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The Influence of Metal–Support Interactions on the Accurate Determination of Ru Dispersion for Ru/TiO_2

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Titania-supported Ru catalysts have been characterized by TEM, ^1H NMR, and H_2 chemisorption to determine the metal particle size, the fraction of the metal surface available for H_2 chemisorption, and the H_2 adsorption capacity of the catalyst, as functions of the reduction temperature. TEM micrographs show that as the reduction temperature rises from 573 to 773 K, the average particle size of Ru remains the same but the surface of the particles is covered to an increasing extent by an amorphous layer of titania. Quantitative estimates of the fraction of the Ru particle surface available for H_2 chemisorption were obtained by ^1H NMR. The NMR spectra also show that a fraction of the adsorbed H_2 spills over onto the support and that as a consequence measurements of total H_2 chemisorption overestimate the number of Ru sites available for H_2 adsorption. The implications of these results for the correct calculation of Ru dispersion and the determination of turnover frequencies for reactions carried out over Ru/TiO_2 are discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Partial encapsulation of metal particles supported on titania can occur during either catalyst preparation or reduction (1–8). In the former case, dissolution of a small portion of the support and subsequent precipitation of the dissolved material together with the metal precursor during drying can result in the deposition of oxide over the newly formed metal particles. In the latter case, coverage of the metal particles by titania occurs due to partial reduction of the support and migration of suboxide species on to the surface of the metal particles. Studies conducted with both supported metal catalysts and model catalysts comprised of a metal foil or single crystal decorated by metal oxide moieties have shown that the dispersed oxide can act either as an inhibitor or promotor [e.g., (1–5) and references cited therein]. Thus, for example, decoration of Rh by TiO_x causes a reduction in the activity of Rh for the hydrogenation of small olefins and the hydrogenolysis of ethane, but causes an enhancement in the rates of CO and CO_2 hydrogenation, and NO reduction.

The present investigation was undertaken to obtain a quantitative estimate of the extent of Ru particle encapsulation by titania for titania-supported Ru. The size of the dispersed particles was determined from TEM micrographs and the amount of H_2 adsorbed on the catalyst surface was determined by ^1H NMR and volumetric chemisorption. It is shown that volumetric chemisorption does not provide an accurate measure of Ru dispersion or the fraction of Ru atoms not covered by titania. The true particle size can be determined by TEM and the fraction of exposed Ru atoms can be determined from ^1H NMR. The effects of reduction temperature on extent of Ru particle encapsulation are examined.

EXPERIMENTAL

Catalyst Preparation

Titania-supported Ru catalysts were prepared by incipient wetness impregnation of TiO_2 (Degussa P-25) with an aqueous solution of $Ru(NO)(NO_3)_3$ (Johnson-Matthey). The impregnated titania was air dried at 383 K for 16 h and then sieved to 30–60 mesh. The dried catalyst was reduced at 473 K in a flow of H_2 and passivated in He containing 1000 ppm of O_2 at room temperature. Since the precursor solution contained a significant amount of Na as a contaminant (Na/Ru = 0.88), the passivated catalyst was washed repeatedly in boiling water. The washed catalyst was dried at 383 K in vacuum for 3 h and reduced at 473 K in flowing H_2, after which it was passivated in He containing 1000 ppm O_2 at room temperature. The final catalyst is referred to as $Ru/TiO_2(A)$. A second sample of titania-supported Ru, designated as $Ru/TiO_2(B)$, was

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prepared by impregnation of TiO_2 with an excess aqueous solution of $Ru(NO)(NO_3)_3$ at pH 8, followed by filtration and water rinsing of the impregnated TiO_2. This sample was then dried, reduced, washed with boiling water, and then reduced again in the same manner as Ru/TiO_2(A). A sample of Ru/SiO_2 was prepared by following the same procedure as that used to prepare Ru/TiO_2(A). Cab-O-Sil L-90 was used as the support in this case.

The weight loading of Ru was determined by X-ray fluorescence. The weight loadings were 4.76% for Ru/TiO_2(A), 1.52% for Ru/TiO_2(B), and 4.90% for Ru/SiO_2. The Na content, determined by ICP, was 100–200 ppm for all three catalysts.

Electron Microscopy

Catalysts were ground to a fine powder and then dry-dispersed onto a carbon-coated copper grid and evaporated. Micrographs were obtained on a Topcon 002B transmission electron microscope operated at 200 kV, with a nominal point-to-point resolution of 1.9 Å. Ru particles were identified by using a combination of selected-area diffraction techniques and measurement of the lattice-fringe spacings. Approximately 100 Ru particles were measured using image processing techniques (9). Images of the Ru particles were digitized and the diameters of the particles were determined using the NIH Image software (version 1.54). This software automatically determines the maximum and minimum diameter of each particle for which the intensity is sufficiently above the intensity of the support. Since the orientation of the Ru particles varies with orientation of the support, the effective diameter of each particle is assumed to be the maximum diameter measured.

^1H NMR

^1H NMR measurements were performed by using a home-built spectrometer operating at a resonance frequency of 250 MHz. An *in situ* NMR probe was constructed at Ames Laboratory following the design of Haddix *et al.* (10). The probe was attached to a volumetric adsorption apparatus and allowed to collect the NMR spectra at various temperatures and adsorbate pressures. In this study, adsorption and reduction temperatures of up to 773 K and H_2 pressures of 5×10^{-6} to 10^3 Torr were used. To avoid baseline artifacts associated with rf pulse breakthrough and receiver recovery, use was made of the proton spin temperature inversion method with an add–subtract of free induction decays on alternate scans. Typically, 500 transients were averaged for each spectrum, using a delay of 0.3 s, which was sufficient to avoid saturation of the resonance corresponding to hydrogen-on-metal. To alleviate tuning problems, all parts of the high frequency rf circuit (except for the NMR coil) were maintained at 300 K regardless of the temperature of the sample. It was determined that only small tuning adjustments were required between 300 and 773 K and that the observed NMR intensities closely followed the Curie–Weiss law. This made it possible to use the room temperature intensity from a sample of water slightly doped with $FeCl_3$ as an external standard for the quantification of the amounts of hydrogen adsorbed on ruthenium. The NMR intensities reported in this work are determined to be accurate to within ±15%. The ^1H background signal of the NMR probe (including an empty tube) was determined separately under the conditions used in this study and found to be negligibly small. The resonance line positions were determined in ppm with respect to tetramethylsilane (TMS), using the δ scale with positive numbers being downfield.

Volumetric H_2 Chemisorption

Prior to measuring the uptake of H_2, the catalyst was reduced in H_2 at a specified temperature for 3 h, evacuated at 473 K for 30 min, and then cooled in vacuum to 373 K. The uptake of H_2 was measured volumetrically at 373 K over the pressure range 75–400 Torr. Since the adsorption of H_2 on Ru is known to be slow, adsorption as allowed to occur for 16 h at 75 Torr, and for 1 h for each higher pressure. Upon completion of the first set of measurements, the catalyst was evacuated to 10^{-6} Torr for 10–30 min and a second isotherm was determined at either 373 or 300 K. The first isotherm gives a measure of the total uptake of H_2 and the second, the reversible uptake of H_2. A measure of the irreversible uptake of H_2 was determined by taking the difference between the extrapolated values of the total and reversible H_2 uptakes at zero pressure.

RESULTS AND DISCUSSION

Figures 1 and 2 show high-resolution TEM micrographs of Ru/TiO2(A) taken after reduction at 573 K and 773 K, respectively. Ruthenium particles with varying amounts of oxide overlayer encapsulation (fully, partially, and unencapsulated) are observed after reduction at 573 K. Unencapsulated Ru particles with clearly exposed faceted surfaces are shown in Fig. 1a, whereas partially and fully encapsulated particles are shown in Fig. 1b. In comparison with reduction at 573 K, reduction at 773 K results in the disappearance of any unencapsulated Ru particles. Only partially and totally encapsulated Ru particles are now observed. In Fig. 2a, a large particle with approximately 30% of its surface exposed is shown. In Fig. 2b, a thin (7–8 Å) amorphous layer is observed to encapsulate the Ru particles supported on anatase.

An average Ru particle size for each of the three cata-

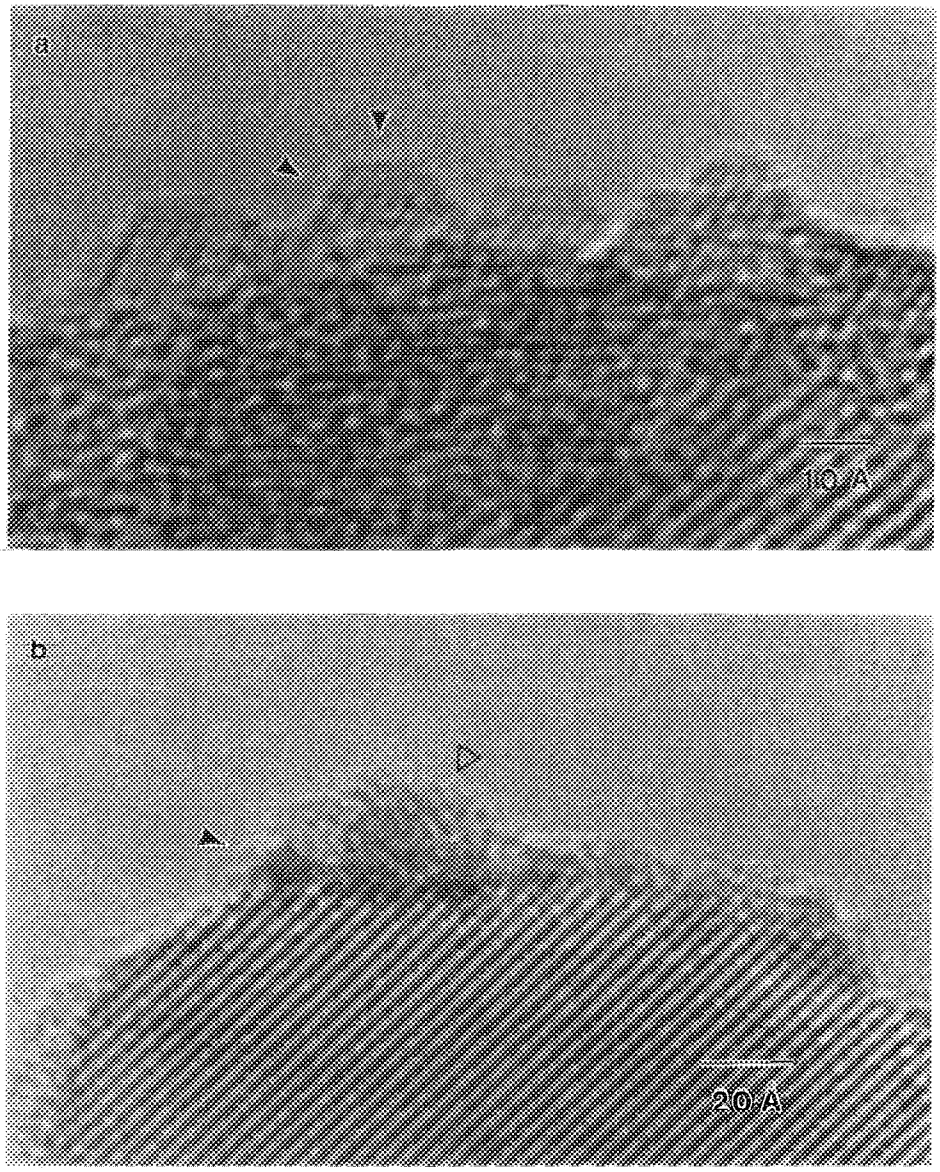

FIG. 1. Micrographs of titania-supported Ru particles [$Ru/TiO_2(A)$] after reduction at 573 K. In (a), the faceted (001) and (101) surfaces of the Ru particles are clearly exposed. In (b), the Ru particles are encapsulated by an amorphous overlayer, indicated by the hollow arrow. Only a small portion of one Ru particle surface is partially exposed (black arrow).

lysts was determined from TEM images. Following reduction at 573 K, the average Ru particle sizes for $Ru/TiO_2(A)$, $Ru/TiO_2(B)$, and Ru/SiO_2 are 15, 8, and 35 Å, respectively. The dispersion of Ru calculated from these average particle sizes are 67% for $Ru/TiO_2(A)$, 100% for $Ru/TiO_2(B)$, and 28% for Ru/SiO_2. Reduction at 773 K has no effect on the average Ru particle size for $Ru/TiO_2(A)$. Reduction of Ru/SiO_2 at 773 K resulted in a rise in the average Ru particles size to 43 Å. No evidence was seen for an amorphous overlayer covering the Ru particles following reduction of this catalyst at either 573 K or 773 K.

Figure 3 shows ^1H NMR spectra obtained after reduction of $Ru—TiO_2(A)$ in H_2 for 2 h and subsequent evacuation to 10^{-6} Torr for 30 min at the reduction temperature. The spectra reveal only one peak at 3 ppm (see inset in Fig. 3) representing hydroxyl groups on the surface of TiO_2. The intensity of this peak decreases monotonically with increasing reduction temperature, which is consistent with observations made by infrared spectroscopy.

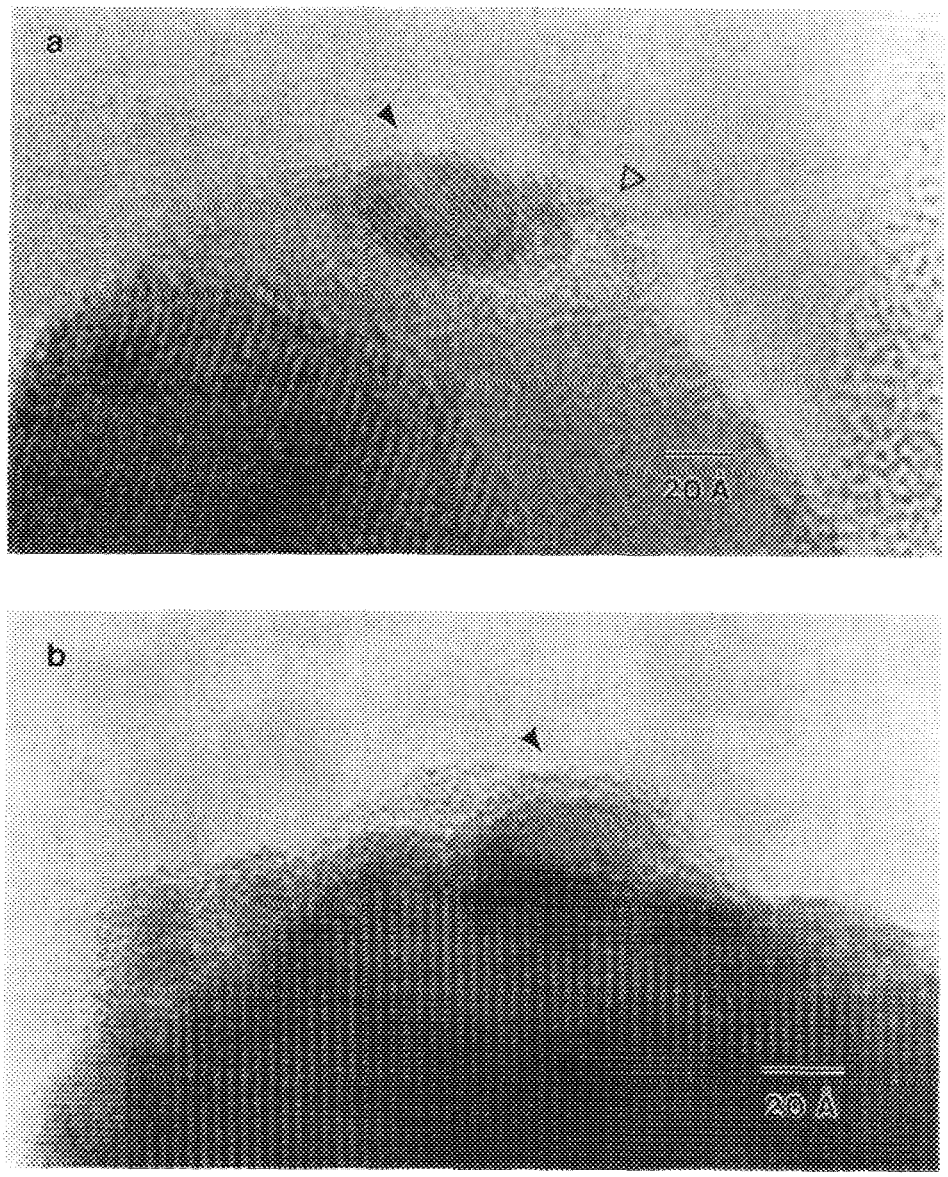

FIG. 2. Micrographs of titania-supported Ru particles [$Ru/TiO_2(A)$] after reduction at 773 K. In (a), the Ru particle (with d_{100} = 2.34 Å fringes visible) is partially encapsulated by an amorphous overlayer (hollow arrow), while a small portion of its surface is exposed (black arrow). In (b), the Ru particles are completely encapsulated by an amorphous overlayer, indicated by the black arrow.

This trend is attributable to the loss of hydroxyl groups due to condensation and the formation of water (11).

^1H NMR spectra taken after reduction of $Ru/TiO_2(A)$ and subsequent 10 min exposure to 400 torr of H_2 at 373 K are presented in Fig. 4a. Two peaks are now observed: one at 3 ppm due to hydroxyl groups on the support and the second at −53 to −64 ppm due to hydrogen adsorbed on Ru (12, 13). For each reduction temperature, the intensity of the 3 ppm peak seen in Fig. 4a is larger than that measured prior to hydrogen dosage, indicating that some of the adsorbed H_2 has spilled onto the TiO_2. ^1H spectra taken after evacuation (10^{-5} Torr) of the reversibly adsorbed H_2 at 300 K for 10 min are shown in Fig. 4b. Following evacuation, the peak associated with H_2 adsorbed on Ru shifts slightly upfield and broadens considerably. This trend is similar to that reported previously for H_2 adsorbed on Ru/SiO_2 (13). The narrowing of the ^1H resonance seen in Fig. 4a was also observed at 300 K (not shown) and is associated with rapid motions of hydrogen on the surfaces of the Ru particles. These motions are restricted after evacuation, as only less mobile, irreversibly adsorbed H atoms are present.

The quantitative estimates of hydrogen uptake on the catalyst surfaces were obtained by comparing the inte-

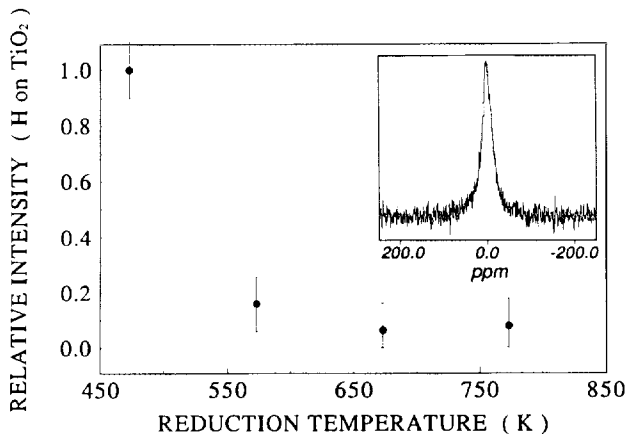

FIG. 3. Relative NMR intensity of the resonance line ascribed to H on TiO_2 versus reduction temperature for Ru/TiO_2(A). The inset show the ^1H NMR spectrum taken after reduction at 473 K.

grated intensities from the NMR spectra with those of a reference sample. The moles of hydrogen adsorbed at a pressure of 400 Torr are designated H_{Ru}, H_{TiO_2}, and H_{total}. Similarly, the moles of hydrogen adsorbed irreversibly are designated $H_{i,Ru}$, H_{i,TiO_2}, and $H_{i,total}$. The amount of hydrogen adsorbed irreversibly on Ru was obtained by integration of the upfield peak in Fig. 4b, whereas the amount of irreversibly adsorbed hydrogen on the support due to spillover was determined by comparing the integrated intensities of the peak at 3 ppm for samples evacuated before and after exposure to hydrogen (Figs. 3 and 4b, respectively). We note that under the conditions used in this study T_1 relaxation times for hydrogen on Ru did not exceed 50 ms. Since the spins resonating at 3 ppm exhibited slower relaxation, the intensity of that peak may be underestimated, as 0.3-s delays were applied between consecutive transients. Consequently, the H_{TiO_2} and H_{i,TiO_2} values reported here represent the lower limits of true hydrogen concentrations on the titania support. The ratio of $H_{i,Ru}$ and $H_{i,total}$ to the total moles of Ru in the sample of Ru/TiO_2(A), Ru_{total}, is plotted in Fig. 5 as a function of the reduction temperature. As the reduction temperature increases from 473 to 773 K, the ratio of $H_{i,Ru}/Ru_{total}$ decreases from 0.33 to 0.11, and the ratio of $H_{i,total}/Ru_{total}$ decreases from 0.54 to 0.12. The difference between these two ratios at each reduction temperature is an estimate of the amount of hydrogen spilled over onto the support. It is evident that hydrogen spillover is significant when the catalyst is reduced at 473 K and decreases monotonically to zero as the reduction temperature is raised to 773 K.

Since the size of the Ru particles in Ru/TiO_2(A) does not change with increasing reduction temperature (see above), the decrease in the ratio of $H_{i,Ru}/Ru_{total}$ seen in Fig. 4 can be attributed to the progressive coverage of Ru particles by an overlayer of TiO_x. As noted above, TEM micrographs of Ru/TiO_2(A) taken after reduction at 773 K clearly show evidence of an amorphous TiO_x layer on the surface of the Ru particles. Similar overlayers have previously been observed by TEM for Rh/TiO_2 reduced at elevated temperatures (14, 15). A measure of the fraction of the Ru particle surface available for H_2 chemisorption can be determined by combining the results obtained from TEM and ^1H NMR. The Ru dispersion obtained from TEM is equal to Ru_{surf}/Ru_{total}, the ratio of Ru atoms at the surface of the particle to the total Ru atoms in the particle. If it is assumed that $H_{i,Ru}/Ru_{exp} = 1$, where Ru_{exp} is the number of exposed Ru atoms in an average particle available for H_2 chemisorption, then the ratio of Ru_{exp}/Ru_{total} can be calculated from the ratio of $H_{i,Ru}/Ru_{total}$ determined by NMR (Table 1). It is evident that for Ru/TiO_2(A) reduced at 573 K $Ru_{exp}/Ru_{surf} = 0.50$ and that the value of this ratio decreases to 0.15 when the reduction temperature is raised to 773 K. For Ru/TiO_2(B), the value of $Ru_{exp}/Ru_{surf} = 0.15$ even when reduction is carried

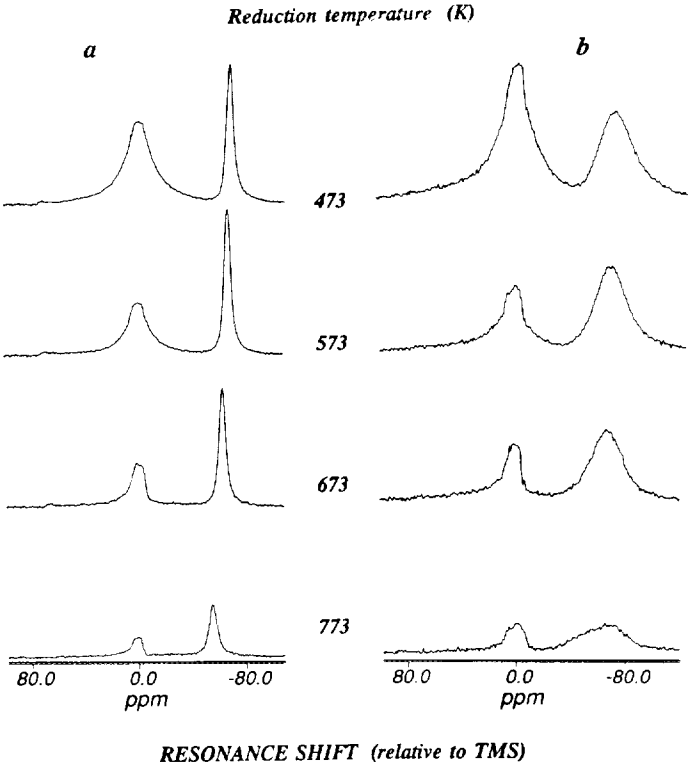

FIG. 4. ^1H NMR spectra of hydrogen on Ru/TiO_2(A) as a function of the reduction temperature. The resonance lines near 0 ppm are ascribed to hydrogen on TiO_2, and the resonance lines near −60 ppm) are ascribed to hydrogen on Ru. Column (a) show spectra obtained at 373 K and a H_2 pressure of 400 Torr. Column (b) shows spectra obtained at 300 K after 10 min evacuation. The spectra in columns (a) and (b) are plotted using two different intensity scales, each normalized relative to the upper spectrum.

TABLE 1

Hydrogen Uptake on Ru/TiO_2 and Ru/SiO_2 Determined by ^1H NMR and Volumetric Chemisorption

	Catalyst			
	Ru/TiO_2(A)	Ru/TiO_2(B)	Ru/SiO_2	
Ru loading (wt%)	4.76	1.52	4.90	
d_{TEM} (Å)	15	8	35	
$D_{Ru} = Ru_{surf}/Ru_{total}$	0.67	1.00	0.28	
	Reduction temp. (K)			
	573	773	573	573
	^1H NMR measurement			
H_{total}/Ru_{total}[f]	0.63	0.17	1.10	—
H_{Ru}/Ru_{total}[a]	0.33	0.15	0.38	0.48
H_{TiO_2}/Ru_{total}[a,f]	0.30	0.02	0.72	—
$H_{i,total}/Ru_{total}$[e,f]	0.44	0.12	0.63	—
$H_{i,Ru}/Ru_{total}$[e,b]	0.33	0.11	0.15	0.25
$H_{i,TiO_2}/Ru_{total}$[e,b,f]	0.11	0.01	0.47	—
	Volumetric H_2 chemisorption			
H_{total}/Ru_{total}[c]	0.59	0.16	1.12	0.56
H_i/Ru_{total}[e]	0.39	—	0.70	—
H_i/Ru_{total}[d]	0.29	0.09	0.59	0.28

[a] H_{total}: Hydrogen uptake after H_2 adsorption at 373 K, 400 Torr H_2.
[b] H_i: Hydrogen uptake after evacuation (5×10^{-6} Torr) for 10 min at 300 K.
[c] Hydrogen uptake after adsorption at 373 K.
[d] Hydrogen uptake after evacuation at 373 K.
[e] Hydrogen uptake after evacuation at 300 K.
[f] All values for H on TiO_2 obtained from NMR intensities may exhibit systematic deviations because T_1 relaxation times for H on TiO_2 are longer than those for H on Ru.

out at 573 K. This suggests that the smaller Ru particles present in Ru/TiO_2(B) are more easily covered by a TiO_x overlayer than the larger Ru particles present in Ru/TiO_2(A). $Ru_{exp}/Ru_{surf} = 0.96$ for Ru/SiO_2 reduced at 573 K, indicating that virtually all of the surface Ru atoms are available for H_2 adsorption, consistent with the observation by TEM that all of the Ru particle surface is free.

A comparison of several measures of H_2 chemisorption obtained by ^1H NMR and volumetric H_2 chemisorption are presented in Table 1. The ratio of H atoms adsorbed to total Ru atoms, H_{total}/Ru_{total}, measured by ^1H NMR and by volumetric adsorption is virtually the same in each case. Likewise, ^1H NMR and volumetric H_2 chemisorption give reasonably good agreement for the ratio of irreversibly adsorbed H (Ru and TiO_2) and total Ru atoms, $H_{i,total}/Ru_{total}$. The last row of Table 1 lists the value of $H_{i,total}/Ru_{total}$ obtained when evacuation of weakly adsorbed H_2 is carried out at 373 K, the temperature of adsorption. This measure of H_2 chemisorption is frequently used (viz., (1–5)) to determine the apparent dispersion of titania-supported transition metals. Comparison of this value of $H_{i,total}/Ru_{total}$ with the value of Ru_{surf}/Ru_{total} shows that agreement occurs only in the case of Ru/SiO_2. For both Ru/TiO_2(A) and $RuTiO_2$(B) the apparent dispersion obtained from the amount of irreversibly adsorbed H_2 measured at 373 K is significantly smaller than that measured by TEM. Again, this discrepancy is attributable to partial blockage of the Ru particle surface by amorphous titania, and is significant, in spite of the fact that H_i/Ru_{total} (373 K) includes hydrogen spilled over on to the support. What this means is that H_2 chemisorption cannot be used reliably to determine the dispersion of Ru supported on TiO_2, even after reduction at temperatures as low as 473–573 K.

The three methods of catalyst characterization presented here, volumetric hydrogen uptake, ^1H NMR of chemisorbed hydrogen, and TEM, measure different parameters. It is clear from the results of this work that volumetric uptake measurements of hydrogen chemisorption cannot be used as a reliable method for determining the number of exposed metal atom sites in the Ru/TiO_2 system. Irreversible hydrogen spillover from the metal to the support causes this method to overestimate the adsorption of hydrogen on the metal. These results are consistent with similar studies investigating Ru on high-surface-area silica supports (16). Another complication imposed by TiO_2 and other reducible supports occurs under circumstances in which there is partial dissolution of the support and subsequent deposition onto the metal particles. As shown here, ^1H NMR does give an accurate measure of the exposed metal atoms available for chemi-

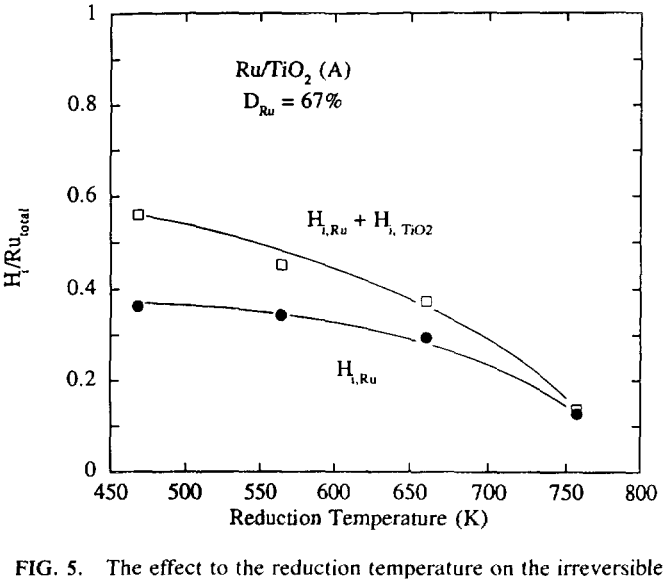

FIG. 5. The effect to the reduction temperature on the irreversible chemisorption of hydrogen on Ru and TiO_2 for Ru/TiO_2(A).

sorption. TEM, on the other hand, indicates the particle size from which the dispersion can be determined assuming no titania overlayer.

The implications of these results for the determination of turnover frequencies on Ru/TiO_2 catalysts is clear. Turnover frequencies based on volumetric uptake of hydrogen cannot be accurate. For low-temperature reduction, this measure overestimates the number of exposed metal atoms, but should become increasingly accurate as the reduction temperature increases and the extent of hydrogen spillover decreases (see Fig. 5). TEM and ^1H NMR present two alternate methods for the calculation of turnover frequencies. TEM indicates the total number of metal atoms on the surface of metal particles, both of those exposed and those covered by the oxide. This basis of turnover frequencies has been used in studies of the effects of metal oxide promoters deposited on metal foils of fixed geometric dimensions. Turnover frequencies based on the number exposed metal atoms (before and after reaction) can be determined from the ^1H NMR results.

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REFERENCES

1. Tauster, S. J., *Acc. Chem. Res.* **20,** 389 (1987).
2. Bell, A. T., *in* "Catalyst Design—Progress and Perspectives" (L. L. Hegedus, Ed.). Wiley, New York, 1987.
3. Burch, R., *in* "Hydrogen Effects in Catalysis" (Z. Paal and P. G. Menon, Eds.). Dekker, New York, 1988.
4. Haller, G. L., and Resasco, D. E., *Adv. Catal.* **36,** 173 (1989).
5. Vannice, M. A., *Catal. Today* **12,** 255 (1992).
6. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 147 (1983).
7. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
8. Sadeghi, H. R., and Heinrich, V. E., *J. Catal.* **87,** 279 (1984).
9. Russ, J. C., "Computer-Assisted Microscopy—The Measurement and Analysis of Images." Plenum, New York, 1990.
10. Haddix, G. W., Reimer, J. A., and Bell, A. T., *J. Catal.* **106,** 111 (1987).
11. Primet, M. P. P., and Mathieu, M. V., *J. Phys. Chem.* **75,** 1216 (1971).
12. Wu, X., Gerstein, B. C., and King, T. S., *J. Catal.* **118,** 238 (1989).
13. (a) Bhatia, S., Engelke, F., Pruski, M., Gerstein, B. C., and King, T. S., *J. Catal.*, in press; (b) Engelke, F., Bhatia, S., King, T. S., and Pruski, M., *Phys. Rev. B* **49,** 2730 (1994).
14. Singh, A. K., Pande, N. K., and Bell, A. T., *J. Catal.* **94,** 422 (1985).
15. Datye, A. K., and Smith, D. J., *Catal. Rev.-Sci. Eng.* **34,** 129 (1992).
16. Uner, D. O., Pruski, M., and King, T. S., submitted for publication.