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Electron Microscopy Study of the Interactions of Rhodium with Titania

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Transmission electron microscopy has been used to study strong metal–support interactions in the Rh/TiO_2 system. Selected-area electron diffraction and X-ray diffraction were used to characterize the TiO_2 support as a function of reduction temperature. A specially prepared sample of TiO_2-promoted Rh/SiO_2 was examined to study the interaction of TiO_2 with Rh metal particles. Temperature-programmed desorption experiments were performed on the Rh/TiO_2 and the TiO_2-promoted Rh/SiO_2 samples to investigate the adsorption of H_2 and CO as a function of catalyst reduction temperature. The suppression of H_2 and CO chemisorption with increasing reduction temperature observed for both samples is attributed to a physical blockage of Rh surface sites by TiO_x moieties.

INTRODUCTION

Considerable attention has been given recently to the interactions of Group VIII metals with titania and other reducible oxides (*1–4*). A common feature of such systems is the suppression of H_2 and CO chemisorption following high-temperature reduction. This phenomenon is attributed to the presence of a strong metal–support interaction (SMSI) (*1*). Several investigators have used transmission electron microscopy to characterize the structure of titania and its manner of interaction with small metal crystallites (*5–10*). Baker *et al.* (*5, 6*) have examined Pt/TiO_2 samples prepared by vapor deposition of Pt on TiO_2 films. Upon reduction at 823 K, the Pt particles assumed a pillbox morphology of hexagonal outline and portions of the substrate were reduced to Ti_4O_7. This behavior was considered to be indicative of SMSI. In a subsequent study, Baker *et al.* (*7*) examined the behavior of Ag and Ag + Pt deposited on TiO_2. Reduction of Ag/TiO_2 at 823 K produced no change in Ag particle morphology and no evidence of Ti_4O_7. When Pt was introduced to the sample, the Ag particles took on a pillbox shape and the support underwent reduction to Ti_4O_7. The authors concluded that the function of Pt is to dissociate H_2, thereby providing a source of H atoms for converting TiO_2 to Ti_4O_7. More recently, Simoens *et al.* (*8*) have examined Ni/TiO_2 samples prepared in a manner similar to that used to prepare the Pt/TiO_2 samples of Baker *et al.* (*5*). From transmission electron microscopy and complementary data derived from *in situ* ferromagnetic resonance spectra and Auger spectra, the authors proposed that the SMSI properties of Ni are brought about by a migration of titanium–oxygen moieties onto the Ni particles. Further support of this model has been presented by Baker *et al.* (*9*) based on studies of Pd/TiO_2 samples by electron microscopy and H_2 chemisorption. It was concluded that the concurrent suppression of H_2 adsorption and absorption upon high-temperature reduction is attributable to reduction of TiO_2 to Ti_4O_7 which leads to the simultaneous formation of mobile titanium suboxide species which migrate onto the Pd particles. It should be noted, though, that while the "decoration" model seems quite plausible, it has been questioned by Kelley

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et al. (*10*), based on data from ion scattering spectroscopy, transmission electron microscopy, and electron energy-loss spectroscopy.

In the present paper, transmission electron microscopy and selected-area electron diffraction have been used to characterize the interactions of Rh with TiO_2. Catalyst samples were prepared both in the form of Rh supported on TiO_2 and TiO_2-promoted Rh supported on SiO_2. These catalysts are of considerable interest since they exhibit particularly high activities for both CO hydrogenation (*11, 12*) and NO reduction (*13, 14*). The results of this study support the "decoration" model proposed recently by a number of authors (*8, 15–21*), and provide insights concerning the nature of the titanium-oxide moieties covering the Rh particles.

EXPERIMENTAL

Catalyst preparation. The supported catalysts were prepared using $RhCl_3 \cdot 3H_2O$ (Aldrich Chemicals) as the metal precursor. Samples of 4 and 25 wt% Rh were prepared by incipient wetness impregnation of the support with a solution of $RhCl_3$ dissolved in deionized water. The support materials used were Cab-O-Sil HS-5 Silica (BET surface area, 300 m^2/g) and Degussa P25 titania (BET surface area, 50 m^2/g). An additional sample of Rh/TiO_2 was prepared by ion exchange using the method of Resasco and Haller (*22*). The metal content of this sample was determined by X-ray fluorescence to be 0.51 wt% Rh. Following introduction of $RhCl_3$, each sample was dried overnight in a vacuum oven at 338 K, and calcined in a 21% O_2/He mixture at 773 K for 1 h. Portions of each sample were then reduced in H_2 at 573, 773, and 1073 K for at least 2 h.

A TiO_2-promoted Rh/SiO_2 sample was prepared in the following manner. A 4 wt% Rh/SiO_2 catalyst, prepared by impregnation of SiO_2 with a solution of $RhCl_3$, was dried but not calcined. This material was then impregnated with $Ti(OCH_3)_4$ (Alfa Chemicals) dissolved in 1 *N* HCl, by dropwise addition to the point of incipient wetness. The amount of $Ti(OCH_3)_4$ added corresponded to a Ti weight loading of 5%. A blank sample (TiO_2-on-SiO_2) containing no Rh was prepared in a similar manner. Both samples were dried overnight in a vacuum oven at 338 K and calcined in a 21% O_2/He mixture at 773 K for 1 h. Portions of these materials were then reduced in H_2 at 573 and 773 K for at least 2 h.

The Rh weight loading of each sample was determined by X-ray fluorescence. The Rh dispersion was measured by volumetric chemisorption of H_2 at room temperature on samples which were reduced overnight at 573 K. The structure of the titania support was characterized by X-ray diffraction. These analyses were performed on a Siemens Model D500 diffractometer using Cu$K\alpha$ radiation.

Transmission electron microscopy. The supported catalysts were ground to a fine powder and dispersed in deionized water. A drop of the suspension was then placed on a carbon-coated electron microscope grid and evaporated to dryness. Examination of the specimens was carried out in a Jeol 200CX electron microscope equipped with a top-entry goniometer stage and operated in the diffraction and imaging modes. The maximum attainable point-to-point resolution was 2.5 Å. It should be noted that the reduced samples were examined after exposure to air at room temperature. As noted in a recent study (*23*), a Rh/TiO_2 catalyst reduced at high temperature still exhibits a suppression of H_2 and CO chemisorption even after exposure to room-temperature air over long periods of time.

Temperature-programmed desorption of H_2 and CO. The H_2 and CO adsorption capacity of the 0.5 wt% Rh/TiO_2 and the TiO_2-promoted 4% Rh/SiO_2 samples was determined by temperature-programmed desorption. The apparatus used for these measurements has been described previously (*24*). A 30-mg sample of the catalyst was placed in a quartz microreactor and reduced in H_2 for at least 2 h at a temperature in the range 523–773 K. The catalyst was

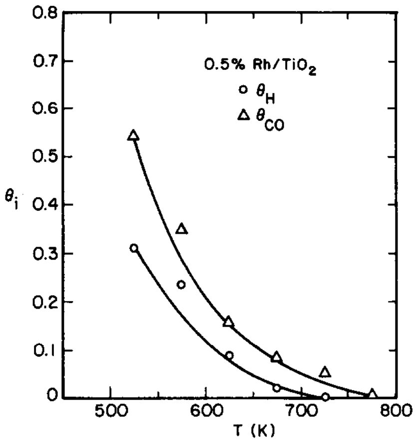

FIG. 1. Effect of catalyst reduction temperature on the maximum H_2 and CO coverage for 0.5% Rh/TiO$_2$.

then evacuated and the temperature ramped under vacuum to 823 K. The sample was subsequently cooled under vacuum to room temperature. The microreactor was repressurized with helium, and either H_2 or CO was pulsed to the reactor to achieve saturation coverage of the catalyst. The catalyst was then ramped to 823 K at a linear heating rate of 1 K/s in a helium stream flowing at 50 cm^3/min. This procedure was repeated for successively higher reduction temperatures, and from the measured amount of H_2 or CO desorbed, the initial coverage of the adsorbate was determined as a function of catalyst reduction temperature.

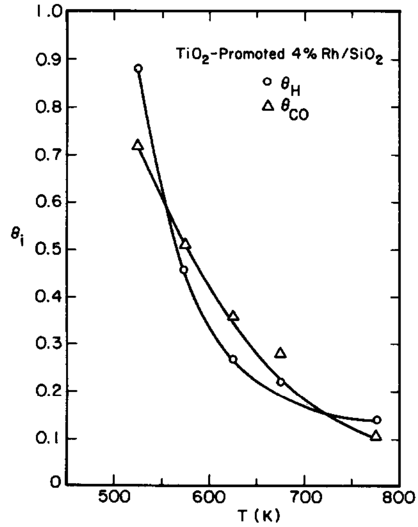

FIG. 2. Effect of catalyst reduction temperature on the maximum H_2 and CO coverage for TiO$_2$-promoted 4% Rh/SiO$_2$.

RESULTS

H_2 and CO Adsorption

The adsorption of H_2 and CO was studied as a function of catalyst reduction temperature for the 0.5 wt% Rh/TiO$_2$-promoted 4% Rh/SiO$_2$ samples. The maximum H_2 and CO coverages are shown in Fig. 1 as a function of catalyst reduction temperature for the 0.5 wt% Rh/TiO$_2$ sample. The uptake of both adsorbates decreases with increasing catalyst reduction temperature, and after reduction at 773 K, diminishes to almost zero. Figure 2 shows the variation in the maximum H_2 and CO coverages as a function of catalyst reduction temperature for the TiO$_2$-promoted 4% Rh/SiO$_2$ sample. Comparison of Figs. 1 and 2 shows that the TiO$_2$-promoted Rh/SiO$_2$ catalyst behaves very similarly to the Rh/TiO$_2$ catalyst. Here again, the uptakes of H_2 and CO decrease with increasing catalyst reduction temperature. The observed decrease in the chemisorption capacity of the TiO$_2$-promoted catalyst is due totally to the promoter, since independent experiments showed that the H_2 and CO chemisorption capacities of an equivalent Rh/SiO$_2$ catalyst did not change when the catalyst was reduced at temperatures between 523 and 773 K.

TiO$_2$ Support

The TiO$_2$ support was examined after various pretreatments. Figure 3 shows an electron diffraction pattern of untreated TiO$_2$ support. Analysis of the electron diffraction pattern indicates that the support is a mixture of the anatase and rutile phases of TiO$_2$. This was also confirmed by X-ray diffraction. The major *d*-line spacings, together with their relative intensities, are given in Table 1. Based on the relative intensity of the principal *d*-line spacings for the anatase and rutile phases of TiO$_2$ (3.54

TABLE 1

XRD *d*-Line Spacings for Degussa P25 TiO_2

d (Å)	Assignment	*I*
3.54	Anatase	1.0
3.27	Rutile	0.47
1.90	Anatase	0.27
1.69	Rutile	0.24

and 3.27 Å, respectively), the support composition was determined to be 70% anatase and 30% rutile. Reduction of the support at 573 or 773 K did not result in any significant changes in the structure. The X-ray diffraction pattern taken after reduction at 773 K shows the support composition is still 70% anatase and 30% rutile. The electron diffraction pattern taken after reduction of the support at 1073 K shows that it has now fully converted to the rutile phase of TiO_2. This conclusion was also confirmed by X-ray diffraction. The anatase phase is stable at low temperatures, but it is known to transform to the rutile phase after H_2 reduction at temperatures above 973 K (*25*). The support color changed from white to deep blue after reduction at 1073 K. This is believed to be due to the creation of oxygen vacancies in the TiO_2 lattice.

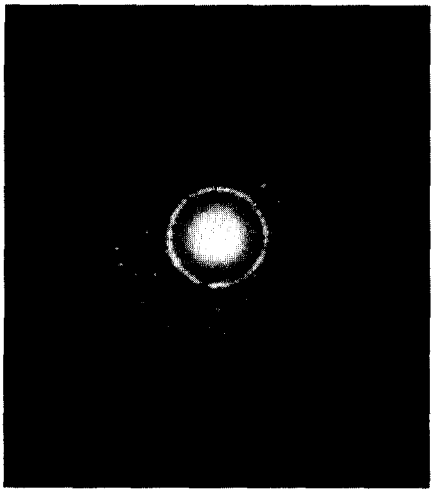

FIG. 3. Electron diffraction pattern of untreated TiO_2.

Rh/TiO_2 Catalysts

The 0.5, 4, and 25 wt% Rh/TiO_2 samples were studied after reduction at 573, 773, and 1073 K. Figures 4, 5, and 6 show the micrographs with the corresponding electron diffraction patterns for the 0.5 wt% Rh/TiO_2 catalyst. The metal particles indicated in the micrographs were identified by selected-area electron diffraction. The particles appear to have a circular shape after reduction at 573 K. Reducing the catalyst at 773 K causes some of the particles to become hexagonal in shape. This shape is retained even after the reduction temperature is raised to 1073 K. The absence of thickness fringes in the metal particles suggests that the particles are fairly flat for reduction temperatures up to 1073 K. Comparison of the micrographs shows no major changes in particle size, thus sintering does not occur during reduction. As with the 0.5 wt% Rh/TiO_2 catalyst, the 4 wt% Rh/TiO_2 catalyst also showed little evidence of sintering upon reduction up to 1073 K. A small amount of sintering was observed when the 25 wt% Rh/TiO_2 catalyst was reduced at 1073 K.

The interface between the Rh particles and the TiO_2 substrate was also examined. Based on electron diffraction studies it was concluded that there is no evidence for any compound formation between the Rh particles and the TiO_2 support. Examination of the catalyst at high resolution verifies that there is a sharp interface between the metal and the support. However, careful examination of the Rh particles following reduction at 1073 K, reveals that some of the Rh particles are covered with a thin layer amorphous material at the edges (see Fig. 6). This material is believed to be TiO_2. The possibility that the amorphous layer is rhodium oxide was considered but discarded based on temperature-programmed reduction spectra which showed that air exposure of reduced Rh/TiO_2 catalysts resulted in the pickup of no more than a monolayer

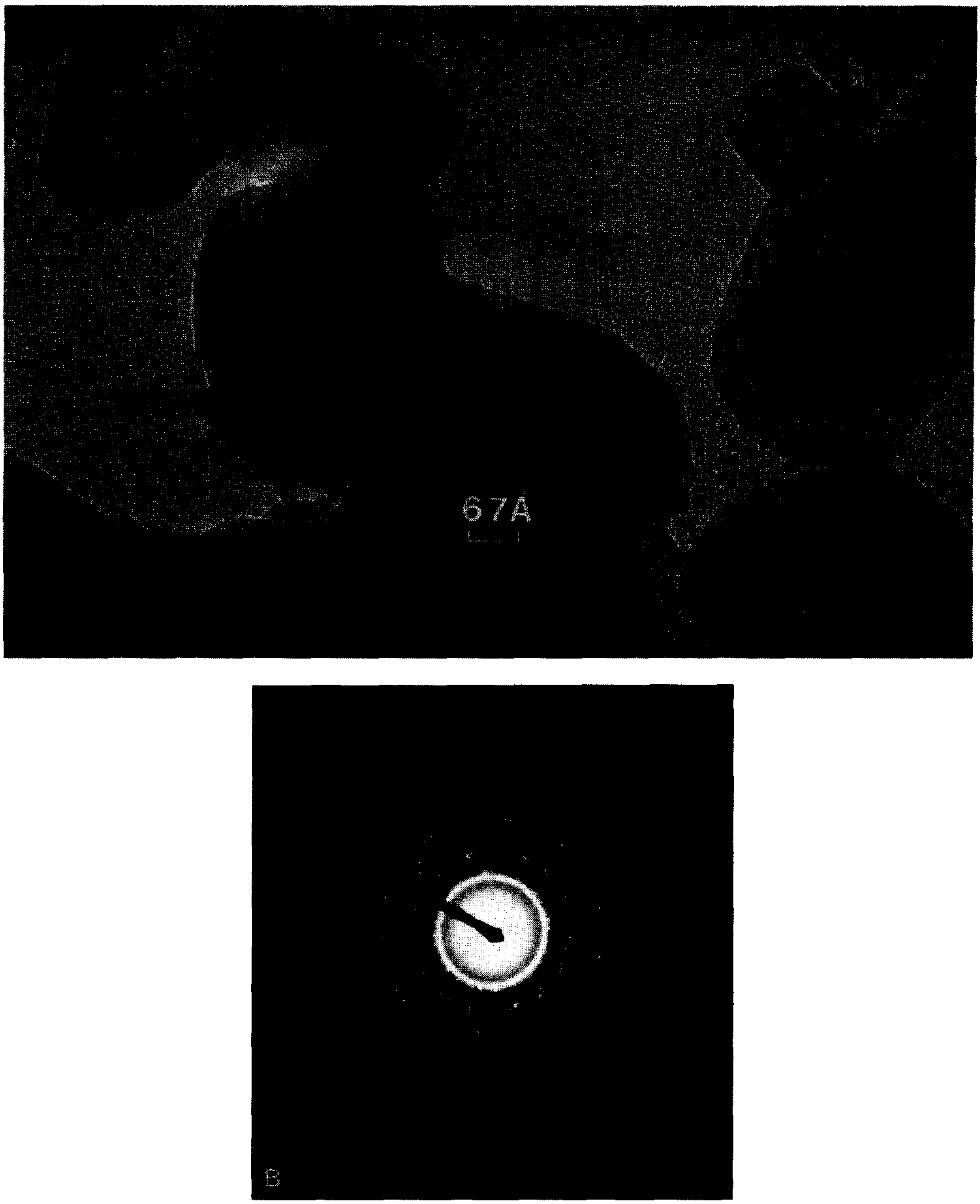

FIG. 4. Micrograph (A) and electron diffraction pattern (B) of 0.5% Rh/TiO_2 after 573 K reduction (1 cm = 67 Å).

of oxygen on the exposed surfaces of Rh particles. The above observations regarding particle shape, morphology and the nature of the metal–support interface were also found to be valid for the 4 and 25 wt% Rh/TiO_2 catalysts.

High-resolution micrographs and the corresponding electron diffraction patterns of the 25 wt% Rh/TiO_2 sample are shown in Figs. 7, 8, and 9 after reduction at 573, 773, and 1073 K. The micrographs show the Rh metal particles on the TiO_2 substrate. Lat-

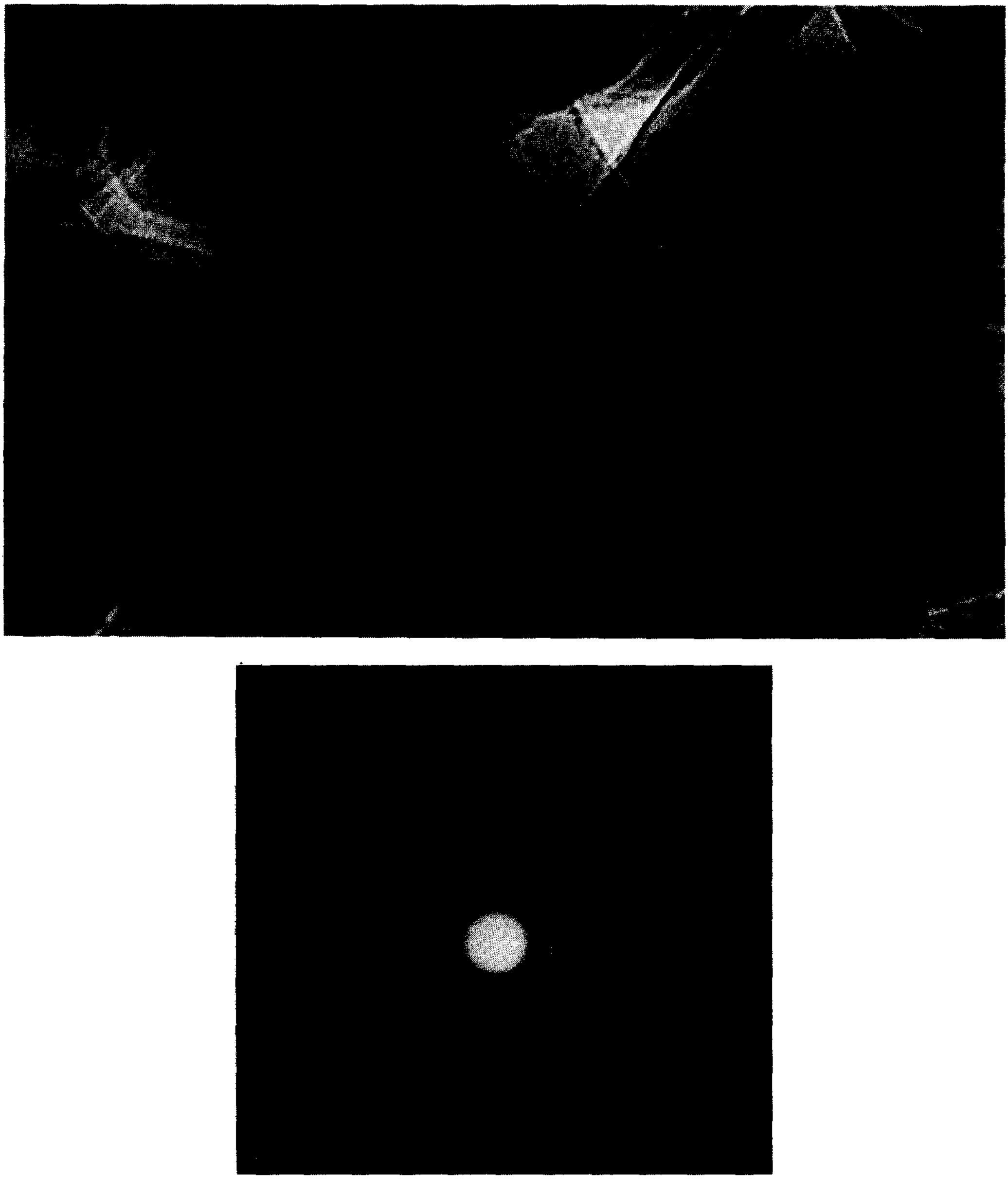

FIG. 5. Micrograph (A) and electron diffraction pattern (B) of 0.5% Rh/TiO_2 after 773 K reduction (1 cm = 67 Å).

tice fringes of the Rh particles and Moiré fringes formed by the overlap of TiO_2 and Rh are clearly visible. The electron diffraction pattern and the lattice fringes of the support correspond to the anatase and rutile phases of TiO_2, for reduction at 573 and 773 K. The high-resolution micrograph and electron diffraction pattern of Fig. 9 shows that the support has transformed entirely to the rutile phase after reduction at 1073 K. The micrograph shows a Rh particle at the edge of the support; again a thin amorphous region of TiO_2 is observed at the edges of the metal particle. The (111) planes of the Rh are resolved with a spacing of 2.2 Å. The electron diffraction pattern of the metal particle shows a continuous diffraction ring, indicating that Rh is present in

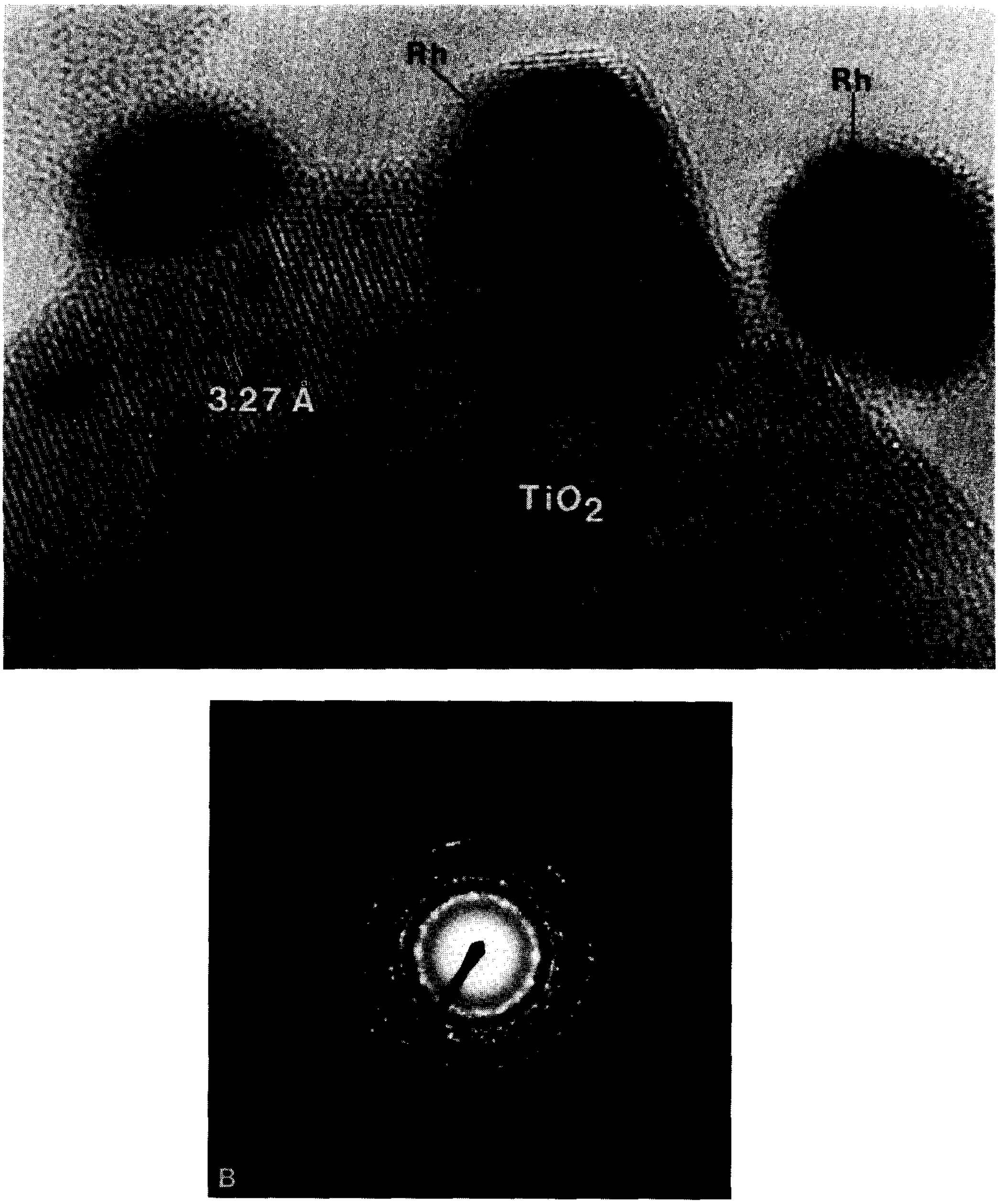

FIG. 6. Micrograph (A) and electron diffraction pattern (B) of 0.5% Rh/TiO_2 after 1073 K reduction.

many crystallographic orientations. From this it is concluded that the Rh metal particle does not exhibit a preferred orientation relative to the TiO_2 support.

Analysis of the electron diffraction patterns show that the support remains a mixture of the anatase and rutile phases of TiO_2 for reduction up to 773 K on the samples of 0.5, 4, and 25 wt% Rh/TiO_2. The support composition was determined by X-ray diffraction to be 70% anatase and 30% rutile for reduction of the supported catalyst up to 773 K. Reduction of these catalyst samples at 1073 K results in a transformation of the support to the rutile phase of TiO_2. This is identical to the behavior observed for the

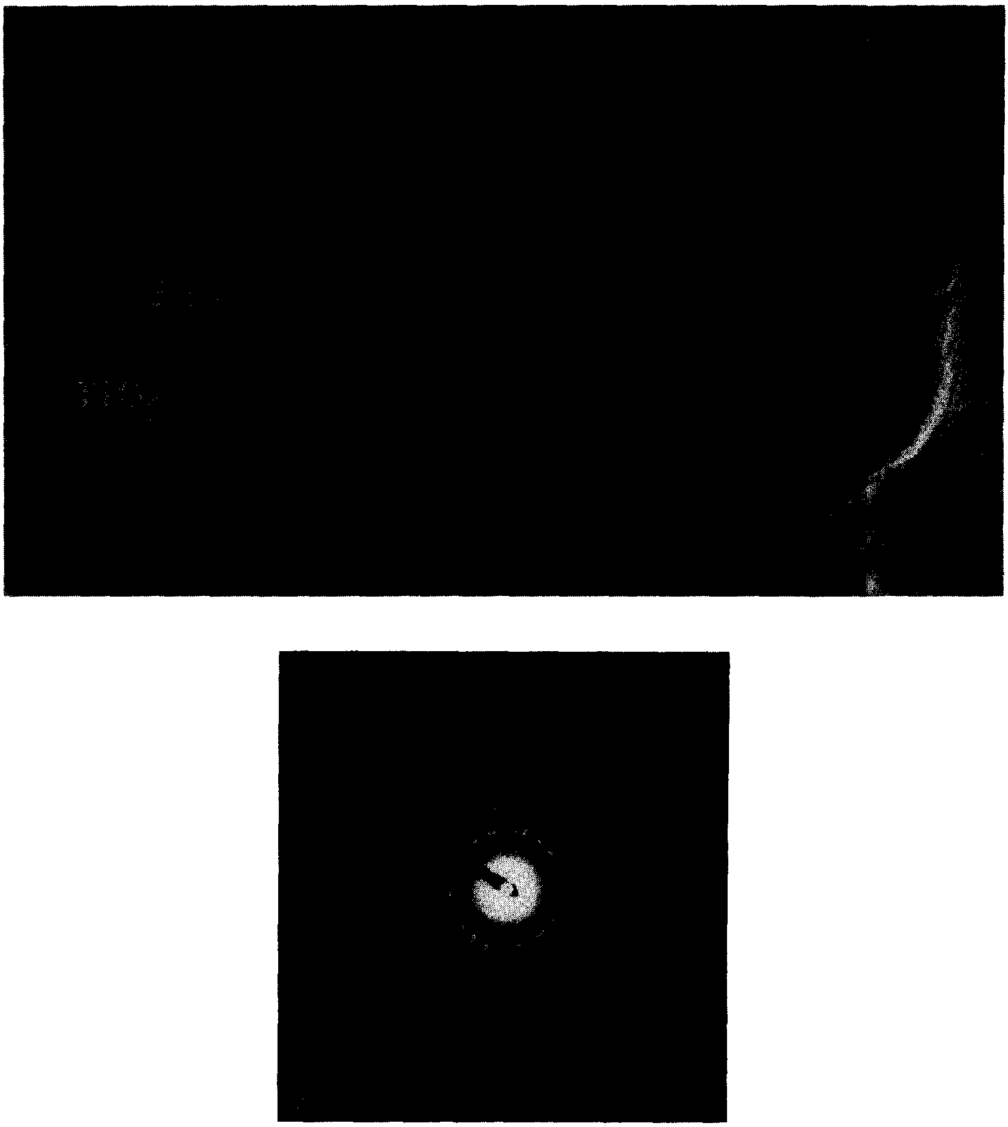

FIG. 7. Micrograph (A) and electron diffraction pattern (B) of 25% Rh/TiO_2 after 573 K reduction.

TiO_2 support in the absence of the metal, and suggests that the anatase-to-rutile phase change is unaffected by the presence of the Rh metal particles.

The supported catalyst samples were carefully examined for any evidence of crystalline Ti_4O_7 or other suboxide phases by both electron diffraction and X-ray diffraction. No evidence was found for any crystalline suboxide phases on the 0.5, 4, or 25 wt% Rh/TiO_2 samples for reduction temperatures up to 1073 K.

TiO_2-Promoted Rh/SiO_2 and TiO_2-on-SiO_2

The micrographs for the TiO_2-promoted Rh/SiO_2 sample reduced at 573 and 773 K are shown in Figs. 10 and 11. Since the SiO_2 support is amorphous it does not exhibit any structure. The Rh particles indicated in the micrographs were identified by selected-area electron diffraction. The uniformity of optical density across the metal particles suggests that they are fairly flat. Examination of a Rh/SiO_2 catalyst of equiv-

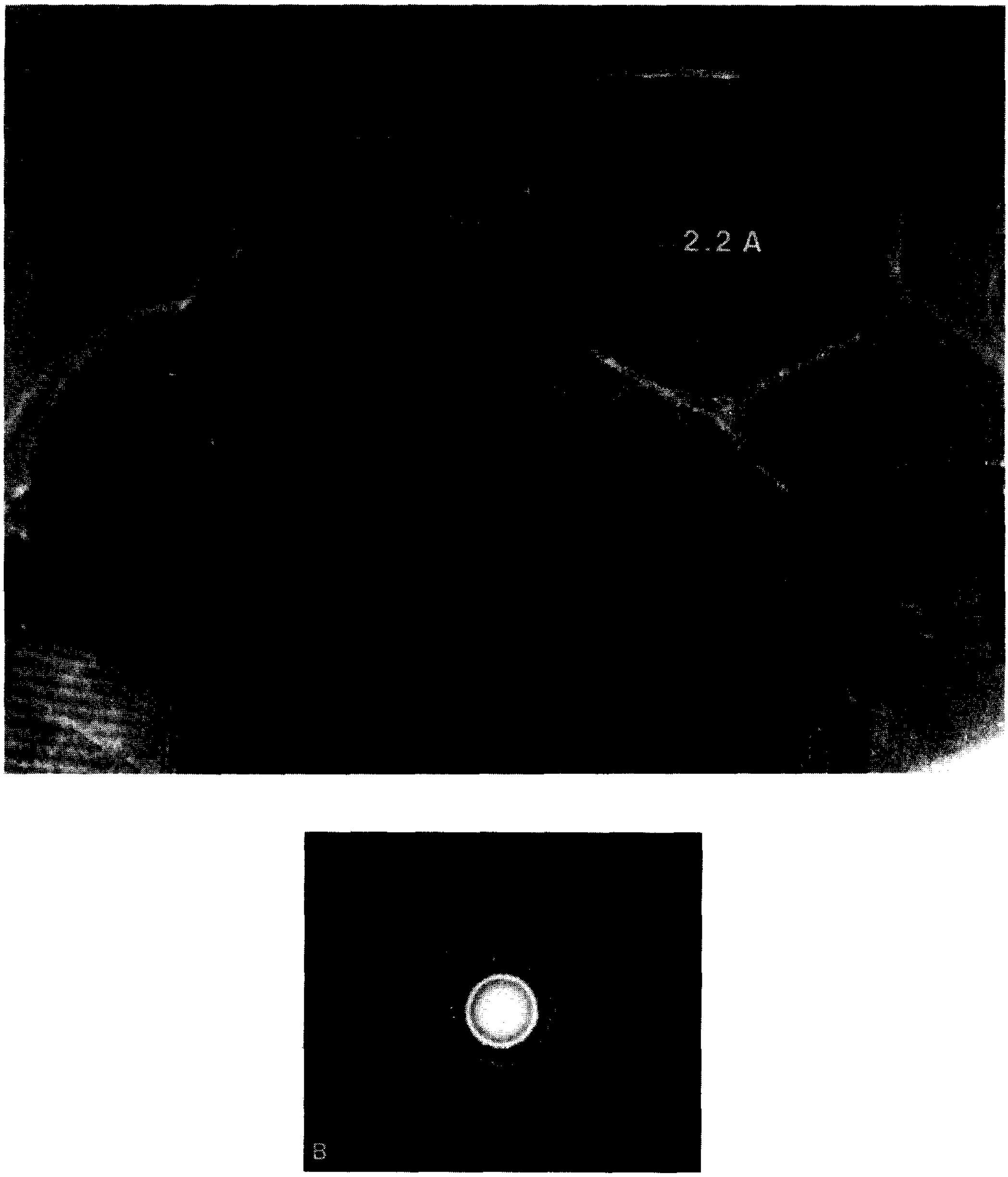

FIG. 8. Micrograph (A) and electron diffraction pattern (B) of 25% Rh/TiO_2 after 773 K reduction.

alent metal weight loading also showed that the Rh particles are flat. These observations suggest that the metal particle morphology is not influenced by the presence of the promoter. Following reduction at 573 K, Fig. 10 shows that only very small regions of crystalline TiO_2 are formed; hence most of the promoter must be present as amorphous titania. Reduction at 773 K results in the generation of relatively large platelets of crystalline TiO_2. The platelets were identified as the rutile form of TiO_2 based on selected-area electron diffraction and the spacing of the lattice fringes. Defocussing experiments confirmed that the rutile platelets lie on top of the metal particle rather than between the metal particle and the SiO_2 support. The appearance of

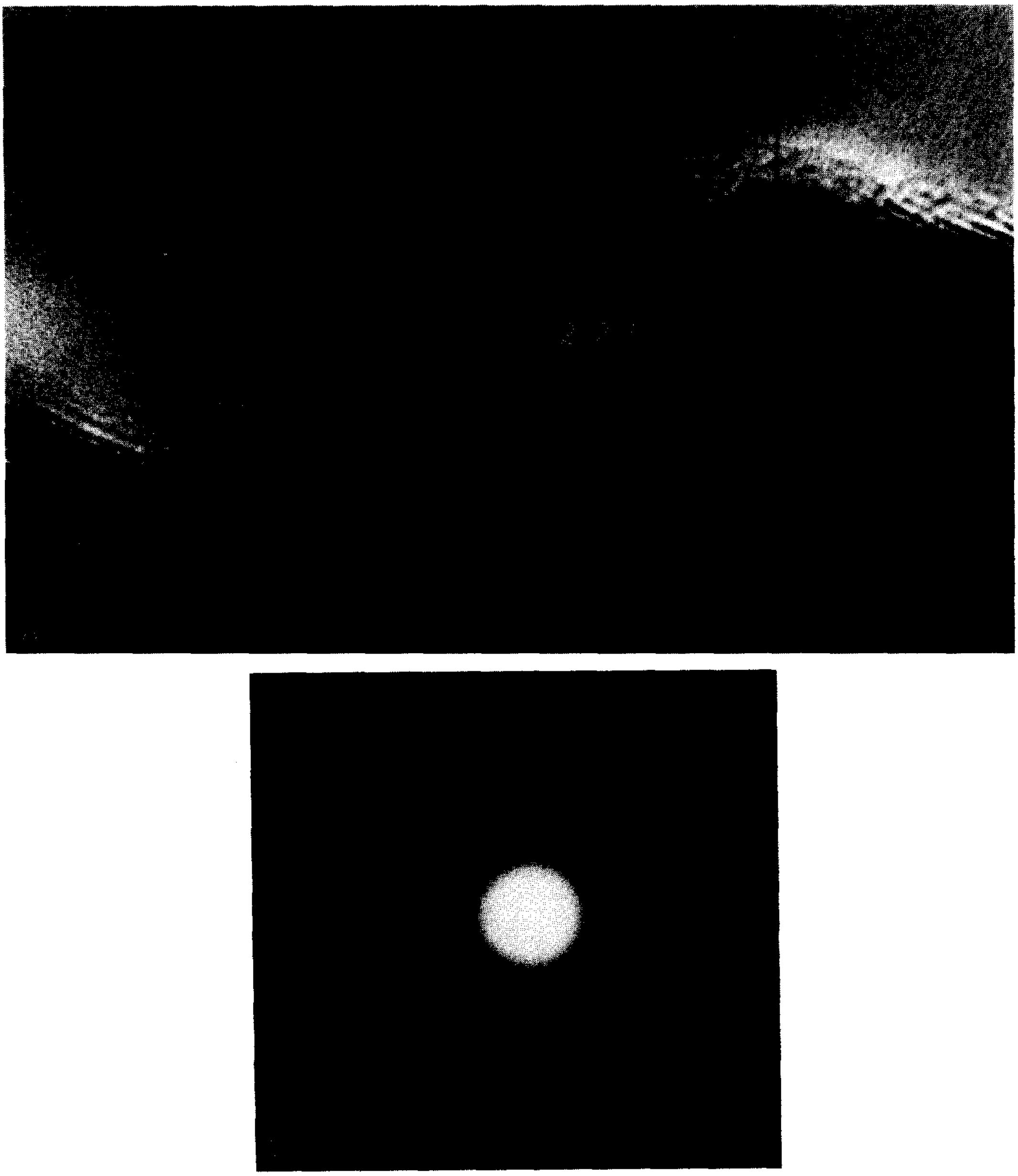

FIG. 9. Micrograph (A) and electron diffraction pattern (B) of 25% Rh/TiO$_2$ after 1073 K reduction.

the platelets primarily in the vicinity of Rh particles suggests that Rh nucleates or promotes the formation of the TiO$_2$ platelets.

The role of the Rh particles in the formation of crystalline TiO$_2$ platelets is further supported by observation of the TiO$_2$-on-SiO$_2$ sample. Figures 12 and 13 show low- and high-magnification micrographs of the TiO$_2$-on-SiO$_2$ sample reduced at 773 K. The major features in Fig. 12 are large agglomerates of TiO$_2$. The structure and composition of these features is confirmed by measurements of the lattice spacings obtained from Fig. 13. It should be noted that the appearance of the TiO$_2$-on-SiO$_2$ sample reduced at 573 K is very similar to that of a sample reduced at 773 K. Thus, in the absence of Rh metal particles, the TiO$_2$ pro-

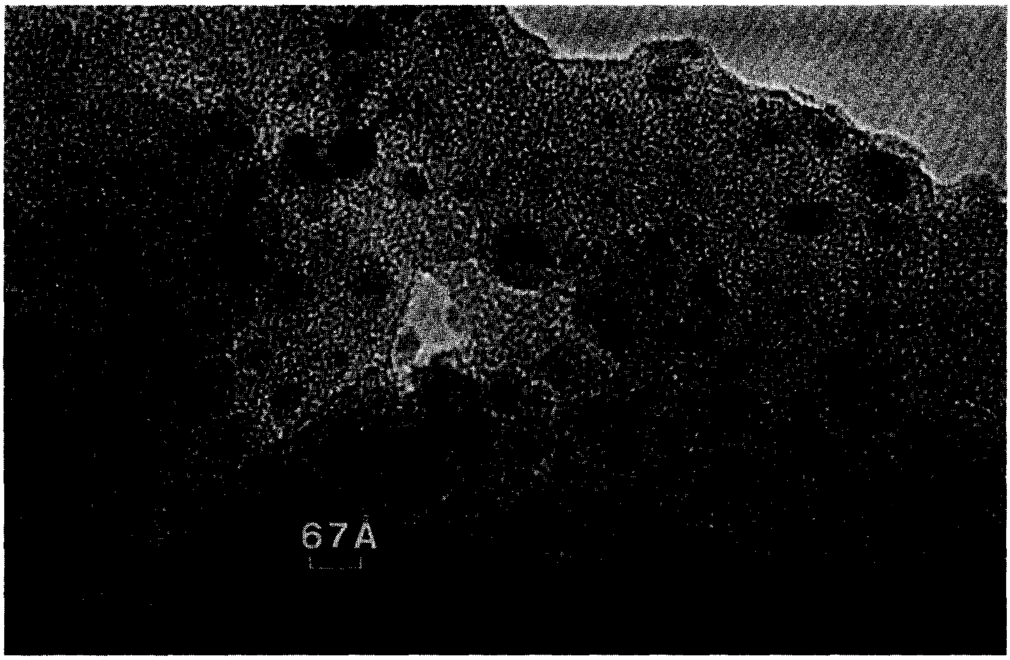

FIG. 10. Micrograph of TiO_2-promoted 4% Rh/SiO_2 after 573 K reduction.

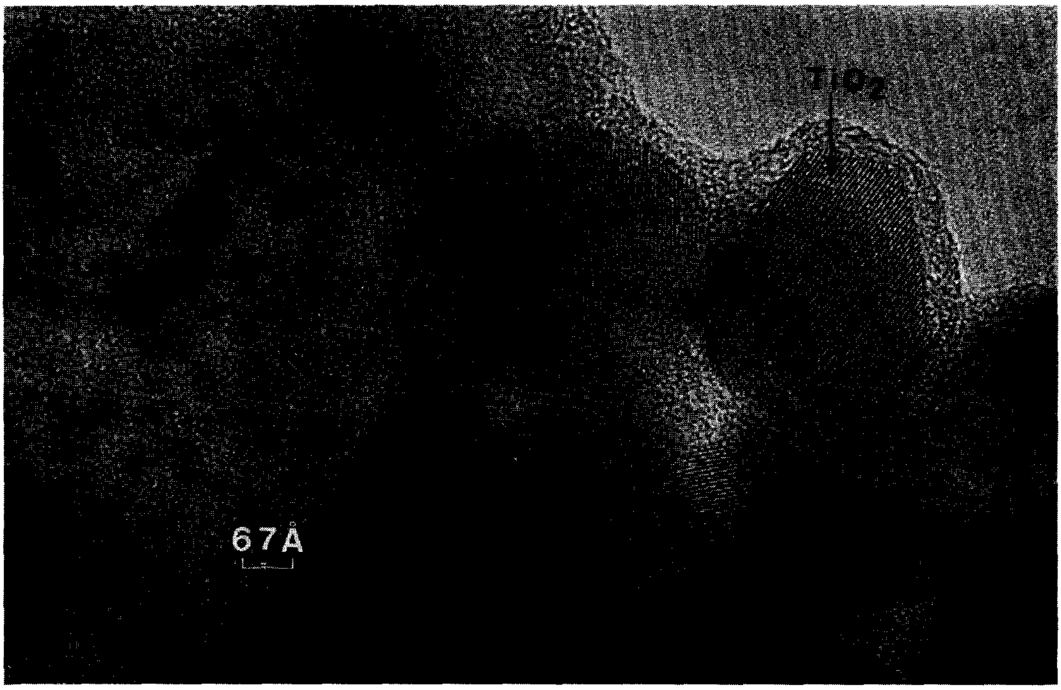

FIG. 11. Micrograph of TiO_2-promoted 4% Rh/SiO_2 after 773 K reduction.

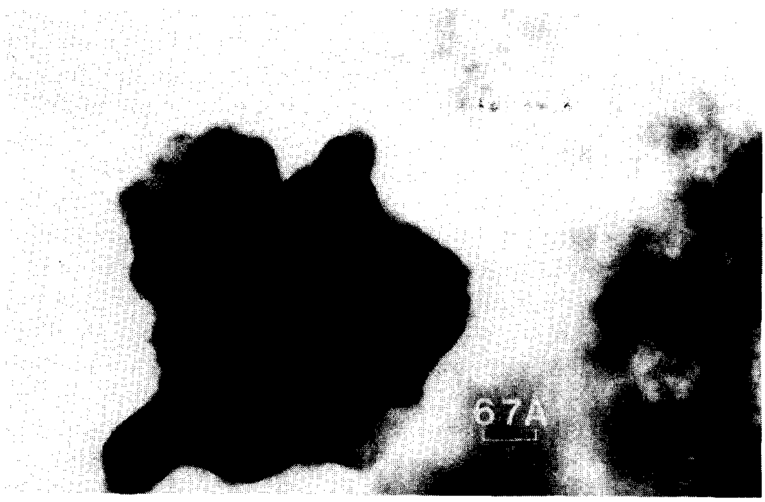

FIG. 12. Micrograph of TiO_2-on-SiO_2 after 773 K reduction.

moter does not disperse over the SiO_2 support and does not form crystalline platelets with increasing reduction temperature.

DISCUSSION

Various theories have been proposed to explain the suppression of H_2 and CO chemisorption of TiO_2-supported metals reduced at elevated temperatures (>523 K). The earliest proposal was that electron transfer occurs from the support to the metal, thereby altering the electronic properties of the metal (*26*). While such an interpretation might be plausible for very small

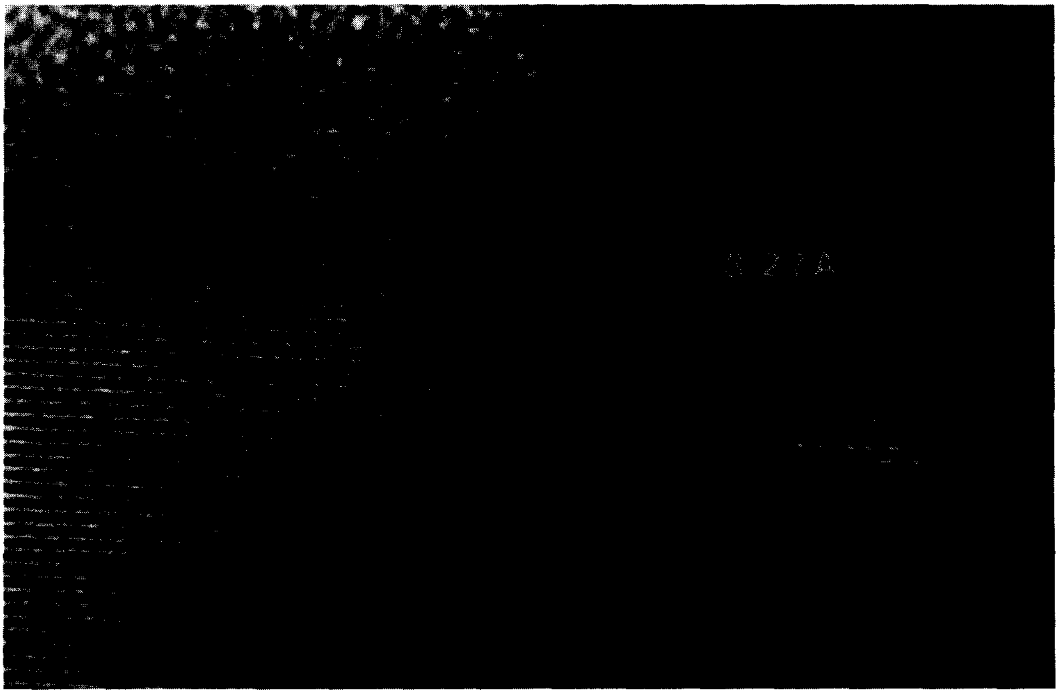

FIG. 13. High-resolution micrograph of TiO_2-on-SiO_2 after 773 K reduction.

crystallites ($d < 15$–20 Å), the observation of suppressed chemisorption in systems with relatively large crystallites ($d > 30$ Å) (*15, 27–29*), casts doubt on the electron transfer model. Baker *et al.* (*5–7, 9*) and Simoens *et al.* (*8*) have observed the formation of crystalline Ti_4O_7 upon high-temperature reduction of TiO_2 on which crystallites of Pt, Pd, or Ni are present. This has led to the inferrence that Ti_4O_7 may be involved in some fashion with the suppression of H_2 and CO chemisorption. A third interpretation, based on the results of AES studies by numerous authors (*8, 19–21*), is that chemisorption is suppressed due to the decoration of the supported crystallites by TiO_x moieties.

The micrographs obtained in the present study for both Rh/TiO_2 and TiO_2-promoted Rh/SiO_2 show no evidence of crystalline Ti_4O_7 formation as the reduction temperature is increased up to 1073 K. The only crystalline phases of TiO_2 observed are anatase and rutile. The conversion of anatase to rutile proceeds readily after reduction of the catalysts at 1073 K, but appears not to be influenced by the presence of Rh. Based on these observations it is concluded that the presence of crystalline Ti_4O_7 is not necessary for the suppression of H_2 and CO chemisorption.

The boundaries of the Rh crystallites seen in all of the micrographs are sharp and there is no evidence from electron diffraction for the formation of new phases through the reaction of Rh and TiO_2. The formation of a Rh–Ti alloy while possible in principle would not be expected to occur, because the temperature of reduction is considerably lower than that required for complete reduction of TiO_2 to Ti metal (>1973 K). Thus, we can discount the possibility that Rh–Ti alloy or compound formation is responsible for the suppression of H_2 and CO chemisorption.

The micrographs in Figs. 6 and 11 support the idea that during high-temperature reduction, titania species migrate onto Rh particles, resulting in the decoration and/or complete coverage of the particles. In the high-resolution micrograph shown in Fig. 6, amorphous titania can be seen covering a portion of the exposed surface of a Rh particle. Such patches of titania were not observed when Rh/TiO_2 samples were reduced at 573 K. In the case of TiO_2-promoted Rh/SiO_2, reduction at 773 K results in the formation of well-defined platelets of rutile, some of which lie over Rh particles (see Fig. 11). When such samples are reduced at 573 K, the TiO_2 remains amorphous and only very small regions of crystalline TiO_2 are observed. The formation of rutile platelets appears to be induced or catalyzed by the presence of the Rh particles. In the absence of Rh, the titania forms large clumps on the SiO_2 support, as shown in Fig. 12.

While no evidence was found in these studies for crystalline Ti_4O_7 or other suboxide phases of TiO_2, one cannot exclude the possibility that amorphous portions of the support undergo a partial reduction. Temperature-programmed reduction (TPR) spectra of Rh/TiO_2 (*23*) show two peaks, a low-temperature peak at 373 K which can be associated with the reduction of Rh and a broad peak at 523–773 K which is ascribed to a partial reduction of the support. The size of the latter peak corresponds to 0.83 Rh monolayer equivalents. The TPR spectrum of a Rh/SiO_2 catalyst shows only a single low-temperature peak which is attributed to reduction of the metal. These results suggest that Rh particles supported on TiO_2 assist in a partial reduction of the support. This conclusion is similar to that reached by Baker *et al.* (*7, 9*) for Pt/TiO_2 and Pd/TiO_2.

The mechanism by which titania species migrate onto the surface of Rh is not understood. It is possible that during reduction, hydrogen chemisorbed on the metal spills over onto the support and reduces amorphous portions of the support. This may release TiO_x or $Ti(OH)_x$ moieties which then wet the Rh particles and spread out across their surface. The TiO_x moieties on the metal particles can physically block sites for H_2 and CO chemisorption and can also alter the chemisorption properties of metal sites in the vicinity of the TiO_x moieties. When a sufficient number of these species accumulate, they may react to form either amorphous or crystalline titania. Such a picture would explain how Rh particles contribute to the formation of rutile platelets during the high-temperature reduction of TiO_2-promoted Rh/SiO_2.

CONCLUSIONS

The following conclusions may be drawn from this investigation:

(1) The progressive suppression of H_2 and CO chemisorption on Rh/TiO_2 and TiO_2-promoted Rh/SiO_2 catalysts with increasing temperature of reduction appears to be due to a partial coverage of the Rh particle surface by amorphous and/or crystalline titania.

(2) There is no evidence from electron micrographs or selected-area electron diffraction for the formation of crystalline Ti_4O_7 or Rh–Ti compounds during high-temperature reduction of Rh/TiO_2 or TiO_2-promoted Rh/SiO_2.

(3) The shape and size of Rh particles supported on SiO_2 and TiO_2 are comparable. Consequently, the suppression of H_2 and CO chemisorption on Rh/TiO_2 samples cannot be attributed to changes in the metal particle morphology.

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