

TiO₂/SiO₂ photocatalysts at low levels of loading: preparation, structure and photocatalysis

Tsunehiro Tanaka^{*}, Kentaro Teramura, Takashi Yamamoto, Sakae Takenaka, Satohiro Yoshida, Takuzo Funabiki

Department of Molecular Engineering, Kyoto University, Kyoto 606-8501, Japan

Received 24 July 2001; received in revised form 21 August 2001; accepted 21 August 2001

Abstract

The effect of precursor on the dispersion and photocatalytic performance of titanium oxide supported on silica has been investigated. The catalysts were prepared by a simple impregnation method with three kinds of titanium complexes of different ligands (dipyrrolymethanato (DPM), acetylacetonato (acac), isopropoxide (O-*i*Pr)) abbreviated to D-TS, A-TS, and I-TS. The UV/Vis diffuse reflectance, Raman, XAFS spectroscopic study showed that surface titanate of D-TS is isolated TiO₄ species, and that of I-TS is a mixture of rutile and anatase crystallites. The surface state of A-TS is the intermediate between D-TS and I-TS. TiO₂/SiO₂ samples were more active than bulk TiO₂ and partial oxidation selectivity of TiO₂/SiO₂ samples are higher than that of TiO₂ in photo-oxidation of propane. Products distribution over TiO₂/SiO₂ was drastically varied with the surface titanates. The activity for photo-assisted selective catalytic reduction (SCR) of NO with ammonia was found for D-TS. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photo-oxidation; TiO₂/SiO₂; XANES; Raman; SCR

1. Introduction

Silica-supported titanium oxide has been reported to exhibit different photocatalytic performance from that titania itself does [1–6]. This is partially explained in terms of the interaction between titanium oxide and silica, and also of the different structure of surface titanate from that of bulk titania. Relation among surface titanium oxide structure, preparation method and loading amount has been extensively studied [7]. Wachs and coworkers [8] discussed the relation between structure of surface titanate and catalytic activity. They classified the surface structure of TiO₂/SiO₂ as a function of the loading amount and concluded that surface TiO₄ species which is realized at a low level of loading exhibits the highest activity for oxidation of methanol. In the present paper, we attempted to prepare TiO₂/SiO₂ catalysts with the different kinds of surface species at the same loading level. By combining UV/Vis diffuse reflectance, XAFS, and Raman spectroscopies, the structure of the surface titanate of the thus prepared catalysts was determined. In the present paper, we discuss the relation between structure and photocatalytic performance of TiO₂/SiO₂.

2. Experimental

2.1. Materials

Silica support (BET specific surface area 630 m² g⁻¹) was prepared by the hydrolysis of twice-distilled silicon tetraethoxide [9]. The catalyst samples [6] were prepared by impregnation of the silica with a toluene solution of bis(isopropylato)-bis(pivaroylmethanato) titanium(IV) (Ti(DPM)₂(O-*i*Pr)₂), bis(acetylacetonato)oxo-titanium(IV) (TiO(acac)₂) and tetrakis(isopropylato) titanium(IV) (Ti(O-*i*Pr)₄) for 2 h under reflux condition. The filtrate was calcined for 5 h at 773 K. The loading of titanium was adjusted to 0.6 wt.% as TiO₂. The catalyst samples will be referred to D-TS, A-TS and I-TS, respectively. As references, three kinds of bulk TiO₂, JRC-TIO-1 (anatase), JRC-TIO-3 (rutile) and JRC-TIO-4 (a mixture of rutile and anatase, identical with P25 Degussa) were kindly supplied from Japan Catalysis Society.

2.2. Characterization

UV/Vis diffuse reflectance spectra (DRS) were recorded with a Perkin-Elmer Lambda 19 spectrometer equipped with a labsphere RSA-PE-19 reflectance spectroscopy accessory.

^{*} Corresponding author. Tel.: +81-75-753-5693; fax: +81-75-753-5925. E-mail address: tanaka@dcc.moleng.kyoto-u.ac.jp (T. Tanaka).

The reflectance of barium sulfate was used for the calculation of Kubelka–Munk function.

The laser Raman spectra were measured with a JASCO NRS-2000 spectrometer using the 514.5 nm line of Ar⁺ laser emission with a resolution of 4 cm⁻¹. The laser power was 200 mW as an output and Raman emission signal at each shift was accumulated for 3 s for reference bulk samples and for 300 s for catalyst samples.

X-ray absorption experiment at Ti K-edge was carried out at BL-7C station with a Si(1 1 1) two-crystal monochromator in Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan, with a ring energy of 2.5 GeV and stored current 280–330 mA (Proposal No. 93G-170). The higher harmonics were eliminated with low angle reflections by a double silicon mirrors and X-rays were concentrated by a sagittal focus. The data collection was performed for the sample without exposure to the air in a X-ray fluorescent mode at room temperature.

2.3. Reactions

The photo-oxidation of propane over the catalyst [10,11] was carried out with a conventional low-pressure gas-circulation system with a quartz reactor (dead volume = 277 cm³) and a 250 W ultrahigh pressure mercury lamp as a light source [12]. The catalyst was irradiated for a given time at room temperature with a reflection by a cold mirror which reduces infrared rays under an atmosphere of propane and oxygen. The products were analyzed by GC. No products were formed without catalysts and/or irradiation.

Photo-reduction of NO with ammonia [13] was carried out with the same style as described above. The reactant gas (¹⁵NO 20 μmol corresponding to 0.2 kPa, NH₃ 20 μmol to 0.2 kPa, O₂ 0–40 μmol to 0–0.4 kPa, and Ar 255 μmol, a diluent) was mixed for 30 min before contact with the catalyst and then admitted to the reactor. The gas composition at a given time was determined by a quadrupole-type mass spectrometer calibrated by Ar²⁺ internal standard. The 10 μmol of molecular amount in the reaction apparatus corresponds to 1000 ppm concentration against an atmospheric pressure.

3. Results and discussion

3.1. Characterization of TiO₂/SiO₂ samples

As a photocatalyst, the wavelength distribution of the absorbed light is one of the important properties regardless of the quantum yield. Fig. 1 shows the UV/Vis diffuse reflectance spectra (UV/Vis DRS) of three kinds of the samples together with the reference compounds, TIO-4 (a mixture of anatase and rutile), TIO-1 (typical anatase) and TIO-3 (typical rutile). TIO-4 is known as a mixture of anatase and rutile and exhibits the spectrum showing

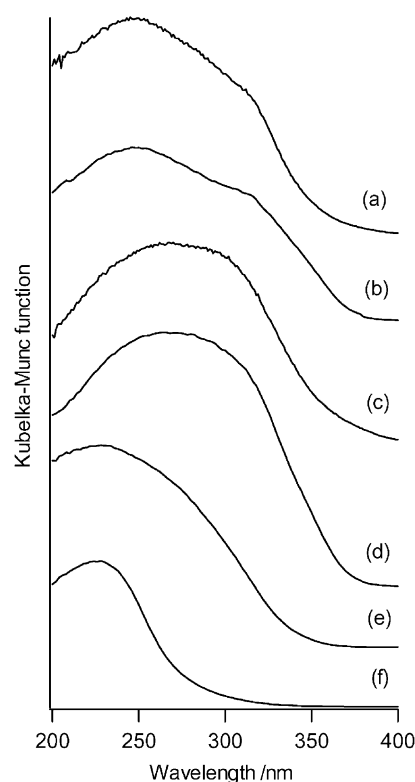


Fig. 1. UV/Vis DRS of: (a) TIO-4 (a mixture of anatase and rutile); (b) TIO-1 (anatase); (c) TIO-3 (rutile); (d) I-TS; (e) A-TS; (f) D-TS.

the mixed profile of anatase and rutile. Absorption edge of rutile is found to be at the shorter wavelength than that of anatase. The spectrum of I-TS is very similar to that of TIO-4 except for the blue shift of the bandgap due to the presence of smaller particles. The resemblance of the spectral feature between I-TS and TIO-4 would show that formed TiO₂ particle over silica is also a mixture of anatase and rutile. On the other hand, D-TS has a single absorption band at 220 nm, indicating the formation of isolated TiO₄ unit [8,14]. The spectrum of A-TS exhibits the intermediate feature between I-TS and D-TS. The spectrum of A-TS exhibits the absorption peak at 250 nm but tailing part to long wavelength shows that the absorption edge is very similar to I-TS. This may be due to the result that surface titanate is the mixture of molecular titanate and aggregated titanate.

Fig. 2 shows the Raman spectra of reference TiO₂ compounds. Anatase shows four strong Raman bands at 140, 392, 512 and 634 cm⁻¹ [15,16]. Of these, intensity of the band at 140 cm⁻¹ is extremely strong and the presence of this band is the indication of the formation of anatase [8,16]. On the other hand, rutile also exhibits the three characteristic bands but relative intensities for rutile bands are a little weaker than those for anatase. In case of TIO-4 including 30% of rutile, the Raman spectrum consists of four strong bands due to anatase and very tiny ones due to rutile. On this basis, we carried out to record Raman spectra of the catalyst samples and silica, as shown in Fig. 3. Because of

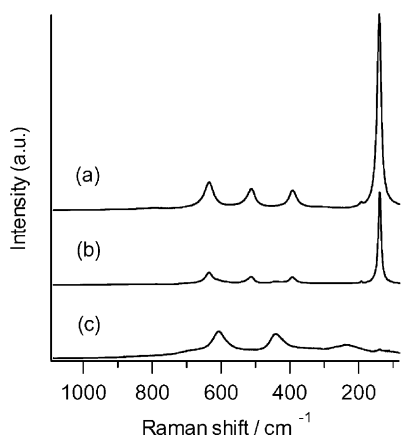


Fig. 2. Raman spectra of reference TiO_2 samples: (a) TIO-1 (anatase); (b) TIO-4 (a mixture of anatase and rutile); (c) TIO-3 (rutile).

the low loading, all the spectra of the catalyst samples lack the bands due to Ti–O–Si [8,17]. The spectral feature for D-TS is the same as that for silica. This is consistent with the result of UV/Vis DRS. In case of A-TS, a small band at 144 cm^{-1} due to the presence of anatase crystallite was found. On the contrary, I-TS sample showed clear bands due to anatase. The intensity of 144 cm^{-1} band for I-TS is 1/500 times smaller than that for TIO-4 is reasonable although the intensity is not directly proportional to the concentration. The bands for rutile were not seen but this does not deny the presence of rutile like TIO-4 case. This Raman result show that I-TS includes TiO_2 crystallite as found in the case of UV/Vis DRS.

From UV/Vis DRS and Raman spectra, we conclude that surface titanate species of D-TS consists of isolated TiO_4 species, and that of I-TS does of a mixture of anatase and rutile crystallites. The surface species of A-TS is in between. In our previous work [6], we carry out the analysis of EXAFS and obtained the structural parameters around a Ti atom in $\text{TiO}_2/\text{SiO}_2$ samples as shown in Table 1. As it is now clear from the results above, the surface species of A-TS and I-TS are a mixture and the result from EXAFS should be

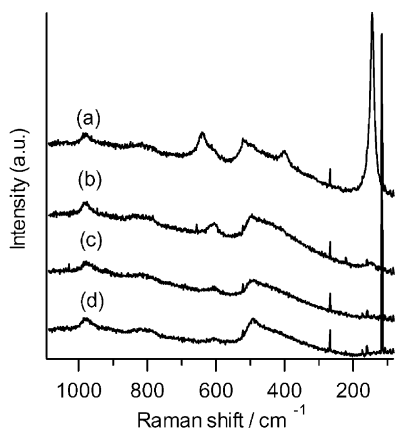


Fig. 3. Raman spectra of $\text{TiO}_2/\text{SiO}_2$ samples and SiO_2 : (a) I-TS; (b) A-TS; (c) D-TS; (d) SiO_2 .

Table 1
Ti–O structural parameters determined by curve fitting of EXAFS^a

Sample	Coordination number	R (Å) ^b	Δ^2 (Å ²) ^c	R factor (%) ^d
D-TS	4.1	1.79	−0.0016	7.5
A-TS	4.0	1.89	0.0014	2.3
	1.0	1.99	−0.0064	–
I-TS	4.0	1.88	−0.0017	10.1
	2.0	2.01	−0.0017	–

^a Curve fitting was performed on k^3 -weighted EXAFS in the k range $3.5\text{--}12\text{ \AA}^{-1}$ with an empirical parameters extracted from Na_3VO_4 [21].

^b Ti–O bond distance.

^c Debye–Waller factor deviation from that of the reference.

^d R factor is defined as a square root of $(\sum(\text{residual})^2 / \sum(\text{data})^2)$.

regarded as an average information. Therefore, we cannot recognize the data for A-TS in Table 1 as it is. As for titanium compounds, a better structural information is obtained by XANES than EXAFS summarized in Ref. [18]. Fig. 4 shows the XANES spectra of the catalyst samples. In case of D-TS, the intense pre-edge peak is characteristic of tetrahedrally coordinated titanium atoms. The height and energy position of the pre-edge peak is 0.65 and 4969.6 eV (0.4 eV resolution), indicating the TiO_4 structure. It is evident that I-TS sample has the octahedrally compounds judging from the pre-edge peak. The post-edge feature is the mixture of anatase and rutile consistently with UV/Vis DRS result. But the post-edge feature is not a simple sum of the spectra of rutile and anatase [19] indicating the presence of amorphous state due to probably the interaction between surface titanate and silica. Again, A-TS sample is in between. The spectrum

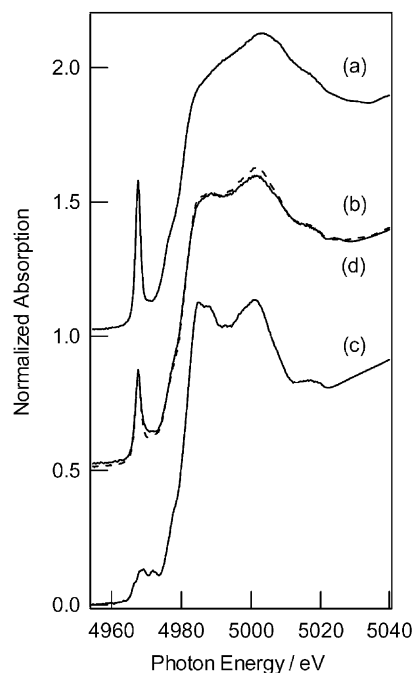


Fig. 4. XANES spectra at Ti K-edge of: (a) D-TS; (b) A-TS; (c) I-TS; (d) dotted, simulated spectrum, $0.45 \times (a) + 0.55 \times (b)$.

Table 2
Photo-oxidation of propane over bulk TiO₂ and TiO₂/SiO₂ catalysts^a

Catalyst	Time (min) ^b	Conversion (%) ^c	Selectivity (%)					
			C ₃ H ₆	C ₂ H ₄	CH ₃ CHO	C ₂ H ₅ CHO	(CH ₃) ₂ CO	CO _x
TIO-4	10	12.1	2	1	tr	0	13	84
I-TS	20	12.6	1	2	1	tr	95	0
A-TS	45	12.9	4	5	19	5	67	0
D-TS	30	11.1	9	7	31	5	28	18

^a Amount of catalysts: 200 mg, each 70 μmol of propane and oxygen were introduced.

^b Irradiation time.

^c Based on introduced propane.

for A-TS has the smaller pre-edge peak at the same position as the case of D-TS. We have thought that if A-TS is an intermediate state between D-TS and I-TS, A-TS XANES spectra should be simulated by superimposing D-TS and I-TS with pertinent weight which shows the fraction of isolated species and aggregated species [20]. In Fig. 4, the simulated spectra are shown as a broken curve. The weights for D-TS and I-TS were 45 and 55%, indicating that almost half of Ti atoms in A-TS sample are present as isolated TiO₄ and the rest as aggregated ones.

3.2. Photocatalytic performance

We have carried out the photocatalytic oxidation of propane [10,11] over TiO₂/SiO₂ catalysts. As shown in Fig. 1, the three samples showed the variety of UV/Vis DRS and we cannot compare the activity of the catalysts simply. Because our light source is 250 W ultrahigh pressure Hg lamp which exhibits discontinuous distribution of wavelength, we could not determine photo-efficiency of the catalysts quantitatively. Therefore, in the present work, we gave up the determination of intrinsic activity of the catalyst. Instead, we controlled the reaction time to obtain the same conversion level of propane and compared the products selectivity. Therefore, the reaction time is the measure of the apparent activity. Table 2 summarizes the result. TIO-4 is the most active but I-TS showing the similar UV absorption distribution to TIO-4 in Fig. 1 is much more active than TIO-4 by taking the Ti concentration into account. Any way, on the basis of the concentration of TiO₂, TiO₂/SiO₂ catalysts are more active than bulk TiO₂. The characterization result showed that I-TS is the mixture of anatase and rutile, which is roughly speaking the same as TIO-4. We expected the similar products selectivity of I-TS to TIO-4. However, in case of I-TS, reacted propane is converted quantitatively to acetone and in case of TIO-4, total oxidation is the main reaction path. These result shows that I-TS is not the simple mixture of TiO₂ crystallites and silica but TiO₂ crystallites are interacted with silica. In case of D-TS consisting of a single TiO₄ species, acetaldehyde and acetone were the main product together with various other products. The striking point of the data is that over A-TS. Again, the products distribution is the intermediate between

those obtained for D-TS and I-TS. This is occasional but the selectivities to acetone and acetaldehyde are almost the half between the sums of those of D-TS and I-TS. This clearly shows the reactivity difference among surface titanate.

The reactivity difference between D-TS and bulk TiO₂ is also found in NO selective catalytic reduction with ammonia (photo-assisted NO SCR). Fig. 5(a) shows the time course of evolution of nitrogen and conversion of NH₃ and NO_x in the absence of catalyst sample after 30 min homogeneous reaction with the mixture of ¹⁵NO 20.0 μmol, NH₃ 20.0 μmol, O₂ 20.0 μmol and Ar 255 μmol. Because free energy of the reaction, NO₂ + NH₃ → N₂ + (3/2)H₂O + (1/4)O₂ at room temperature is negative, the reaction proceeds sponta-

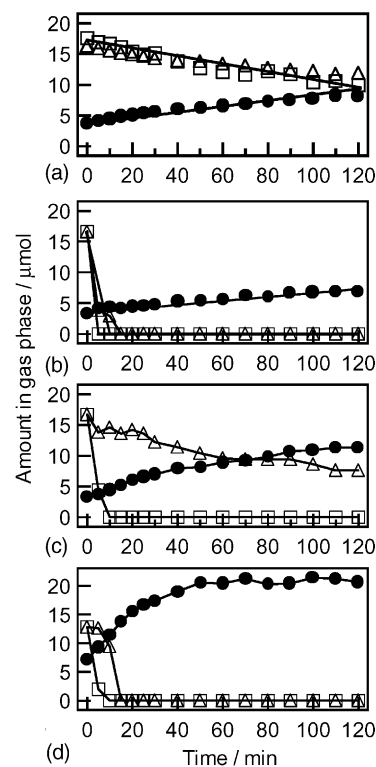


Fig. 5. Time course of N₂ (circle), NO_x (triangle), and NH₃ (square) in gas phase for NO–NH₃–O₂ reaction: (a) without catalyst in the dark; (b) over TIO-4 in the dark; (c) over D-TS in the dark; (d) over irradiated D-TS.

neously. Therefore, NO and NH₃ were gradually decreased. In the presence of TIO-4 as shown in Fig. 5(b), NO and NH₃ were removed from the gas phase very fast both in the dark and under irradiation. This shows that TiO₂ is a good adsorbent for NO and NH₃. However, the evolution rate of nitrogen was not accelerated from the homogeneous reaction very much even under irradiation. This suggests that TiO₂ is not active for photo-assisted NO SCR. As shown in Fig. 5(c), in the presence of D-TS in the dark, nitrogen evolution curve and NO decay curve is almost the same with those found in homogeneous reaction although NH₃ was removed very fast. D-TS works as an adsorbent of ammonia but it does not accelerate NO SCR reaction in the dark. On the other hand, irradiation of D-TS brought about acceleration of NO decay and evolution of N₂, and after 60 min irradiation, quantitative amount of N₂ was formed. The test reaction may show the reactivity difference between TIO-4 and D-TS. In case of TIO-4, NO and ammonia molecules are tightly adsorbed on TiO₂ so that the mutual association is not frequent. On the other hand, ammonia is adsorbed on D-TS in the dark and a NO molecule would be adsorbed on an excited surface cluster composed of ammonia and surface titanate. The driving force of NO adsorption presumably involves an exciton because NO is a naturally free radical. However, the clarification of the reaction mechanism is now under progress.

References

- [1] R.W. Matthews, J. Catal. 113 (1988) 549.
- [2] H. Inoue, T. Matsuyama, B. Liu, T. Sakata, H. Mori, H. Yoneyama, Chem. Lett. (1994) 653.
- [3] C. Anderson, A.J. Bard, J. Phys. Chem. B 101 (1997) 2611; M. Anpo, K. Chiba, J. Mol. Catal. 74 (1992) 207.
- [4] M. Anpo, K. Chiba, J. Mol. Catal. 74 (1992) 207.
- [5] S. Yoshida, S. Takenaka, T. Tanaka, H. Hirano, H. Hayashi, Stud. Surf. Sci. Catal. 101 (1996) 871.
- [6] S. Yoshida, S. Takenaka, T. Tanaka, T. Funabiki, J. Phys. IV (Colloque C2) 7 (1997) 859.
- [7] X. Gao, I.E. Wachs, Catal. Today 51 (1999) 233, and references therein.
- [8] X. Gao, S.R. Bare, J.L.G. Fierro, M.A. Banares, I.E. Wachs, J. Phys. Chem. B 102 (1998) 5653.
- [9] S. Yoshida, T. Matsuzaki, T. Kashiwazaki, K. Mori, K. Tarama, Bull. Chem. Soc. Jpn. 47 (1974) 1564.
- [10] T. Tanaka, S. Takenaka, T. Funabiki, S. Yoshida, Chem. Lett. (1994) 1588.
- [11] S. Takenaka, T. Kuriyama, T. Tanaka, T. Funabiki, S. Yoshida, J. Catal. 155 (1995) 196.
- [12] T. Tanaka, M. Ooe, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 1 82 (1986) 35.
- [13] T. Tanaka, K. Teramura, T. Funabiki, Phys. Chem. Chem. Phys. 2 (2000) 2681.
- [14] D. Trong On, L. Le Noe, L. Bonnevot, Chem. Commun. (1996) 299.
- [15] C. Li, G. Xiong, J. Liu, P. Ying, Q. Xin, Z. Feng, J. Phys. Chem. B 105 (2001) 2993.
- [16] S. Srinivasan, A.K. Datye, M. Hampden-Smith, I.E. Wachs, G. Deo, J.M. Jehng, A.M. Turek, C.H.F. Peden, J. Catal. 131 (1991) 260.
- [17] S. Pei, G.W. Zajac, J.A. Kaduk, J. Faber, B.I. Boyanov, D. Duck, D. Fazzini, I.T. Morrison, D.S. Yang, Catal. Lett. 21 (1993) 333.
- [18] F. Farges, G.E. Brown Jr., J.J. Rehr, Phys. Rev. B 56 (1997) 1809.
- [19] T.M. Salama, T. Tanaka, T. Yamaguchi, K. Tanabe, Surf. Sci. Lett. 227 (1990) L10.
- [20] T. Tanaka, T. Yamamoto, Y. Kohno, T. Yoshida, S. Yoshida, Jpn. J. Appl. Phys. Suppl. 38 (1) (1999) 30.
- [21] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 1 84 (1988) 2987.