

## Evidence for Slow Uptake of Hydrogen by Titania-Supported Metal Samples: Consequences for Estimating Metallic Surface Areas

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The uptake of hydrogen by titania-supported Ni, NiFe, and Pt samples was investigated at room temperature following reduction at 770 K. The hydrogen uptake was low for each sample (e.g., zero for Pt/TiO<sub>2</sub>) as determined by adsorption measurements. After the samples were subsequently equilibrated with gaseous hydrogen at ca. 40 kPa for extended periods of time (ca. 15–20 h), hydrogen desorption measurements were determined. Significant amounts of hydrogen strongly held by the samples were observed in this manner. Metal particle sizes estimated from these hydrogen uptakes were in good agreement with particle sizes determined by X-ray line broadening and transmission electron microscopy. The hysteresis between the adsorption and desorption measurements was indicative of slow hydrogen adsorption. Titania-supported Pt samples were also observed to adsorb CO weakly, and Ni(CO)<sub>4</sub> was formed slowly when Ni/TiO<sub>2</sub> was exposed to CO at room temperature. These data are discussed in terms of the presence of titanium species (TiO<sub>x</sub>) on the surfaces of the metal particles, and the possible migration of hydrogen from metal particles to adjacent regions of the titania support.

### INTRODUCTION

The nature of "strong metal-support interactions" for Group VIII metals supported on titania has received considerable attention in the recent literature (e.g., (1–10)). In agreement with the original findings of Tauster *et al.* (11, 12), essentially all investigators have found that the room temperature chemisorption of hydrogen and carbon monoxide is suppressed after titania-supported metals are reduced at temperatures near 770 K. This behavior has posed two important questions. From a fundamental point of view, what causes this apparent suppression of chemisorption, and, from a practical point of view, how can one measure the metallic surface area if the metal does not chemisorb hydrogen or carbon monoxide?

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In recent publications (13, 14), it has been suggested that strong metal support interactions may be at least partially due to the presence of titanium species (e.g., TiO<sub>x</sub> with 1 < x < 2) on the surfaces of titania-supported metal particles. In addition to blocking a fraction of the metallic surface, these titanium species may also modify the chemical properties of neighboring surface metal atoms. In general, these titanium species may not only decrease extents of chemisorption but they may also alter rates of chemisorption on titania-supported metal surfaces. The present paper addresses the existence of slow and/or weak adsorption phenomena when titania-supported metal samples are exposed to hydrogen or carbon monoxide at room temperature. Such phenomena may provide a means for determining the metallic surface areas of titania-supported samples after reduction at 770 K, and they may also provide information about the nature of strong metal-support interactions.

## EXPERIMENTAL

*Materials and Sample Preparation*

The TiO<sub>2</sub> support used in this study was obtained from Degussa (P-25), and it was cleaned prior to sample preparation in the manner described by Munuera *et al.* (15) and Santos *et al.* (14). The following samples were prepared by incipient wetness impregnation of TiO<sub>2</sub> using 0.25 ml of aqueous solution per gram of support: 7.4% Ni/TiO<sub>2</sub>, 1.07% Pt/TiO<sub>2</sub>, 2.5% Pt/TiO<sub>2</sub>, 4.9% Pt/TiO<sub>2</sub>, and 5.23% Ni–0.55% Fe/TiO<sub>2</sub>. These loadings are expressed in weight percent, as determined from chemical analyses of the samples (Galbraith Laboratories). The metal salts used in these impregnations were Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> for the 1.07% Pt/TiO<sub>2</sub> sample, H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O for the 2.5% and 4.9% Pt/TiO<sub>2</sub> samples, and Fe(NO<sub>3</sub>)<sub>3</sub>. The FeNi/TiO<sub>2</sub> sample was prepared by coimpregnation. Following impregnation, all samples were dried overnight in air at ca. 380 K.

Hydrogen (99.95%) was purified by passage through a Pd thimble (Serfass) prior to use during sample reductions or for chemisorption measurements. Carbon monoxide (Matheson, CP grade 99.5%) was passed through copper turnings at ca. 530 K followed by activated molecular sieves (5A) at ca. 190 K. The purified gas was then stored in a glass bulb for later uses during chemisorption measurements. Helium (99.995%) used in dead-volume determinations was purified and stored in a manner similar to the carbon monoxide, except that the molecular sieve trap was cooled to 77 K. Oxygen uptakes were also measured for several samples, and the oxygen (99.7%) was purified by passage through molecular sieves (5A) at ca. 190 K.

*Chemisorption Measurements*

All chemisorption studies were carried out using a glass, high vacuum (ca. 10<sup>-4</sup> Pa) system which has been described elsewhere (16). Pressure measurements during chemisorption studies were made with a Texas

Instruments precision pressure gauge. Samples (ca. 0.5 g) were placed in a flow-through quartz cell for pretreatment and subsequent chemisorption measurements.

Reduction of all samples was carried out in flowing hydrogen (ca. 400–500 cm<sup>3</sup> (NTP)/min). For the Pt/TiO<sub>2</sub> samples, the temperature was first increased to ca. 500 K for at least 2 h and then to 770 K for 1 h, as described by Tauster *et al.* (11). The nickel-based catalysts were reduced according to the procedure outlined by Shen *et al.* (17). This included at least 3 h at 710 K and 1 h at 770 K. Following reduction, the samples were evacuated for 1 h at 720 K and cooled to room temperature under vacuum, as described by Tauster *et al.* (11). A known quantity of hydrogen was then dosed into the sample cell, and the pressure was monitored until it appeared to reach a constant value. This typically took about 1–2 h. Additional doses of hydrogen were successively admitted into the sample cell, and an apparent hydrogen adsorption isotherm was thereby determined. When the hydrogen pressure reached 30–45 kPa (250–350 Torr), the dosing was terminated, and the gaseous hydrogen was allowed to equilibrate with the sample for about 15–20 h. During the equilibration process, the total hydrogen pressure was monitored. It was determined accordingly that the uptake of hydrogen was essentially complete after about 15 h. Normally, equilibration was allowed to proceed for 15–20 h. A hydrogen desorption isotherm was then collected. This was accomplished by expanding the gas from the sample cell into a previously evacuated, known volume, and monitoring the pressure until it reached a constant value. This was done 6–7 times, until the hydrogen pressure decreased to about 5 kPa. Approximately 30–40 min was allowed for equilibration of the first desorption step, and subsequent desorption steps took about 10–15 min. It should be noted that the use of desorption isotherms to study slow chemisorption processes has been suggested previously by Dalla Betta (18). Fol-

lowing hydrogen adsorption and desorption measurements, the sample was evacuated at room temperature. Helium doses were then added successively into the sample cell, and the dead-volume of the cell was determined from the corresponding pressure readings. For selected samples, carbon monoxide chemisorption measurements were also performed. These samples were reduced as described above, followed by evacuation at 720 K and cooling to room temperature. Adsorption and desorption measurements were then carried out at room temperature, as described above for hydrogen. The sample was subsequently evacuated at this temperature for about 0.2 h (to a pressure of ca.  $10^{-1}$  Pa), and the CO adsorption and desorption measurements were repeated. The use of two sets of adsorption data separated by a brief evacuation is necessary to separate the contributions from "weak adsorption and strong chemisorption." The first measurements include contributions from both forms of adsorption, while the second set of measurements is due primarily to the more weakly adsorbed CO. Carbon monoxide adsorption measurements were also carried out at 190 K for the 4.9% Pt/TiO<sub>2</sub> sample.

As suggested by the work of Smith *et al.* (5), the oxygen uptake of the nickel-based samples was also measured at room temperature. In short, these samples were reduced and evacuated in the above manner, and oxygen was dosed successively into the sample cell to determine the oxygen uptake as a function of the oxygen pressure. Typically, at least 2 h were required for the oxygen pressure to reach a constant value after each dose.

#### Particle Size Measurements

X-ray line-broadening determinations of metal particle sizes (larger than ca. 5 nm) were carried out using a Phillips diffractometer operating with CuK $\alpha$  radiation and nickel filters. This was done following the procedures outlined by Klug and Alexander (19).

Transmission electron microscopy studies of titania-supported samples were performed using a JEOL 100 B microscope. The microscope was operated at 100 kV with a 30- $\mu$ m objective aperture inserted for contrast. Magnifications were calibrated using carbon replica gratings. The titania samples were prepared for microscopic analysis by adding the powdered sample to methanol, grinding the suspension in a mortar and pestle, and dispersing the sample in the methanol using an ultrasonic cleaner. A drop of this suspension was then placed onto a Formvar film supported on a copper grid.

Metallic dispersions  $D\%$  (or percentages exposed) were calculated from the chemisorption measurements assuming that each surface metal atom chemisorbs one hydrogen atom or one oxygen atom. The uptakes of H and O by the titania-supported metals were determined by extrapolating the results of adsorption and desorption measurements to zero pressure and subtracting the corresponding uptakes by blank TiO<sub>2</sub>. For the case of CO, the first and second sets of adsorption/desorption data (i.e., before and after evacuation at room temperature or 190 K) were subtracted at a pressure of 15 kPa to show only the contribution from strongly adsorbed species. The sizes of the metal particles  $d$  (units of nm) were then estimated by the approximate relation:  $d = 80/D\%$ .

#### RESULTS

The results of hydrogen adsorption and desorption measurements on 7.4% Ni/TiO<sub>2</sub> are shown in Fig. 1. Extrapolation of the hydrogen adsorption data to zero pressure gives an uptake of about 20  $\mu$ mol/g; however, similar extrapolation of the desorption results gives the larger value of 45  $\mu$ mol/g. The observation that the apparent hydrogen adsorption isotherm for titania-supported nickel shows a nonzero uptake, even after reduction at 770 K, is in agreement with the work of Smith *et al.* (5). Yet the present results also show the existence

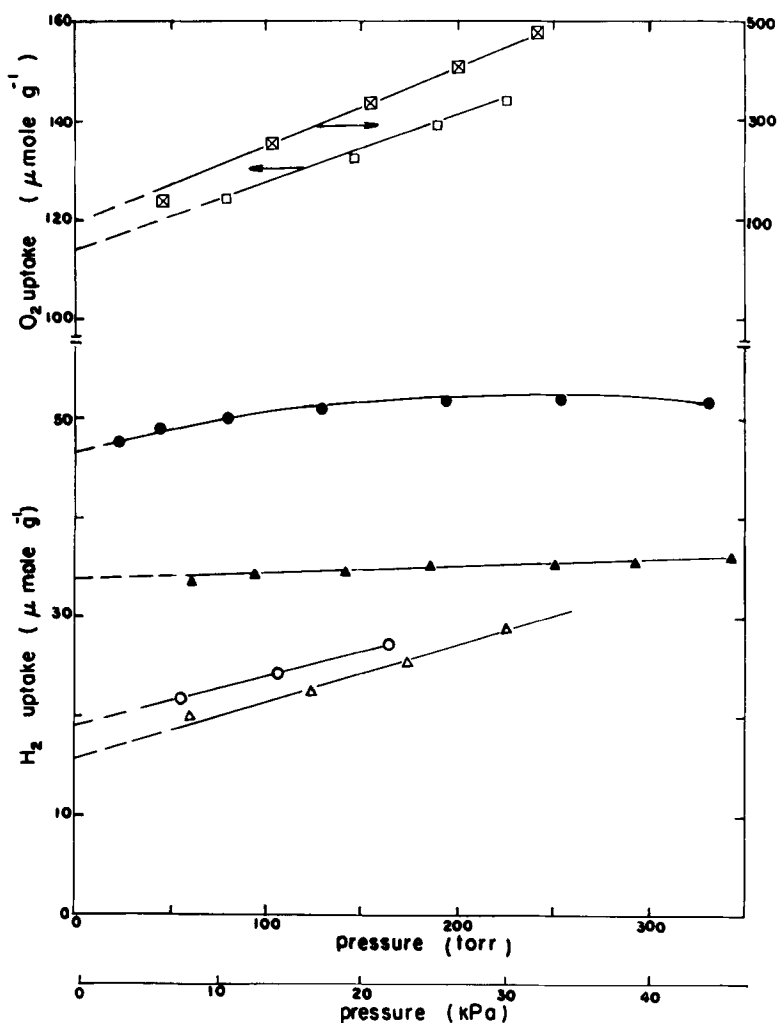


FIG. 1. Hydrogen and oxygen uptakes of 7.4% Ni/TiO<sub>2</sub> and 5.23% Ni-0.55% Fe/TiO<sub>2</sub> samples at 295 K following hydrogen reduction at 770 K. (○, △) H<sub>2</sub> uptakes from adsorption measurements on Ni/TiO<sub>2</sub> and NiFe/TiO<sub>2</sub>, (●, ▲) H<sub>2</sub> uptakes from desorption measurements on Ni/TiO<sub>2</sub> and NiFe/TiO<sub>2</sub>, respectively; (□, ⊠) O<sub>2</sub> uptakes from adsorption measurements of Ni/TiO<sub>2</sub> and NiFe/TiO<sub>2</sub>, respectively.

of an additional slow adsorption phenomenon which is responsible for the greater uptake determined by the desorption measurements. Also shown in Fig. 1 are the results of exposing the 7.4% Ni/TiO<sub>2</sub> sample to oxygen. Extrapolation of these data to zero pressure gives an uptake of about 115 μmol/g. Consistent with the results of Smith *et al.* (5), the oxygen uptake is greater than the hydrogen uptake determined by adsorption measurements. Furthermore, it can be seen that the hydrogen

uptake determined by desorption measurements is between these above two values. In addition, the hydrogen uptake determined in this manner is not sensitive to the hydrogen pressure (35–45 kPa) used during equilibration of the sample prior to desorption measurements. The results of analogous adsorption/desorption studies of the 5.23% Ni-0.55% Fe/TiO<sub>2</sub> sample are also shown in Fig. 1. It can be seen that the zero-pressure intercept of the hydrogen desorption is about a factor of 2 larger than

that for the hydrogen adsorption measurements. In contrast, when these experiments were performed on a 6.1% Ni-0.5% Fe/ $\text{Al}_2\text{O}_3$  sample, the hydrogen uptake determined from desorption measurements was only about 15% larger than that from adsorption measurements.

Representative hydrogen adsorption and desorption measurements for the 1.07, 2.5, and 4.9% Pt/ $\text{TiO}_2$  samples are shown in Fig. 2. The zero-pressure intercepts of the apparent adsorption isotherms for all samples are essentially zero, in agreement with all previous studies of Pt/ $\text{TiO}_2$  catalysts. In contrast, however, the hydrogen desorption data extrapolate to zero pressure with uptakes from about 7–11  $\mu\text{mol/g}$ , indicating the existence of a slow hydrogen adsorption phenomenon.

To determine whether the increased up-

takes determined by hydrogen desorption compared to hydrogen adsorption measurements were due to slow adsorption (or absorption) by the support, experiments were conducted on blank titania. The support was reduced and evacuated in a similar manner as the Pt/ $\text{TiO}_2$  samples (during which the titania turned blue), followed by hydrogen desorption studies at room temperature. Extrapolation of these desorption data to zero pressure gave an uptake of about 2  $\mu\text{mol/g}$ . Thus, the higher uptakes of the Ni/ $\text{TiO}_2$  and Pt/ $\text{TiO}_2$  samples are due to effects of the metals on the support. Table 1 summarizes the H/M ratios (i.e., hydrogen atoms per total number of metal atoms) determined from the hydrogen adsorption and desorption measurements for all of the samples of this study. (The desorption uptakes were corrected for the 2- $\mu\text{mol/g}$  uptake of

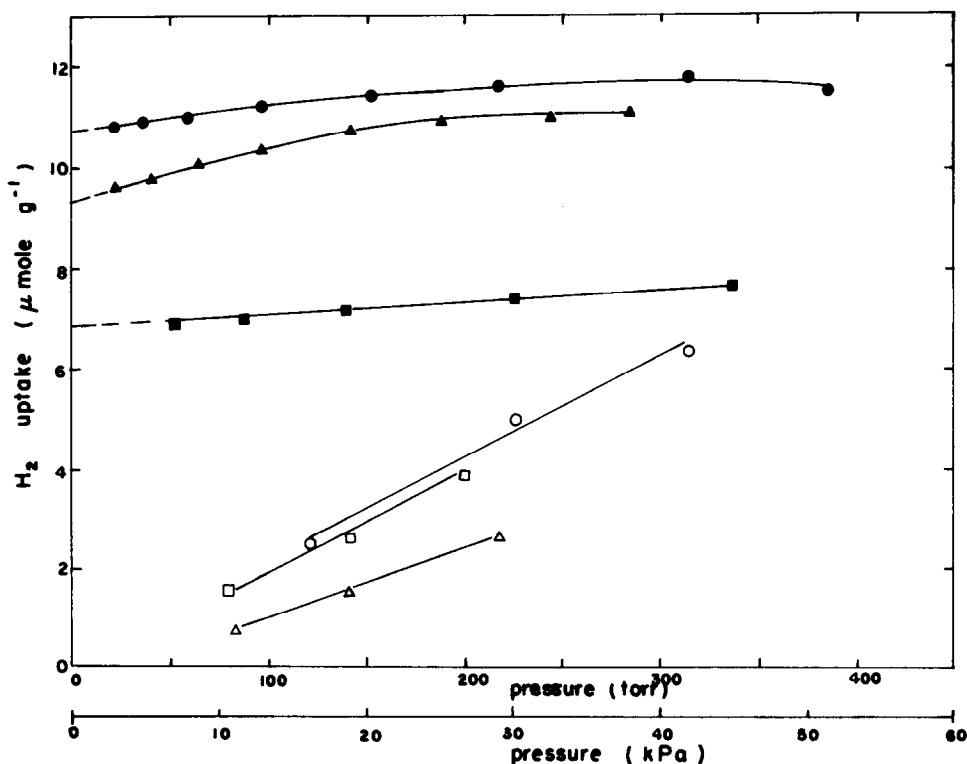


FIG. 2. Hydrogen uptakes of 1.07, 2.5, and 4.9% Pt/ $\text{TiO}_2$  samples at 295 K following hydrogen reduction at 770 K. ( $\Delta$ ,  $\square$ ,  $\circ$ )  $\text{H}_2$  uptakes from adsorption measurements on 1.07, 2.5, and 4.9% Pt/ $\text{TiO}_2$ , respectively; ( $\blacktriangle$ ,  $\blacksquare$ ,  $\bullet$ )  $\text{H}_2$  uptakes from desorption measurements on 1.07, 2.5, and 4.9% Pt/ $\text{TiO}_2$ , respectively.

TABLE 1

Hydrogen, Oxygen, and Carbon Monoxide Uptakes for Titania-Supported Samples at 295 K following Reduction at 770 K

Sample	H <sub>2</sub> , Adsorption		H <sub>2</sub> , Desorption		O <sub>2</sub> , Adsorption		CO, Adsorption	
	Uptake ( $\mu\text{mol/g}$ )	H/M	Uptake ( $\mu\text{mol/g}$ )	H/M	Uptake ( $\mu\text{mol/g}$ )	O/M	Uptake ( $\mu\text{mol/g}$ )	CO/M
7.4% Ni/TiO <sub>2</sub>	19	0.03	46	0.07	114	0.17	Ni(CO) <sub>4</sub> formation	
5.23% Ni } 0.55% Fe } /TiO <sub>2</sub>	16	0.03	34	0.07	100	0.19	Ni(CO) <sub>4</sub> formation	
1.07% Pt/TiO <sub>2</sub>	0	0	9.5	0.27	—	—	8	0.14
2.5% Pt/TiO <sub>2</sub>	0	0	7	0.08	—	—	5	0.04
4.9% Pt/TiO <sub>2</sub>	0	0	11	0.07	—	—	7	0.03
Blank TiO <sub>2</sub>	0	—	2	—	7	—	0	—

the support.) Also included in this table are the O/M ratios (i.e., oxygen atoms per total number of metal atoms) for the Ni/TiO<sub>2</sub> and NiFe/TiO<sub>2</sub> samples, after subtraction of the 7- $\mu\text{mol/g}$  O<sub>2</sub> uptake of blank titania determined in separate experiments.

Carbon monoxide adsorption and desorption data at room temperature for the 4.9% Pt/TiO<sub>2</sub> sample are shown in Fig. 3 (before and after evacuation of CO at room temperature). Unlike the behavior of hydrogen, the adsorption and desorption data superimpose, suggesting that these data in fact represent equilibrium isotherms. Subtracting the two isotherms at 15 kPa gives a value  $\Delta_{\text{CO}}$  of about 7  $\mu\text{mol/g}$ , corresponding to the amount of strongly held CO on the sample. Also shown in Fig. 3 are two desorption isotherms collected for blank TiO<sub>2</sub>. At a CO pressure of 15 kPa the difference between these isotherms is negligible. Thus, the strongly held CO on Pt/TiO<sub>2</sub> is related to the presence of Pt. Carbon monoxide desorption measurements were also performed on the 1.07 and 2.5% Pt/TiO<sub>2</sub> samples at room temperature, and the corresponding amounts of strongly held CO are given in Table 1.

If one compares the first adsorption isotherms at 15 kPa (i.e., before evacuation of the CO at room temperature) for 4.9% Pt/

TiO<sub>2</sub> and blank TiO<sub>2</sub>, then it can be seen in Fig. 3 that the presence of Pt leads to an increase in the extent of CO adsorption by about 11  $\mu\text{mol/g}$  at a pressure of 15 kPa. This corresponds to the total amount of CO which is weakly or strongly held on the Pt/TiO<sub>2</sub> samples. To confirm the above result that both weakly and strongly adsorbed CO molecules are associated with Pt, CO adsorption measurements were carried out at 190 K on the 4.9% Pt/TiO<sub>2</sub> sample. The rationale for decreasing the adsorption temperature was to increase the coverage by weakly adsorbed CO at a given CO pressure. Accordingly, the amount of CO adsorbed at ca. 15 kPa and the amount of CO remaining on the surface after evacuation to ca. 1 Pa should increase upon decreasing the temperature from 295 to 190 K. Thus, the difference  $\Delta_{\text{CO}}$  between the two CO isotherms collected before and after evacuation of the CO (i.e., the amount of so-called strongly held CO) should increase as the temperature is decreased. For the 4.9% Pt/TiO<sub>2</sub> sample, this difference between CO isotherms was about 127  $\mu\text{mol/g}$  at 190 K, compared to the aforementioned value of 7  $\mu\text{mol/g}$  measured at room temperature. Blank TiO<sub>2</sub> showed a difference  $\Delta_{\text{CO}}$  equal to 115  $\mu\text{mol/g}$  at 190 K. Subtracting the values of  $\Delta_{\text{CO}}$  for Pt/TiO<sub>2</sub> and TiO<sub>2</sub> suggests

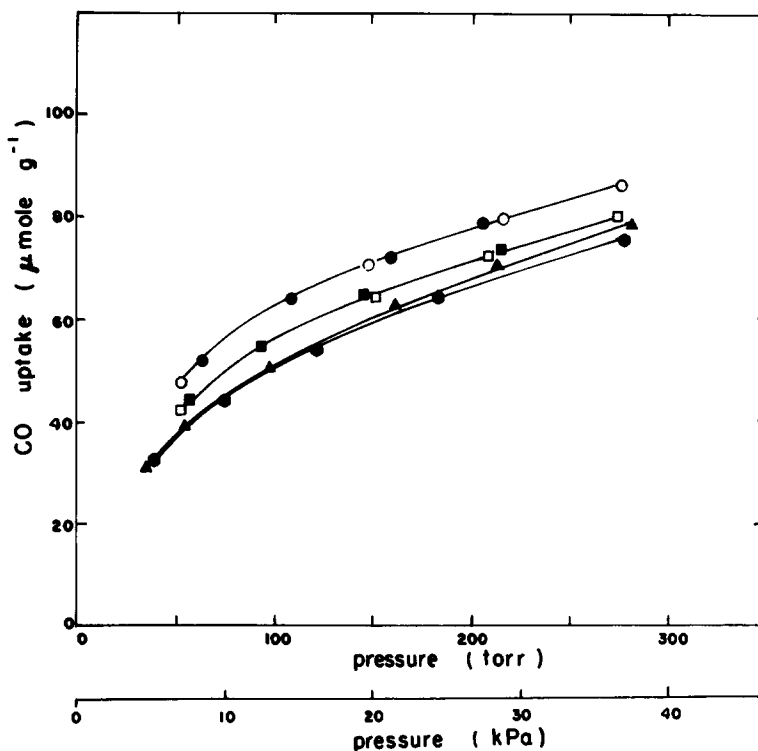


FIG. 3. Carbon monoxide uptakes of 4.9% Pt/TiO<sub>2</sub> sample and blank TiO<sub>2</sub> at room temperature following hydrogen reduction at 770 K. (○, ●) First CO isotherm for 4.9% Pt/TiO<sub>2</sub> from adsorption and desorption measurements, respectively; (□, ■) Second CO isotherm for 4.9% Pt/TiO<sub>2</sub> from adsorption and desorption measurements, respectively; (▲) First desorption isotherm for blank TiO<sub>2</sub>; (●) Second desorption isotherm for blank TiO<sub>2</sub>.

that at 190 K about 12  $\mu\text{mol}$  of CO are associated with Pt on 4.9% Pt/TiO<sub>2</sub> per gram of sample.

Carbon monoxide chemisorption measurements on metallic nickel at room temperature are complicated by the formation of volatile Ni(CO)<sub>4</sub>. It has been reported, however, that the formation of nickel carbonyl is suppressed when nickel is supported on titania (2). Accordingly, CO chemisorption measurements were attempted on the 7.4% Ni/TiO<sub>2</sub> sample. The sample was exposed to CO at a pressure of about 40 kPa, and the total pressure over the sample was monitored versus time. Even after 35 h the total pressure continued to decrease, suggesting the formation of Ni(CO)<sub>4</sub>. To test this hypothesis, a glass appendage of the apparatus was immersed in a dry ice-acetone bath (190 K) to freeze

any gaseous Ni(CO)<sub>4</sub>. It was thereby determined that about 100  $\mu\text{mol}$  of condensable species were present per gram of sample after ca. 50 h exposure to CO. Positive proof for the presence of Ni(CO)<sub>4</sub> was obtained by quickly removing the dry ice-acetone bath and heating the glass appendage to ca. 350 K: a nickel mirror formed during this procedure. Thus, it must be concluded that while strong metal-support interactions between nickel and titania may inhibit the formation of Ni(CO)<sub>4</sub>, these interactions do not eliminate this reaction at room temperature.

Table 2 shows the average metal particle sizes estimated from the hydrogen uptakes for the titania-supported Ni, NiFe, and Pt samples of this study. For the Ni and NiFe samples, oxygen uptakes were also used to estimate particle sizes. X-ray diffraction

TABLE 2

Average Metal Particle Sizes for Titania-Supported Samples after Reduction at 770 K

Sample	H <sub>2</sub> , Adsorption <i>d</i> (nm)	H <sub>2</sub> , Desorption <i>d</i> (nm)	O <sub>2</sub> , Adsorption <i>d</i> (nm)	X-ray <i>d</i> <sub>200</sub> (nm)	TEM
7.4% Ni/TiO <sub>2</sub>	26.7	11.4	4.7	11	—
5.23% Ni 0.55% Fe } /TiO <sub>2</sub>	25	12.3	4.3	11	—
1.07% Pt/TiO <sub>2</sub>	Very large	3	—	Peak not detectable	4
2.5% Pt/TiO <sub>2</sub>	Very large	10	—	10	—
4.9% Pt/TiO <sub>2</sub>	Very large	11	—	13	—

peaks for the (200) planes of these FCC metals were observable for all samples except 1.07% Pt/TiO<sub>2</sub>. The results of line-broadening analyses of these peaks are summarized in Table 2. For the 1.07% Pt/TiO<sub>2</sub> sample, where no X-ray diffraction peaks were detected for Pt, transmission electron microscopy was used to estimate an average Pt particle size.

Figures 4 and 5 are representative transmission electron micrographs of blank TiO<sub>2</sub> and 1.07% Pt/TiO<sub>2</sub> after reduction at 770 K and exposure to air at room temperature. A large number of small particles are present in micrographs of the 1.07% Pt/TiO<sub>2</sub> sample which are not apparent in the TiO<sub>2</sub> blank. For comparison with adsorption measurements, an area-average Pt particle size  $\langle d \rangle$  was estimated from the sizes  $d_i$  of 100 particles using the relation (20)

$$\langle d \rangle = \frac{\sum_i d_i^3}{\sum_i d_i^2}$$

The value of 4 nm determined in this manner agrees well with the 3-nm value obtained from the hydrogen desorption measurements (see Table 2). It should be noted that transmission electron microscopy studies were also performed on the other titania-supported samples of this paper. However, it can be seen in Fig. 4 that the titania blank shows a number of contrast features with dimensions of 10 nm and

larger. Since the metal particles on these other samples were about 10 nm in size (e.g., see the X-ray diffraction results of Table 2), it was difficult to distinguish the metal particles from the features of the support in the transmission electron micrographs.

## DISCUSSION

### *Adsorptive Properties of Titania-Supported Metal Samples*

The most striking observation of this study is that hydrogen apparently adsorbs on titania-supported samples after reduction at ca. 770 K, if the uptakes are determined by desorption measurements after the sample has equilibrated with the gas phase for long periods of time (ca. 15–20 h). This is in contrast to the small extents of chemisorption determined by traditional adsorption measurements. Indeed, Table 2 shows that the metallic particle sizes estimated from these hydrogen desorption measurements are in fair agreement with the sizes determined by X-ray line broadening or transmission electron microscopy.

Metallic particle sizes estimated from hydrogen adsorption measurements and oxygen uptake determinations are also listed in Table 2. The former measurements give particle sizes which are too large, as expected from previous studies (e.g., (11,





FIG. 4. Transmission electron micrograph of blank  $\text{TiO}_2$  following hydrogen reduction at 770 K.

12)). Consistent with the work of Smith *et al.* (5), oxygen uptake measurements on nickel-containing samples give particle sizes which are in approximate agreement with the results of X-ray diffraction. These sizes based on oxygen uptakes appear to be

too small, but it is difficult to make a quantitative comparison since the shape of the particle size distribution is not known. In addition, the metal particles are probably not spherical in shape (e.g., (21, 22)) and this also complicates the comparison of av-

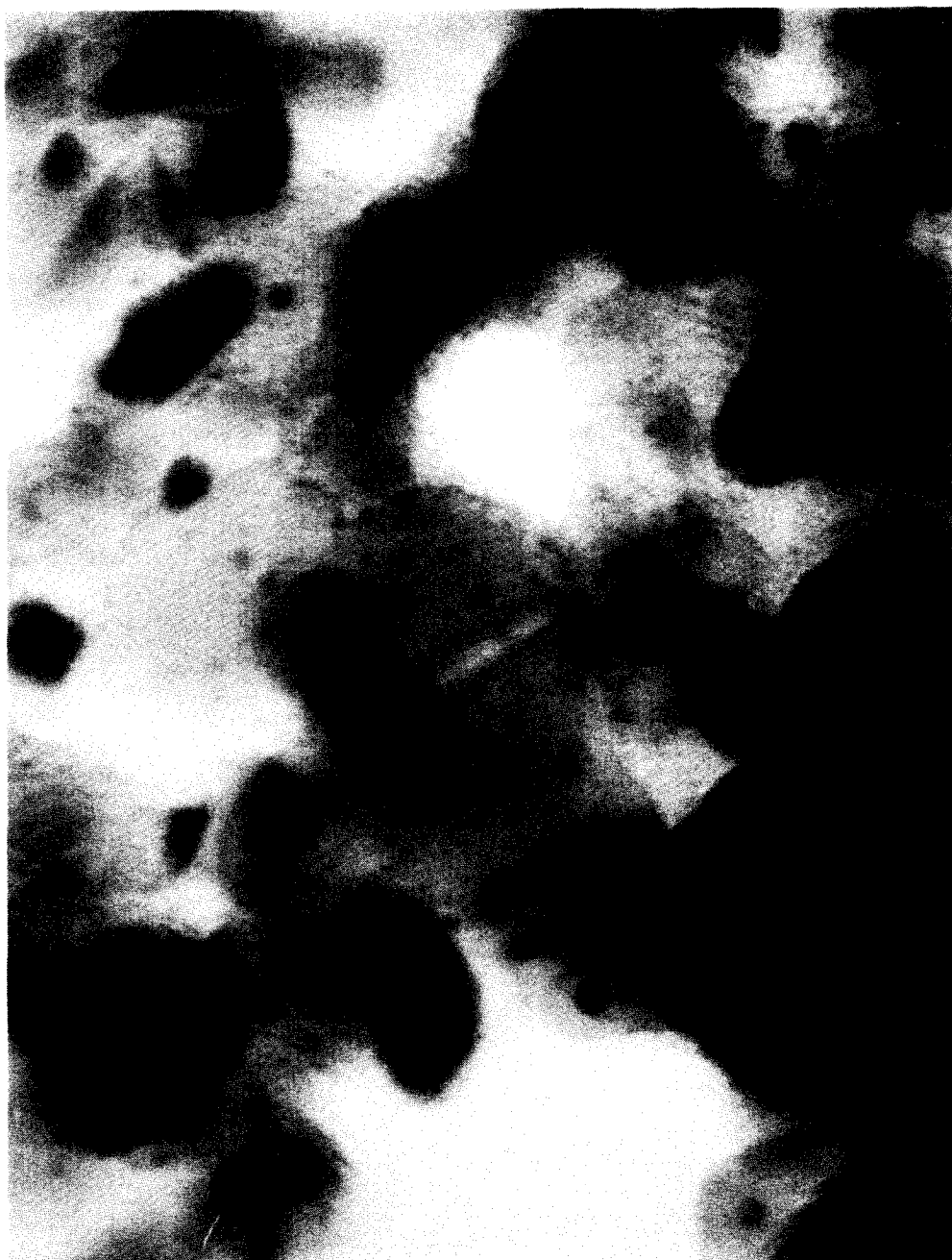


FIG. 5. Transmission electron micrograph of 1.07% Pt/TiO<sub>2</sub> sample following hydrogen reduction at 770 K.

erage particle sizes determined by different techniques.

In short, the results of this study show that in addition to oxygen uptake determinations, hydrogen desorption measure-

ments can be used to estimate particle sizes of titania-supported metals. Further studies will be required to assess the quantitative validity of this desorption technique.

It is appropriate at this point to address

the possible origins of this slow hydrogen uptake by titania-supported samples. In general, hydrogen may be adsorbed by both the metal particles and the titania support. This has been shown by Gajardo *et al.* (23) in nuclear magnetic resonance studies of hydrogen adsorbed on Rh/TiO<sub>2</sub> samples. Furthermore, the hydrogen associated with the support may be present in at least two forms: associated with Ti<sup>3+</sup> cations or present as hydroxyl groups. Consider first the role of Ti<sup>3+</sup> cations. Electron spin resonance studies have revealed the presence of Ti<sup>3+</sup> in reduced or evacuated samples of titania (24–28). Studies of oxygen adsorption on titania have suggested that at least a fraction of these Ti<sup>3+</sup> cations may be located at or near the surface (25–28). Furthermore, the presence of Group VIII metals is known to facilitate reduction of titania (e.g. (4, 6, 7, 29)). Hence, the increased hydrogen uptake of titania-supported metal samples, compared to blank TiO<sub>2</sub>, can be understood in terms of a greater concentration of Ti<sup>3+</sup>. In addition, the correlation of the hydrogen uptake measurements (from desorption studies) with the results of metal particle size determinations by X-ray diffraction and electron microscopy can be explained by assuming that the amount of Ti<sup>3+</sup> formed is related to the surface area of the metal particles. For example, it has been proposed by Huizinga and Prins (4) that the Ti<sup>3+</sup> cations formed during the reduction of Pt/TiO<sub>2</sub> are located near the Pt particles. In addition, Knotek (30) has shown that Ti<sup>3+</sup> cations at or near the surface are capable of adsorbing hydrogen. It should be noted that using X-ray photoelectron spectroscopy, Sexton *et al.* (7) and Chien *et al.* (8) could not detect the presence of Ti<sup>3+</sup> near the surface of Rh/TiO<sub>2</sub> samples after reduction at ca. 770 K. It was concluded that Ti<sup>3+</sup> is more stable in the bulk than at the surface of titania and that the Ti<sup>3+</sup> formed on the titania surface during hydrogen reduction of titania-supported metal samples may diffuse into the support at ca. 770 K. This would suggest

that if Ti<sup>3+</sup> cations are responsible for the slow hydrogen uptake observed in the present study, then these cations may be located beneath the surface. Moreover, the fact that the reduced titania blanks did not show this slow hydrogen uptake would suggest that molecular hydrogen must first be dissociated by the Group VIII metal particles, followed by the diffusion of atomic hydrogen into the reduced titania support. Evidence for such a process (for the absorption of hydrogen by titanium films) has been reported by Kasemo *et al.* (31) and Kasemo and Törnqvist (32).

Besides Ti<sup>3+</sup>, it must be considered that titania may adsorb hydrogen as OH groups due to spillover of atomic hydrogen from the metal to the support. Huizinga and Prins (4) suggested that OH groups were formed on titania upon exposure of Pt/TiO<sub>2</sub> to hydrogen at room temperature. Under similar conditions, Chen and White (9) reported the slow formation of OH groups on Pt/TiO<sub>2</sub> samples. In addition, Knotek (30) has shown that hydrogen may be bonded to titania as OH groups on the surface or in subsurface regions. The correlation of the hydrogen uptake with the metal particle size measurements suggests that if OH groups are formed on titania, these groups may be in the vicinity of the metal particles. Indeed, this is consistent with the model of Huizinga and Prins (4) according to which OH groups are formed near the interface between the metal particles and the titania support. This is also consistent with the model (13, 14) in which TiO<sub>x</sub> species are on the surface of titania-supported metal particles, since these species may also form OH groups.

It is apparent from the above discussion that the slow hydrogen uptake observed in this study can be interpreted in terms of slow adsorption (or absorption) of hydrogen by regions of the titania support which are near the metal particles (and TiO<sub>x</sub> species which are on the metal particles).

The role of the metal particles in this adsorption of hydrogen must now be consid-

ered. It seems likely that one function of the metal particles is to dissociate molecular hydrogen, followed by the migration of atomic hydrogen from metal atoms to titania (4, 9, 23, 29). The rate of this slow adsorption process may be limited by the rate of surface diffusion and/or the rate of dissociative hydrogen adsorption. Furthermore, the small hydrogen uptakes observed in adsorption studies of titania-supported metals suggest that the titania support decreases the binding energy of hydrogen to the metal surface (9, 33). In fact, it is possible that a decrease in the strength of hydrogen adsorption may be related to a decrease in the rate of dissociative hydrogen adsorption on the metal. In particular, it will be suggested below that strong metal-support interactions between Group VIII metals and titania may be the result of electronegative titanium species (e.g.,  $\text{TiO}_x$ ) on the surface of the metal particles. These titanium species not only block a certain fraction of the metal surface, but they may also decrease the rates and strengths of hydrogen and carbon monoxide adsorption on the remaining, accessible metal surface sites. The recent work of Chen and White (9) suggests that at least for Pt, the primary effect of strong metal-support interactions is to decrease the strength of hydrogen adsorption on the metal surface, since the Pt/ $\text{TiO}_2$  samples studied by these authors catalyzed H-D exchange at room temperature.

The results of CO adsorption/desorption measurements reported in this study provide information complementary to that obtained from the hydrogen adsorption/desorption studies. For example, the slow uptake of hydrogen by titania-supported Pt samples was not observed for CO in analogous adsorption/desorption experiments. This verifies that the slow hydrogen uptake is related to the rates of hydrogen dissociation and/or surface diffusion of atomic hydrogen, since CO does not dissociate on Pt at the temperatures of this study (e.g. (34)). In addition, evidence that strong-metal interactions between Pt and titania lead to

weaker adsorption on the metal surface is provided by the observation that the extent of CO adsorption on Pt/ $\text{TiO}_2$  was increased by decreasing the temperature from 295 to 190 K. Specifically, this behavior can be attributed to the effects of metal-support interactions because CO adsorption normally reaches saturation coverage on Pt at room temperature for the CO pressures used in the present study (e.g. (11, 12)).

Finally, comment should be made about the slow rate of  $\text{Ni}(\text{CO})_4$  formation over titania-supported nickel, compared to nickel on other supports (e.g.,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) (2). The results of the present study indicate that the rate of  $\text{Ni}(\text{CO})_4$  formation over Ni/ $\text{TiO}_2$  at room temperature is about  $10^{10}$  molecules/ $\text{cm}^2 \cdot \text{s}$  (i.e., ca.  $100 \mu\text{mol Ni}(\text{CO})_4$  formed in 35 h for a sample with a hydrogen uptake of ca.  $45 \mu\text{mol}$ ). This is at least an order of magnitude slower than that rate observed over single crystal nickel surfaces at room temperature and similar CO pressures (35), in agreement with the findings of Vannice and Garten (2). It is possible that the slow rate of  $\text{Ni}(\text{CO})_4$  formation over Ni/ $\text{TiO}_2$  could be related to a decrease in the strength of CO adsorption on Ni caused by the titania support, (i.e., an electronic effect) and/or a partial blocking of the Ni surface by  $\text{TiO}_x$  species.

#### *Possible Model to Explain Adsorptive Properties of Titania-Supported Metals*

Since the above results indicate that strong metal-support interactions between Group VIII metals and titania lead to decreases in the strengths of hydrogen and carbon monoxide adsorption, and perhaps also a decrease in the rate of hydrogen adsorption, this paper closes with a model to explain these results. The principal assumption of this model is that  $\text{TiO}_x$  species are present on the surfaces of titania-supported metal particles following reduction at high temperatures (13, 14).

One simple effect of  $\text{TiO}_x$  species on metal particles is to physically cover surface metal atoms, thereby decreasing the

adsorption capacity and catalytic activity of the metal particles. Yet, these surface species may also perturb the chemical and catalytic properties of the neighboring surface metal atoms which may still be accessible to gaseous molecules. It has been generally proposed that strong metal-support interactions are due to electron transfer from  $Ti^{3+}$  to Group VIII metals (e.g. (35)). Similarly, it has also been proposed that the role of alkali metal promoters on Group VIII metals is to transfer electrons to the metal (e.g. (37, 38)). Herein lies an apparent paradox. Electron transfer from  $Ti^{3+}$  to the metal apparently suppresses hydrogen and carbon monoxide adsorption, while electron transfer from alkali metals to Group VIII metals facilitates the adsorption of these molecules. The role of these surface additives is apparently more complicated than the simple direction of electron transfer.

To resolve this problem, reference is given to studies of the interaction of potassium with metallic iron surfaces and the chemical consequences of these interactions (38–42). As expected from the electropositive nature of potassium, work function measurements have demonstrated that adsorption of potassium is accompanied by electron transfer from potassium to iron. Importantly, the chemical consequences of this addition of potassium to the iron surface are localized near each potassium atom. For example, each potassium atom creates one surface site on iron which binds molecular nitrogen more strongly than iron alone (42). This has been interpreted in terms of a lowering of the "local work function" near each potassium atom. This leads to an increase in the binding energy of molecular nitrogen to the surface and to an increase in the rate of dissociative nitrogen adsorption. Analogously, it has been found that the presence of electronegative species (e.g., O, C, Cl, S, P) on metal surfaces decreases the rates of hydrogen and carbon monoxide adsorption and also decreases the strengths of adsorption (e.g. (38)). That

is, electronegative additives have the opposite effect of alkali metal additives. It is thus now postulated that one origin of strong metal-support interactions is the presence of electronegative  $TiO_x$  species on the surfaces of titania supported metal particles. According to the above arguments, these species could decrease the strengths of hydrogen and carbon monoxide adsorption. In addition, they could decrease the rate of dissociative hydrogen adsorption in a way analogous to the manner by which potassium increases the rate of dissociative nitrogen adsorption on iron.

#### CONCLUSIONS

The slow uptake of hydrogen on titania-supported metal samples (i.e., Ni, NiFe, and Pt on  $TiO_2$ ) at room temperature was evidenced by the difference between hydrogen adsorption measurements carried out over a period of several hours and hydrogen desorption studies following prolonged exposure (ca. 15–20 h) to hydrogen at a pressure of about 40 kPa. The hydrogen uptakes determined by such desorption measurements provide estimates for metallic particle sizes which are in agreement with those sizes determined by X-ray line broadening or transmission electron microscopy. This slow hydrogen uptake can be attributed to the bonding of hydrogen to  $Ti^{3+}$  or to the formation of hydroxyl groups on titania. A correlation exists between the extent of hydrogen uptake and the metal particle size, suggesting that this bonding takes place at regions of the titania support which are near metal particles or on  $TiO_x$  species which may be present on the surface of the metal particles.

In general, the metal-support interactions which take place between Pt and titania upon reduction in hydrogen at 770 K appear to decrease the heats of hydrogen and carbon monoxide adsorption on the metal surface. It is also possible that the rate of hydrogen dissociation may be decreased. In addition, for Ni/ $TiO_2$  samples, the rate of  $Ni(CO)_4$  formation at room tem-

perature is decreased compared to the corresponding rates over Ni supported on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> and the rate over Ni single-crystal surfaces. These results can be understood in terms of the presence of TiO<sub>x</sub> species on the surfaces of these titania-supported metals.

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