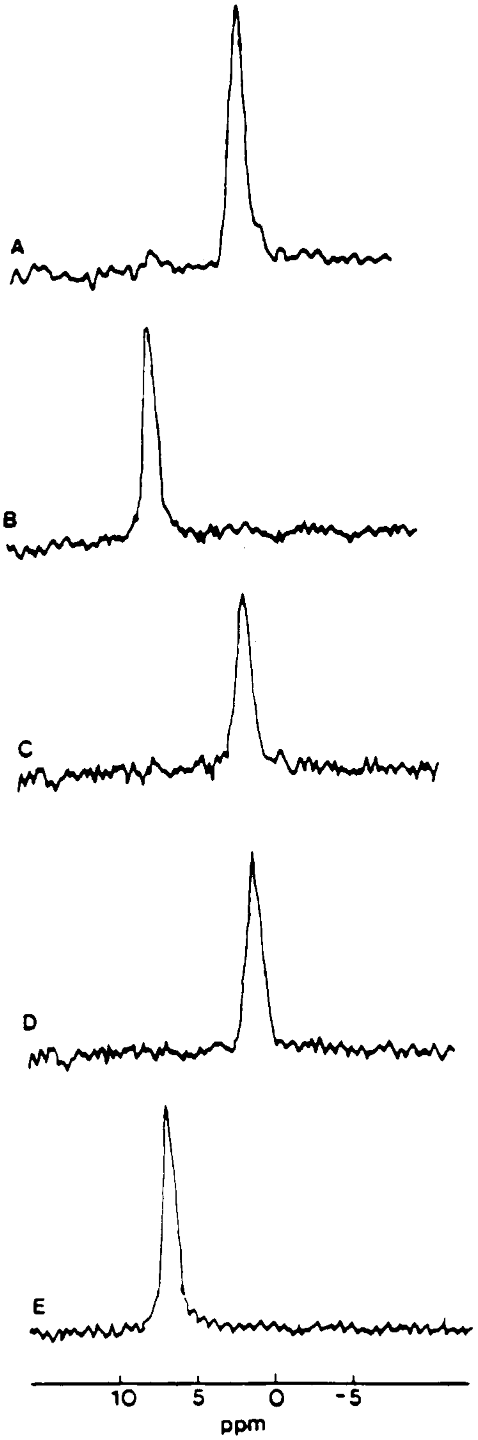

Figure 4. ^{1}H NMR spectra of the 0.7 wt % Rh/TiO$_2$ sample: (A) spectrum obtained after exposure of the reduced sample to (H$_2$, 500 torr, 298 K) 30 torr of benzene at 298 K; (B) spectrum obtained after exposure of the calcined sample to 30 torr of benzene at 298 K; (C) spectrum obtained after exposure of the calcined sample to 15 torr of cyclohexane at 298 K; (D) spectrum obtained after exposure of the reduced sample (H$_2$, 500 torr, 298 K) to 15 torr of cyclohexane at 298 K; (E) spectrum obtain after *prolonged* exposure of the reduced sample (H$_2$, 500 torr, 298 K) to flow of Ar saturated with C$_6$H$_6$ vapor at 298 K.

change and the appearance of Ti^{3+} resonances in the ESR spectrum (Figure 1). The NMR spectrum of this material still shows only the resonance centered at δ 5 ppm (Figure 3). None of the extremely mobile, upfield-shifted hydrogen species, observed for similar samples reduced at 573 K,[4,5] are seen in this spectrum. It should be noted that previous NMR investigations have shown rhodium hydride species to be centered at δ 0 ppm.[3-6] Other workers[14,15] have attributed highly upfield-shifted resonances to the existence of a rhodium hydride species. NMR-detectable amounts of rhodium hydride species might not form at room temperature. If such species are formed, they still might not be visible in the NMR due to the paramagnetism of some of the rhodium.

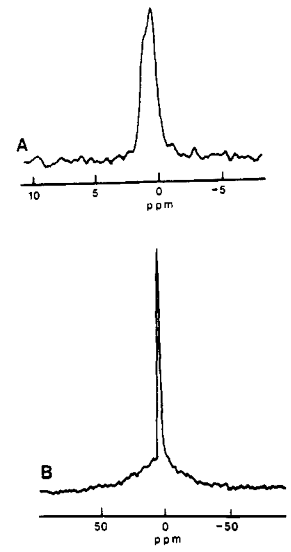

Figure 5. ^{1}H NMR spectra of a sample of 0.7 wt % Rh/TiO$_2$ after exposure to 500 torr of hydrogen at 298 K and subsequent exposure to 30 torr of benzene at 298 K: spectrum A shows an expanded view of the resulting cyclohexane resonance while spectrum B illustrates that the resonance due to the -OH species is still present after the hydrogenation reaction has occurred.

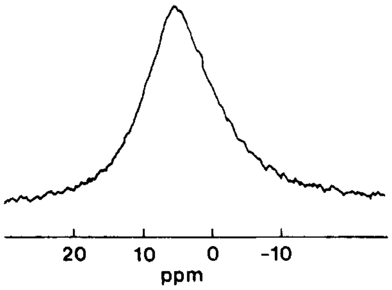

Figure 6. ^{1}H NMR spectrum of a calcined sample of 3.8 wt % Rh/TiO$_2$ after exposure to 30 torr of benzene at 298 K.

Supported metals are frequently used as hydrogenation catalysts, and one of the classical reactions over such catalysts is the hydrogenation of benzene. The result of exposing a sample of previously reduced Rh/TiO$_2$ (0.7 wt %; reduction at 298 K) to 30 torr of benzene at 298 K is given in Figure 4A. A single resonance with a full width at half-maximum of 1.2 ppm centered at δ 0.5 ppm is the only feature in this spectrum. The spectrum of benzene on the calcined, *but unreduced*, Rh/TiO$_2$ is shown in Figure 4B. The single resonance in this spectrum is located at 6.8 ppm. Exposure of a calcined, unreduced, Rh/TiO$_2$ catalyst to cyclohexane results in a single resonance (Figure 4C) centered at δ 0.5 ppm. Exposure of the reduced 0.7 wt % Rh/TiO$_2$ catalyst to cyclohexane results in the NMR spectrum of Figure 4D, which also shows a resonance at δ 0.5 ppm. Extensive exposure of a previously reduced sample to benzene in an argon flow results in the spectrum shown in Figure 4E. Obviously, the benzene has been hydrogenated by species produced during the exposure of the surface to H$_2$ at 298 K in the previous step, resulting in the appearance of cyclohexane. It is also obvious from Figure 4E that these species can be exhausted by prolonged exposure to benzene. On a wider scale than that of Figure 4, it can be observed that, during this process, the hydroxyl

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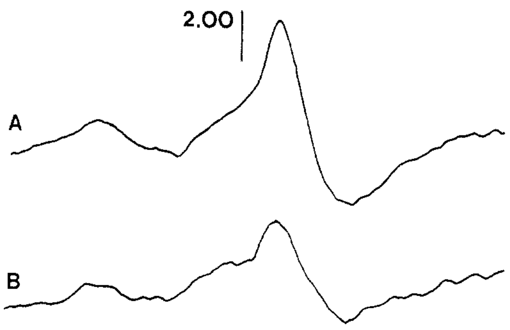

Figure 7. Ambient temperature ESR spectra of the 0.7 wt % Rh/TiO_2 catalyst: (A) after exposure to 500 torr of H_2 at 298 K and subsequent evacuation to 25 × 10^{-3} torr; (B) after further treatment of this sample with 30 torr of benzene at 298 K.

groups present before addition of benzene are still present (Figure 5) after no further cyclohexane is produced.

The data presented in Figures 4 and 5 illustrate the resolution obtainable for the 0.7 wt % Rh/TiO_2 catalyst. Figure 6 gives the NMR spectrum of benzene adsorbed on a calcined 3.8 wt % Rh/TiO_2 catalyst. The single resonance is shifted slightly (δ 5.5 ppm) and is substantially broader (fwhm = 11.6 ppm) than the resonance of benzene on the 0.7 wt % Rh/TiO_2 catalyst (Figure 4B). This broadening is a function of metal-particle size dispersion which is larger on the 3.8 wt% Rh/TiO_2 sample than on the 0.7 wt % Rh/TiO_2 sample. This phenomenon will be more fully described in a future publication.[16]

The hydrogenation of benzene can be observed via proton NMR spectroscopy of the benzene itself. Since the benzene participates in a reaction with an active hydrogen species derived from the species which produces Ti^{3+} (Figure 7A), the hydrogenation may also be monitored via the depletion of Ti^{3+} as hydrogenation progresses (Figure 7B). The important implication of this result is that the species produced by the interaction of hydrogen with the metallized surface and that produces Ti^{3+}, i.e., the spillover hydrogen, must also participate in the hydrogenation reaction.

Conclusions

The reduction of TiO_2 surfaces by hydrogen is a facile process at 298 K if Rh is present on the surface. No similar processes are detected when TiO_2 alone is exposed to H_2 at 298 K. The reduction is postulated to occur via production of hydrogen atoms which spillover to the support, resulting in the formation of $Ti^{3+}OH^-$ units. The process is partially reversible, as seen by the effect of outgassing on the ESR spectrum of this material. Two types of Rh^{2+} species are formed during reduction at 298 K, one of which is reversibly removed by outgassing at 298 K. Carbon monoxide adsorption occurs in such a way as to decrease the number of Rh^{2+} species in the sample, presumably by the formation of rhodium carbonyls. The carbon monoxide adsorption can "poison" surface sites where reduction occurs, as can be seen from the preadsorption experiments. Benzene is hydrogenated to cyclohexane by catalysts of this type, even when hydrogen is preadsorbed. Reaction of benzene continues until some surface species, but not the initially present hydroxyl groups ($Ti^{4+}OH^-$), is exhausted. The results strongly imply that the species reducing the surface, the spillover hydrogen, does participate in the benzene hydrogenation.

Registry No. Rhodium, 7440-16-6; titanium dioxide, 13463-67-7; benzene, 71-43-2; atomic hydrogen, 12385-13-6; carbon monoxide, 630-08-0.

Low-Resolution Microwave Studies of Substituted Ethyl- and Isopropylbenzenes

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A single conformation exists in ethylbenzenes with the ethyl C–C bond lying in a plane orthogonal to the benzene ring. This conclusion results from the observation that asymmetrically substituted ethylbenzenes each display only a single band series in low-resolution microwave (LRMW) spectra whereas any other conformation of the ethylphenyl fragment would result in two spectroscopically distinguishable species. LRMW spectra of isopropylbenzene derivatives display three spectroscopically distinguishable band series, two of which correspond to the conformation with the methine C–H bond eclipsed with the benzene ring and syn or anti with respect to an unsymmetrical phenyl substituent. The third series is much more intense, has a $B + C$ value which is the average of the syn and anti forms, and is consistent with the superposition of spectra of torsionally excited species.

Introduction

The barrier to internal rotation of the methyl group in toluene is exceedingly small, 14 cal/mol (5 cm^{-1}).[1] The most stable conformation has not been characterized. Many studies have reported on the most stable conformation of ethylbenzene but their conclusions conflict. From the chemical shift of the methylene protons of ethylbenzene in CCl_4 solution,[2] the skew form (methyl

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