Spectroscopic Characterization of TiO$_2$/SiO$_2$ Catalysts

ASUNCIÓN FERNANDEZ,* JÜRGEN LEYRER,† AGUSTÍN R. GONZÁLEZ-ELIPE,*
GUILLERMO MUNUERA,* AND HELMUT KNÖZINGER†

*Instituto de Ciencias de Materiales de Sevilla, Universidad de Sevilla, P.O. Box 1115, 41071 Sevilla,
Spain, and †Institut für Physikalische Chemie, Universität München, Sophienstrasse 11,
8000 Munich 2, West Germany

TiO$_2$/SiO$_2$ (7 wt% TiO$_2$) has been prepared via modification of the SiO$_2$ surface by reaction with Ti[OCH(CH$_3$)$_2$]$_4$. Physical characterization of the material was performed by means of XRD, diffuse reflectance spectroscopy (DRS), XPS, and low-temperature IR spectroscopy of adsorbed CO. TiO$_2$ exists in highly dispersed form on the SiO$_2$ surface. Interestingly, a quantum size effect leads to a shift of the absorption edge of TiO$_2$ toward higher energy. XPS difference spectra indicate the formation of Ti^{3+} during reduction. This is confirmed by CO adsorption in the temperature range $80 < T \leq 300$ K. IR spectroscopy of adsorbed CO provides advantages over XPS in that it responds exclusively to coordinatively unsaturated Ti^{3+} sites which are located and exposed in the surface. © 1988 Academic Press, Inc.

INTRODUCTION

Titania supported on SiO$_2$ or Al$_2$O$_3$ has been found in the past few years to be of increasing interest as a catalyst or support. This research was motivated by the fact that TiO$_2$ belongs to the class of the so-called SMSI (strong metal–support interaction) supports and by the observation that transition metals supported on this type of carrier developed higher activities than when supported on unmodified SiO$_2$ or Al$_2$O$_3$ (1–4). Lisitsyn et al. (5) have demonstrated that Ti ions on the SiO$_2$ surface increased the dispersion of cobalt and led to increased relative yield of light hydrocarbons and ethanol during CO hydrogenation.

The modification of the support oxide can typically be performed by reacting alkoxides Ti(OR)$_4$ with surface hydroxyl groups of SiO$_2$ or Al$_2$O$_3$. Reichmann and Bell (6, 7) have followed the state of titanium on SiO$_2$ supports during the various stages of preparation by laser Raman spectroscopy (LRS) and X-ray diffraction (XRD). Stranick et al. (8) reported on a detailed spectroscopic characterization by means of XPS, LRS, and XRD of TiO$_2$/Al$_2$O$_3$ as a function of the Ti loading. In the present paper we discuss the nature of a similar TiO$_2$/SiO$_2$ preparation with special emphasis being paid to the nature and oxidation states of surface Ti^{x+} coordination sites.

EXPERIMENTAL

A TiO$_2$/SiO$_2$ sample containing 7 wt% TiO$_2$ was prepared by incipient wetness impregnation of Aerosil SiO$_2$ ($S_{BET} = 200$ m^2 g^{-1}) from an n-hexane (Merck, p.a.) solution of Ti(OCH(CH$_3$)$_2$)$_4$ (Tilcom). After drying in flowing N$_2$ for 1 h at 295 K and for 2 h at 673 K, the material was calcined in air at 873 K for 10 h. For comparative purposes a second sample was prepared as a physical mixture (TiO$_2$ + SiO$_2$) containing 7 wt% TiO$_2$ (Degussa P-25, 56 m^2 g^{-1}) and 93 wt% SiO$_2$ (Aerosil, 200 m^2 g^{-1}).

XRD was performed on a Philips PW 1060 diffractometer. Transmission electron microscopy (TEM) was carried out on an ISI SS40 instrument equipped with a Kevex 8000 EDAX analyzer. Diffuse reflectance spectra (DRS) were recorded with a Perkin–Elmer Type 554 UV–Vis spectrometer equipped with an integrating sphere.
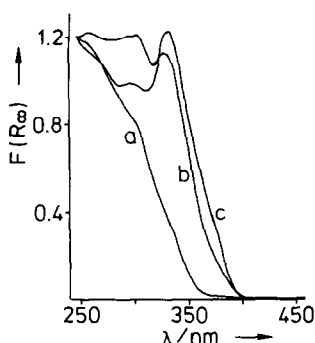
489

FIG. 1. Diffuse reflectance spectra of (a) TiO_2/SiO_2; (b) TiO_2 + SiO_2; and (c) pure TiO_2 (P-25).

X-ray photoelectron spectra were recorded on a Leybold-Heraeus LHS-10 spectrometer using $MgK\alpha$ radiation (1253.6 eV) for excitation and a pass energy of 50 eV. Binding energies (B.E.) were referenced to the Si $2p$ level of Si^{4+} at 103.3 eV. Sample pellets were mounted on a tantalum sample holder which could be heated resistively. The spectrometer was interfaced to an HP-1000 E computer. A straight baseline was used for peak area calculations. Atomic percentages were estimated using the sensitivity factors provided by Leybold-Heraeus.

Infrared spectra of thin, self-supporting wafers (typically 20 mg cm^{-2}) were recorded on a Perkin–Elmer 580B spectrometer at a spectral slit width of 5.2 cm^{-1} in the carbonyl stretching region; the wavenumber accuracy was ±2 cm^{-1}. Spectra were recorded after in situ thermal or reduction treatments before and after CO adsorption in the pressure range up to 40 Torr (1 Torr = 133.3 Pa) at 80 K and at constant equilibrium pressure (40 Torr) at increasing temperatures (80–300 K), so as to obtain information on the relative stability of individual CO adsorption states.

RESULTS AND DISCUSSION

The XRD analysis of the calcined TiO_2/SiO_2 sample showed no detectable reflections of crystalline TiO_2 phases. In contrast, the TiO_2 + SiO_2 physical mixture clearly showed the principal diffraction peaks of anatase and rutile typical for the Degussa P-25 product. Electron microscopy demonstrated the presence of spherical and porous particles in the TiO_2/SiO_2 sample and EDAX analysis indicated homogeneously distributed TiO_2 at the spatial resolution of the EDAX analysis (0.1 μm). Reichmann and Bell (6) reported the formation of anatase with crystallite sizes of 7–8 nm for a similarly prepared material containing, however, 25% TiO_2.

UV–Vis reflectance spectra supported the high dispersion of TiO_2 in the TiO_2/SiO_2 sample. Figure 1 compares the optical spectra of TiO_2/SiO_2 (spectrum a) with those of the physical mixture and of pure TiO_2 (P-25) (spectra b and c, respectively). It can clearly be seen that the absorption edge of TiO_2/SiO_2 is shifted toward lower wavelengths and becomes spread over a wider energy range compared to the physical mixture and pure TiO_2. A high-energy shift of the absorption edge is characteristic for small particles of TiO_2. Analogous trends have been observed by Nozik et al. (9a) and by Henglein et al. (9b) when studying the optical properties of colloidal semiconductor particles for which the absorption edge clearly shifted to lower wavelengths as the particle size decreased. This phenomenon can be interpreted as a quantum size effect.

Further information on the dispersion of the TiO_2 phase in TiO_2/SiO_2 was obtained by XPS when carried out in comparison with the physical mixture TiO_2/SiO_2. The results of a quantitative analysis are summarized in Table 1. It is obvious from the data that the amount of Ti detectable by

TABLE 1

Atomic Percentages and Ratios Obtained from XPS Spectra of TiO_2/SiO_2 and TiO_2 + SiO_2 Samples

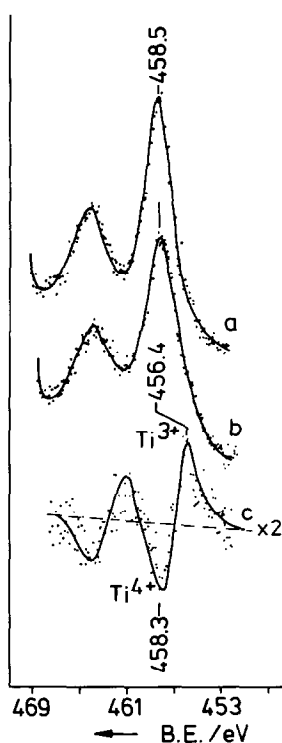| Sample	O(1s)	Ti(2p)	Si(2p)	Ti/Si
TiO_2/SiO_2	69.7	1.3	28.9	1/22
TiO_2 + SiO_2	65.3	0.5	34.2	1/67

FIG. 2. Ti $2p$ photoelectron spectra of TiO₂/SiO₂: (a) calcined; (b) reduced in H₂ at 773 K; (c) difference spectrum (b) − (a).

H₂ at T $\geq$ 723 K, the sample adopted the blue–gray color characteristic of the formation of Ti^{3+} ions. The Ti $2p$ photoelectron peak of TiO₂/SiO₂ after reduction in H₂ at 773 K (spectrum b) is compared with that of the original, unreduced sample (spectrum a) in Fig. 2. The difference spectrum c (spectrum b − spectrum a) clearly indicates the formation of Ti^{3+} at the expense of Ti^{4+}. The formation of Ti^{3+} could not be detected by XPS on pure TiO₂ (P-25) when treated under similar reduction conditions. This result can be interpreted in terms of the higher reducibility of TiO₂ in the TiO₂/SiO₂ sample. An enhanced reducibility of TiO₂ due to its higher dispersion in TiO₂/SiO₂ can in fact not be excluded. However, it must be kept in mind that Ti^{3+} ions could still be formed on the surface of pure TiO₂, these ions remaining undetectable by XPS due to the unfavorable surface-to-bulk ratio. In fact, we have recently reported that an infrared band near 2180 cm^{-1} was observed when CO was adsorbed on TiO₂ (P-25) at 80 K (*11*). This band was assigned to the carbonyl stretching mode of CO coordinated to Ti^{3+} surface sites (*11*). It is interesting to note that this band was observed not only on H₂-reduced samples but also after evacuation at 673 K, thus indicating that oxygen loss and partial surface reduction can occur by simple thermoevacuation. It must therefore be concluded that adsorption of CO at low temperatures and infrared analysis would provide a more surface-sensitive tool for the detection of low-valent cation sites on oxide surfaces than XPS. This is due to the fact that CO is a true surface probe and the carbonyl stretching frequency is sensitive (among other factors) to the oxidation state of a given element to which CO is coordinated (*10, 11*); on the other hand, the electron escape depth in oxides is typically several nanometers, so that small contributions of minority surface sites may not be resolved from the overall emission in XPS.

XPS in the TiO₂ + SiO₂ physical mixture is significantly smaller than that in the TiO₂/SiO₂ sample, although both preparations contain the same percentage of TiO₂, namely 7 wt%. This result clearly points to a high dispersion of the TiO₂ phase in TiO₂/SiO₂, supporting the conclusions drawn above from XRD, TEM, and DRS. Also, both samples contain 1 Ti atom for 19.05 Si atoms. Taking into account that the BET surface area of SiO₂ is approximately four times larger than that of TiO₂ in the physical mixture TiO₂ + SiO₂, one estimates a Ti/Si atomic ratio for this sample of approximately 1/76, in good agreement with the experimental value of 1/67 (see Table 1). The experimental Ti/Si ratio for the TiO₂/SiO sample is much higher, namely 1/22, again pointing to the high dispersion of TiO₂ in this preparation.

When TiO₂/SiO₂ was reduced in flowing

We have therefore applied low-temperature IR spectroscopy of adsorbed CO to
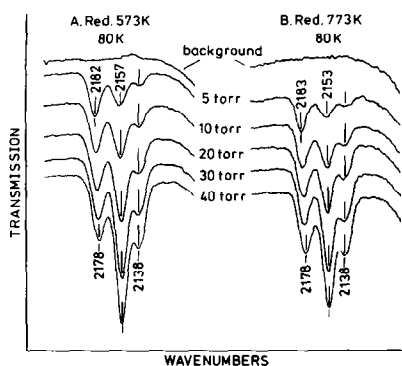
FIG. 3. Carbonyl infrared spectra of CO adsorbed on TiO_2/SiO_2 at 80 K at increasing CO pressure after reduction in H_2 at (A) 573 K and (B) 773 K.

further elucidate the oxidation states of accessible Ti^{x+} coordination sites on TiO_2/SiO_2. Figure 3 shows the development of the spectra in the carbonyl stretching region at 80 K with increasing CO pressure for two TiO_2/SiO_2 samples which were reduced *in situ* in flowing H_2 at 573 and 773 K, respectively. Three bands can be discerned, at 2138, 2153–2157, and 2178–2183 cm^{-1}. The two bands at lower frequency are built up slowly, while that at 2178–2183 cm^{-1} seems to saturate at lower pressures. Band assignments have been given earlier. The band at 2138 cm^{-1} corresponds to the most weakly held species, as shown by its easy desorption at constant CO pressure of 40 Torr when the temperature is raised (Fig. 4). The species is considered to be physically adsorbed CO (*10–12*). The central band around 2153–2157 cm^{-1} is due to H-bonded CO (*12, 13*). The band around 2180 cm^{-1} is brought about by the most stable adsorbed CO species which is still detectable at 200 K in the presence of 40 Torr CO when the other two bands are almost entirely eroded (Fig. 4). This band is assigned to CO coordinated to Ti^{x+} sites (*10*) with the Ti ion most probably being in the 3+ oxidation state (*11*). The position of this band is at 2178 cm^{-1} and shifts slightly toward higher frequency when the coverage decreases (see Fig. 3 for decreasing pres-

sure at 80 K, and Fig. 4 for increasing temperature at a constant pressure of 40 Torr). This frequency shift must be related to an inhomogeneous site distribution. Dynamic dipole–dipole coupling can be excluded, since this effect would lead to shifts toward higher frequency with increasing coverage (*14, 15*). It should be mentioned that identical behavior has been observed previously (*11*) for CO adsorption on bulk TiO_2 (rutile). Also, a band near 2180 cm^{-1} was reported for CO adsorbed on TiO_2 by Tanaka and White (*16*); these authors, however, did not attempt any correlations of this carbonyl stretching frequency with the Ti oxidation state.

H_2 reduction at higher temperatures (compare spectra of series A for 573 K and series B for 773 K in Fig. 4) did not seem to affect significantly the intensity of the band at 2180 cm^{-1} although the relative intensity of the band at 2157 cm^{-1} of the H-bonded CO species was higher for the sample reduced at the lower temperature (series A in Fig. 4).

It is also interesting to note that the Ti^{3+} ← CO adsorption complex on the TiO_2/SiO_2 sample can be formed after evacuation at temperatures higher than approximately 570 K (see Fig. 5) which is again in close analogy with previous results on bulk TiO_2 (*10, 11*). In fact, in this case the intensity of the IR band at 2178 cm^{-1} was always much
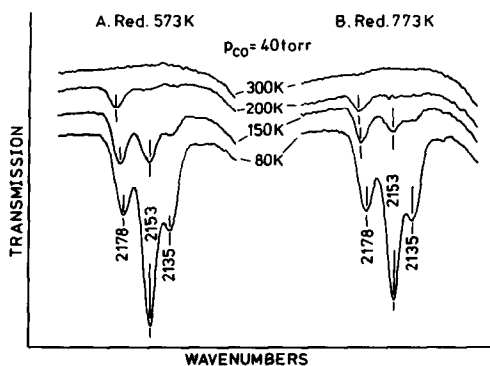

FIG. 4. Carbonyl infrared spectra of CO adsorbed on TiO_2/SiO_2 at 40 Torr CO at increasing temperatures after reduction in H_2 at (A) 573 K and (B) 773 K.
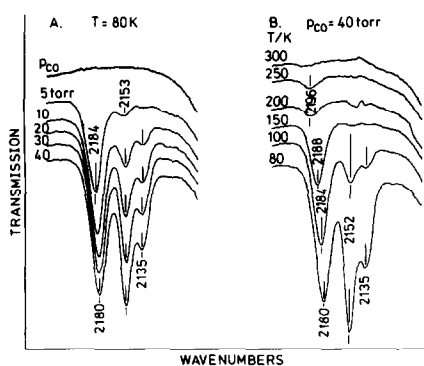
FIG. 5. Carbonyl infrared spectra of CO adsorbed on TiO$_2$/SiO$_2$ after thermoevacuation at 773 K. (A) Adsorption at 80 K and varying CO pressure; (B) adsorption at an equilibrium CO pressure of 40 Torr and varying temperatures.

greater (under similar conditions) than that in the samples reduced at the same temperature with H$_2$. We have previously observed (17) that hydrogen reduction of the TiO$_2$ support in Rh/TiO$_2$ samples leads to incorporation of hydrogen into the oxygen vacancies near the Ti^{3+} species, leading to some kind of Ti–H^{3+} (hydride-like) species as previously reported by Göpel et al. (18) and by Knotek (19) for reduced TiO$_2$ single crystals. This may block CO adsorption. A higher mobility of the reduced TiO$_x$ phase has also been observed (20) upon incorporation of hydrogen into reduced TiO$_2$, which may lead to a removal of exposed Ti^{3+} ions through shear plane formation. In fact, preliminary results using EPR with our TiO$_2$/SiO$_2$ sample indicate a strong coupling of the Ti^{3+} states. This would be consistent with the explanation given for the lower intensity of the band at 2178 cm^{-1} in the samples reduced with hydrogen.

CONCLUSIONS

We conclude from the present results that

(1) highly dispersed TiO$_2$ phases supported on SiO$_2$ can be prepared by reacting Ti(OR)$_4$ precursors with the SiO$_2$ surface and calcination in air;

(2) Ti^{3+} coordination sites can be formed by either H$_2$ reduction or high-temperature evacuation;

(3) the number of such Ti^{3+} coordination sites is lower in the samples more deeply reduced with H$_2$, suggesting that a mechanism is operating which partially removes coordination sites; and

(4) IR spectroscopy of CO adsorbed at low temperatures (80 K) is better than XPS for the detection of these low-valent coordination sites which exist in the surface as overall minority cations.

ACKNOWLEDGMENTS

REFERENCES

1. Rieck, J. S., and Bell, A. T., J. Catal. 99, 262 (1986).
2. Föger, K., and Anderson, J. R., Appl. Catal. 23, 7 (1986).
3. Ichikawa, M., Fukushima, T., and Shikakura, K., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 69. Dechema, Frankfurt-am-Main, 1984.
4. Ichikawa, M., Sekizawa, K., and Shikakura, K., J. Mol. Catal. 11, 167 (1981).
5. Lisitsyn, A. S., Golovin, A. V., Kuznetsov, V. L., and Yermakov, Yu. I., J. Catal. 95, 527 (1985).
6. Reichmann, M. G., and Bell, A. T., Appl. Catal. 32, 315 (1987).
7. Reichmann, M. G., and Bell, A. T., Langmuir 3, 111 (1987).
8. Stranick, M. A., Houalla, M., and Hercules, D. M., J. Catal. 106, 362 (1987).
9. (a) Nozik, A. J., Williams, F., Nenadović, M. T., Rajh, T., and Mićić, O. I., J. Phys. Chem. 89, 397 (1985); (b) Henglein, A., Fojtik, A., and Weller, H., Ber. Bunsenges. Phys. Chem. 91, 441 (1987).
10. Zaki, M. I., Vielhaber, B., and Knözinger, H., J. Phys. Chem. 90, 3176 (1986).
11. Zaki, M. I., and Knözinger, H., Spectrochim. Acta A 43, 1455 (1987).
12. Beebe, T. P., Gelin, P., and Yates, J. T., Jr., Surf. Sci. 148, 526 (1984).
13. Zaki, M. I., and Knözinger, H., Mater. Chem. Phys. 17, 201 (1987).
14. Zecchina, A., Scarano, D., and Garrone, E., Surf. Sci. 160, 492 (1985).

15. Escalona Platero, E., Coluccia, S., and Zecchina, A., *Surf. Sci.* **171,** 465 (1986).
16. Tanaka, K., and White, J. M., *J. Phys. Chem.* **86,** 4708 (1982).
17. Conesa, J. C., Malet, P., Munuera, G., Sanz, J., and Soria, J., *J. Phys. Chem.* **88,** 2986 (1984).
18. Göpel, W., Rocker, G., and Feierabend, R., *Phys. Rev. B* **28,** 3427 (1983).
19. Knotek, M. L., *Surf. Sci.* **91,** L-17 (1980).
20. Munuera, G., González-Elipe, A. R., Espinós, J. P., Conesa, J. C., Soria, J., and Sanz, J., *J. Phys. Chem.* **91,** 6625 (1987).