Optimization of the Volumetric Hydrogen Chemisorption Technique for Dispersions of Ru/SiO$_2$ Catalysts

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Metal dispersions of silica-supported ruthenium catalysts determined by the standard volumetric chemisorption technique were found to be inaccurate due to irreversible spillover of hydrogen to the support. Direct evidence was obtained via *in situ* ^{1}H NMR for an irreversibly bound component of the hydrogen that migrated from the metal to the support on a time scale of tens of minutes or longer at room temperature. It was also shown in this work that hydrogen saturated the surface of the metal particles on a shorter time scale, on the order of minutes. Based on ^{1}H NMR, optimum conditions for the volumetric chemisorption method were determined in order to alleviate the interference of spillover with measurements of hydrogen uptake on the metal. Ruthenium dispersions obtained from the optimized volumetric chemisorption technique were more accurate and agreed well with the results of the ^{1}H NMR method. © 1995 Academic Press, Inc.

INTRODUCTION

The relatively simple nature of hydrogen adsorption on most metals makes it useful as a method to characterize dispersions of supported metal catalysts (1, 2). A disadvantage of this approach is that it may involve inaccuracies due to the presence of irreversibly bound, spilled over hydrogen on the support (3, 4). The amount of this spilled over hydrogen is a strong function of the metal and its dispersion, the support material, the adsorption temperatures, and exposure times (3–10).

The hydrogen chemisorption technique currently used to characterize supported metal catalysts was described by Dalla Betta (1) and Goodwin (2). In this technique, isotherms (typically room temperature) are obtained for the total and weakly bound hydrogen over a pressure range of 0 to 100 Torr. The total hydrogen (H_{total}) isotherm is defined as the total amount of hydrogen taken up by the catalyst. Weakly bound hydrogen (H_{weak}) is defined as that which can be easily removed, for example, by a 10 min evacuation at 10^{-5} Torr. Both H_{total} and H_{weak} isotherms show a linear dependence with pressure in the 0 to 100 Torr range. The hydrogen remaining on the surface after

evacuation is defined as the strongly bound hydrogen (H_{strong}). The amount of H_{strong} is obtained by extrapolating the linear portions of the H_{total} and H_{weak} isotherms to zero pressure and taking the difference between the intercepts. Metal dispersions are calculated assuming an H_{strong}-to-metal stoichiometry of 1. The above technique does not overlook the possibility of the presence of spilled over hydrogen ($H_{spillover}$) on the support. However, it invokes the assumption that $H_{spillover}$ is weakly bound at room temperature and that it can be eliminated by evacuation for a short period of time.

In this paper we report evidence obtained by ^{1}H NMR spectroscopy for an irreversibly bound, spilled over hydrogen on the silica support. We also report conditions for volumetric chemisorption experiments under which dispersion determinations are relatively free from the influence of hydrogen spillover.

METHODS

Catalyst Preparation

All of the catalysts used in this study contained 4 wt% Ru and were prepared via an incipient wetness technique using either ruthenium nitrosyl nitrate (26% Ru, Johnson-Matthey) or a ruthenium nitrosyl nitrate solution (Strem Chemicals, 1.5 wt% Ru). The first catalyst, designated Ru/SiO$_2$(I), was prepared from the ruthenium nitrosyl nitrate obtained from Johnson-Matthey by dissolving the appropriate amount of salt in 2.2 ml water per gram of support. A slurry was prepared by adding the support (Cab-O-Sil HS5) to this solution. It was then dried in air at 383 K for 8 h. Subsequently, the catalyst was reduced and washed in boiling water to remove Na and/or Cl contaminants. A second catalyst, Ru/SiO$_2$(II), was prepared from the ruthenium nitrosyl nitrate solution obtained from Strem Chemicals. The volume of the solution needed to prepare a 4 wt% Ru/SiO$_2$ catalyst was 2.6 ml per gram of support. After the slurry was prepared this catalyst was dried in air overnight and at 383 K for 2 h. By using ^{1}H NMR spectroscopy it was determined that the final catalyst dis-

persions were 10 ± 2 and $28 \pm 4\%$ for Ru/SiO₂(I) and Ru/SiO₂(II), respectively.

Hydrogen Uptake by the Volumetric Method

Hydrogen uptake on the catalysts was measured by the volumetric method using a home-built absorption apparatus described elsewhere (11). About 1 g of catalyst was placed in a Pyrex cell with a coarse frit which enabled the reduction of the catalyst in flowing hydrogen. The cell was heated to 423 K while helium was flowing and maintained at that temperature for about 30 min to remove moisture. The catalysts were reduced in flowing hydrogen for 2 h at temperatures between 623 K and 723 K, and then evacuated to 10^{-6} Torr for 4 h at the reduction temperature. Hydrogen uptake measurements were carried out at temperatures between 293 and 393 K with exposure times varying between 10 min and several hours. Hydrogen adsorption isotherms were determined as described in the introduction.

NMR Experiments

¹H NMR experiments were carried out at a proton resonance frequency of 250 MHz, using a home-built spectrometer and a home-built in situ probe capable of operation at variable temperature and pressure. About 100 mg of unreduced catalyst was placed in the sample chamber of the probe. The sample pretreatment procedure for the in situ NMR experiments was the same as that used in the volumetric method. After reduction and evacuation, hydrogen was dosed onto the sample at the desired temperature and pressure and the NMR spectra were acquired. To study the hydrogen-on-metal resonance located at about −60 ppm (from TMS), 200 to 1000 scans were acquired using a recycle time of 0.4 s. Due to the long spin–lattice relaxation times, the true intensity of the hydrogen-on-support resonance was determined separately by acquiring 10 scans with a recycle time of 50 s. The absolute intensities of NMR peaks were obtained by comparing the integrated signal intensity with that of a water reference sample. To account for inhomogeneities in the pulse lengths along the probe coil the reference water was analyzed in a capillary tube the length of the catalyst samples.

The spilled over hydrogen had a resonance frequency (3 ppm from TMS) and line shape similar to the silanol in the support but it contributed only 3–4% of the total intensity of that resonance. In order to better determine the amount of the spilled over hydrogen via ¹H NMR spectroscopy the resonance intensity of the silanol protons was reduced by deuterium exchange. Deuterium exchange was carried out in situ under D₂O vapor and D₂ gas. A reduced and evacuated catalyst sample (Ru/SiO₂(II)) was first exposed to 15 Torr of D₂O vapor at room temperature. The
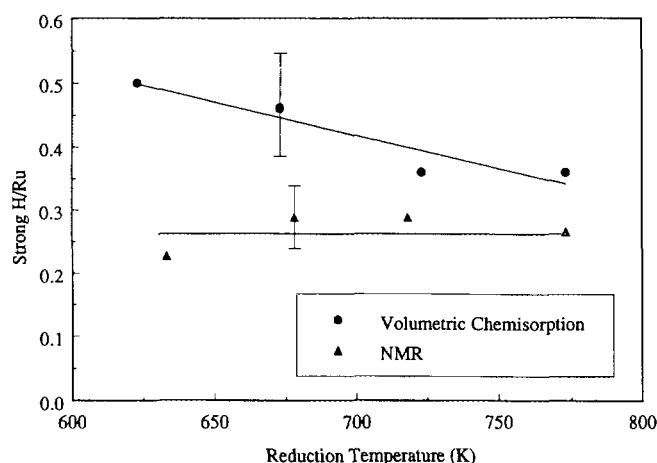

FIG. 1. H_{strong}/Ru obtained from ¹H NMR and volumetric hydrogen chemisorption for Ru/SiO₂(II).

temperature was then gradually increased to 383 K under 500 Torr of D₂, and after 15 min, the D₂O + D₂ mixture was replenished. This procedure was repeated twice before evacuation. The temperature was then gradually raised to 623 K under 500 Torr D₂. The sample was kept at this temperature for two hours and D₂ gas was replenished every 10 min. After two hours, more than 90% of the proton intensity associated with the support was eliminated. Finally, the sample was evacuated at 623 K for 1 h and overnight at room temperature. The amount of spilled over hydrogen was obtained by noting the increase in the diamagnetic resonance of deuterated samples under hydrogen gas.

RESULTS AND DISCUSSION

In Fig. 1 the amounts of irreversibly bound hydrogen on ruthenium (H_{strong}/Ru) obtained from NMR spectroscopy are compared with those found using the standard volumetric technique at room temperature for catalysts reduced at various temperatures. The NMR method determined the ratio H_{strong}/Ru by integrating the hydrogen-on-metal peak measured after a 10 min evacuation. As noted in Fig. 1, the volumetric technique gave a steady decrease of H_{strong}/Ru with increasing catalyst reduction temperature, while ¹H NMR intensities of the hydrogen-on-metal resonance did not appreciably change with reduction temperature. On all catalysts the volumetric method appeared to yield a larger amount of strongly bound hydrogen. The difference between the volumetric and ¹H NMR data directly demonstrates the irreversible spillover process. We also note that the silanol intensity decreases with increasing reduction temperature (not shown, see Ref. 9), which is correlated with dehydroxylation and/or the reduction in hydrogen spillover.
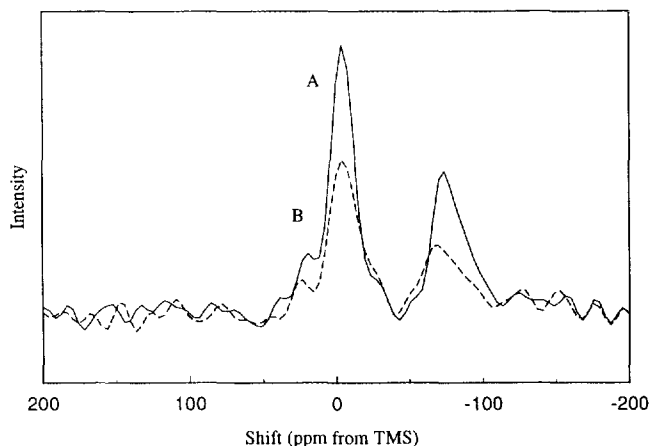
FIG. 2. NMR spectra corresponding to a reduced sample (A) under 20 Torr of hydrogen, and (B) with irreversibly bound hydrogen. The spectra were obtained by accumulating 10 scans at a repetition rate of 50 s and subtracting the NMR spectrum of the sample under vacuum. The ^{1}H NMR measurements were done after extensive deuterium exchange to eliminate most of the hydrogen originally present in the support.

Previously, Wu et al. (11) reported a better agreement between the results of the volumetric technique and ^{1}H NMR spin counting. For example, a Ru/SiO_2 catalyst reduced at 723 K had a dispersion determined by NMR within 15% of the value obtained by the volumetric method (11). This discrepancy is less than half of what is reported in Fig. 1, and was formerly disregarded. We have since conducted a detailed investigation of the line shape of the diamagnetic resonance at about 3 ppm and demonstrated that it consists of an intense narrow peak (3–5 kHz full-width at half-magnitude (FWHM)) superimposed with a broad (~15 kHz FWHM) line centered at the same location (8). The contribution from this broader line to the H/Ru resonance is not negligible and was overlooked in the earlier study.

The quantitative evaluation of the spilled over hydrogen via ^{1}H NMR spectroscopy was done after the silanol protons were exchanged with deuterium as described in the previous section. We first measured the residual ^{1}H background of an evacuated sample. This background signal was then subtracted from the fully relaxed NMR spectra acquired after 20 Torr of hydrogen was introduced into the catalysts (for example, see Fig. 2, spectrum A) and from similar spectra obtained upon subsequent evacuation for 10 min to a pressure of 10^{-5} Torr (see Fig. 2, spectrum B). Thus, the upfield (−65 ppm) and downfield (3 ppm) resonances of Fig. 2, spectrum B, represent hydrogen irreversibly adsorbed on the metal and the irreversibly spilled over hydrogen, respectively. The residual intensity of the 3 ppm resonance was present even after evacuation to 10^{-5} Torr for 10 to 30 min, but disappeared after evacuating the sample for several hours at room temperature. The

intensity due to the protonation of the deuterated silanol groups did not contribute appreciably to the total intensity at 3 ppm. This is due to the relatively short (30 min) time span of the experiment in comparison to the time required for the chemical exchange process at these temperatures (11).

In situ ^{1}H NMR spectroscopy was also used to monitor the time dependence of hydrogen uptake (and spillover) after approximately 20 Torr of hydrogen gas was introduced into the sample and the time dependence of subsequent desorption upon evacuation, all at room temperature. The results of NMR are compared to the volumetric method in Fig. 3. The total amount of hydrogen obtained from the sum of the hydrogen-on-metal and spilled over hydrogen resonances agreed well with the amounts obtained by the volumetric method, both prior to and after evacuation. Also, the results given in Fig. 3 unequivocally show that the total amount of the strongly bound hydrogen found by the volumetric method includes significant spilled over hydrogen in addition to the hydrogen on the metal. The contribution of the spilled over hydrogen remains significant even after prolonged (10 to 30 min) evacuation at room temperature. Clearly, the spillover process and its kinetics have important implications for the determination of metal dispersion using the volumetric technique. We address this problem in more detail below.

The NMR data of Fig. 3 indicate that the amount of hydrogen chemisorption on the metal reached saturation relatively quickly (less than several minutes) with exposure at room temperature. However, the diamagnetic proton resonance associated with hydrogen in the support continued to increase for a long period of time (>24 h, not shown). The analysis of NMR data showed that the rate of hydrogen spillover was initially rapid but slowed with time. This slower process was reported earlier and was
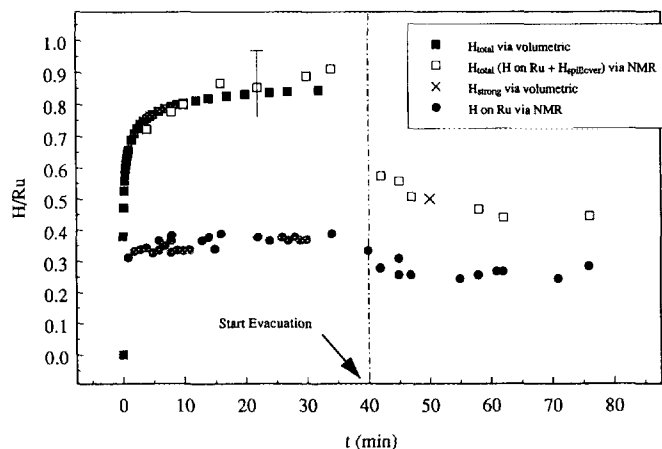

FIG. 3. Quantitative comparison of hydrogen chemisorption and the spillover process at room temperature and initially under 19 Torr H_2 on $Ru/SiO_2(II)$. The catalyst was reduced at 623 K.
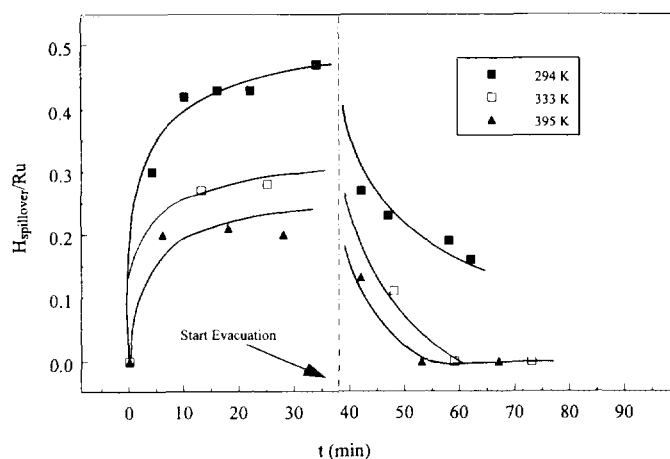
FIG. 4. The temperature dependence of spilled over hydrogen normalized per Ru atom in Ru/SiO$_2$(II) before and after evacuation obtained by *in situ* NMR spectroscopy.

attributed to diffusion-limited motion of the spilled over hydrogen on the silica surface (3, 5). Similar kinetics were observed during evacuation. The hydrogen-on-metal resonance stabilized within a few minutes but the spilled over hydrogen continued to decrease with time.

Given these complicated kinetics and the variety of proposed procedures for performing volumetric chemisorption measurements, we attempted to optimize the parameters for the volumetric method. Because the metal surface was saturated with hydrogen in several minutes (see the NMR experiments shown in Fig. 3) we fixed the hydrogen exposure time at 10 min. Next, an appropriate temperature for the experiment and the duration of evacuation between the total and weak adsorption isotherms was investigated. We found that there was only a small change (<10%) in the H$_{strong}$/Ru amounts determined by NMR over a temperature range of 294 to 350 K using an evacuation time of 10 min. As the temperature of the experiment increased, however, the amount of spilled over hydrogen remaining on the support substantially decreased with evacuation time (see Fig. 4). Within 10 min almost all of the spilled over hydrogen was removed at temperatures of 333 K or higher. The net result of reducing hydrogen exposure time and increasing the temperature during the entire experiment is to minimize the amount of irreversible hydrogen spillover measured by the volumetric technique.

The recommended experimental parameters for the volumetric technique are summarized in Table 1. The apparent dispersions (H$_{strong}$/Ru) for two different catalysts reduced at 623 K were obtained using the volumetric technique for both the "standard" procedure and the procedure based on the recommendations developed in this work. In Table 2, the results of these two volumetric procedures are compared with dispersions determined by ^{1}H

NMR. The optimized volumetric technique and the NMR method gave similar results. The low-dispersion catalyst, Ru/SiO$_2$(I), yielded a dispersion of 10 ± 2% by ^{1}H NMR but the standard volumetric technique gave an apparent dispersion of about a factor of two higher (18 ± 4%). By raising the temperature of the experiment and reducing the exposure time, the dispersion measured by the volumetric method was 13 ± 3%, in better agreement with the NMR result. For the higher dispersion catalyst the optimized volumetric technique and the NMR method gave the same dispersion of 28%.

The ^{1}H NMR investigations clearly demonstrate the hydrogen remaining on the support after evacuation is not associated with the metal particles. However, in the volumetric method for determining dispersion, this same irreversibly adsorbed, spilled over hydrogen is not directly distinguishable from the hydrogen on the metal. It should be noted that increasing the catalyst reduction temperature can have the effect of significantly reducing the amounts of both the reversibly bound and irreversibly bound, spilled over hydrogen on the support (8, 11). Hence, the results of the volumetric method can give the appearance that the metal dispersion is decreasing with increasing reduction temperature when in reality only the irreversibly bound, spilled over hydrogen is reduced. The reduction of spillover appears to be correlated with the partial dehydroxylation of the support. The NMR experiments, on the other hand, indicate that H$_{strong}$ on the metal paticles is unaffected until

TABLE 1

Comparison of Parameters for the Standard and Optimized Volumetric Chemisorption Experiments

	Standard volumetric chemisorption	Optimized volumetric chemisorption
Temperature	294 K	330 to 360 K
Hydrogen exposure time	4 to 10 h	10 min
Evacuation period	10 to 30 min	10 to 20 min

TABLE 2

Apparent Dispersions Obtained from the Standard and the Optimized Volumetric Chemisorption Techniques and from ^{1}H NMR

Catalyst	Ru wt%	Apparent dispersion (H$_{strong}$/Ru)		
		Standard	Optimized	^{1}H NMR
Ru/SiO$_2$(I)	4	0.18 ± .04	0.13 ± .03	0.10 ± .02
Ru/SiO$_2$(II)	4	0.50 ± .10	0.28 ± .06	0.28 ± .04

Note. Catalysts were reduced at 623 K.

significantly higher reduction temperatures are employed. Recent results of a study characterizing the Ru/TiO$_2$ system by ^{1}H NMR and electron microscopy indicated a similar phenomenon (12). Electron microscopy showed that the metal particles were unaffected by reduction temperature in a range where the apparent dispersion determined by the volumetric method varied considerably. In this case, the variation of apparent dispersion with reduction temperature was due to a combination of irreversible hydrogen spillover to the support (noted by ^{1}H NMR) and migration of TiO$_x$ species onto the metal surface.

CONCLUSIONS

An irreversibly bound, spilled over hydrogen species on the silica support clearly interfered with the accurate evaluation of dispersion via the volumetric hydrogen chemisorption technique. The amount of irreversibly bound, spilled over hydrogen was a strong function of the catalyst reduction temperature, hydrogen adsorption temperature, and the exposure and evacuation times. Volumetric chemisorption parameters were optimized to minimize the presence of the irreversibly bound, spilled over hydrogen on Ru/SiO$_2$ catalysts. It was found that dispersions determined by the volumetric method were most reliable when the temperature of the experiment was about 330 to 360 K and the time for both exposure of the catalyst to hydrogen and evacuation was about 10 min. At the temperature recommended the exposure and evacuation times are sufficient to ensure that only hydrogen on the metal is counted in the volumetric method.

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