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Investigation of oxidation states of titanium in titanium silicalite-1 by X-ray photoelectron spectroscopy

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Abstract

Oxidation states of Ti in TS-1 samples prepared by using tetrabutylorthotitanate under various conditions were measured using XPS. Most of the Ti $2p_{3/2}$ spectra comprised of two kinds of core spectra having binding energies of 460.0 ± 0.2 and 457.8 ± 0.2 eV, which were due to framework and extraframework Ti^{4+}, respectively. The existence of the extraframework Ti^{4+} was also ascertained using X-ray diffraction (XRD) and DRUV–Vis. From area intensities of the Ti $2p_{3/2}$ spectra and Si 2p spectrum, x_f of framework Ti and x_{ex} of extraframework Ti were determined and compared with x_g of precursor gel given by the moles of starting materials used, where the x_f, x_{ex}, and x_g represented the atomic ratio of $Ti/(Ti + Si)$. In TS-1 sample (Y.TS-1) series, prepared using vacuum distilled tetrabutylorthotitanate and 2-propanol, low reaction temperature of 273 K, and an ultrasonic wave vibrator at the aging stage of the precursor gel, a linear relationship between x_f and x_g and at $x_g > 0.04$ a plateau of $x_f = 0.03$ were observed, and good correlations between the relative intensity of XRD peak due to TiO_2 and x_g and between x_{ex} and x_g were established in the range of $0.017 \leqq x_g < 0.10$. For other prepared samples, it was, however, difficult to find such regularities. From these results, it was concluded that pure TS-1 samples without extraframework TiO_2 were obtained only in $x_f \leqq 0.013$ and the use of ultrasonic wave vibrator was very effective to facilitate the dispersion of Ti^{4+} in the precursor gel.

Keywords: Titanium silicalite-1; Tetrabutylorthotitanate; Oxidation state of Ti; X-ray diffraction; X-ray photoelectron spectroscopy

1. Introduction

Titanium-substituted silicalite-1 (TS-1) with MFI structure has been noted as one of the very effective catalyst materials in oxidation of a variety of organic compounds at low temperature using dilute hydrogen peroxide solution as an oxidant [1]. Originally, Taramasso et al. [2] had reported the preparation of TS-1, and Huybrechts et al. [3] reported that the best catalysts were obtained by careful hydrolysis of a mixture of silicon and titanium ethoxides with aqueous tetrapropylammonium hydroxide. Since titanium ethoxide is unstable in the presence of water, the improved synthesis procedure using more stable compounds like titanium butoxide [4] was proposed. Tuel [5] also reported that crystallization of TS-1 in the presence of isopropyl alcohol would facilitate its preparation. However, in the preparation of TS-1, the inclusion of extraframework Ti or TiO_2 (anatase) could be unavoidable, especially in the case of $Ti/Si \geqq 0.02$ [5] and 0.025 [6]. Thangaraj et al. [4] reported the possibility to produce the TS-1 with up to 0.091, but Millini et al. [7] have again confirmed that the upper limit of Ti/Si is around 0.025 by the determination method of unit cell parameters of TS-1 using full-profile fitting method for X-ray diffraction (XRD) patterns. The existence of extraframework Ti is one of the most important problems in the synthesis

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of TS-1, because it depresses the catalytic activity of the TS-1 samples in reactions of partial oxidation of phenol [8,9], alkanes [8,10], and alkenes [8]. This influence of the extraframework Ti has been discussed in lowering of catalytic activity of the framework Ti sites [11], blocking of the access of reacting molecule to the sites [12], and promotion of decomposition of hydrogen peroxide to radical species which might increase initialization of radical chain reactions [7,9,11].

On the other hand, in characterization of state and coordination of titanium ions, many literatures using XRD [2,4,6,7], FT-IR [2,4,6,13], DRUV [11,14,15,27], XANES [15,27], EXAFS [15,16,27,28], and MAS–NMR [12] have been reported. However, valuable reports using XPS are not so many, Bittar et al. [10] reported that the Ti $2p_{3/2}$ spectrum at 459.8 eV observed on TS-2 corresponded to tetrahedral coordinated Ti^{4+} and the spectrum line shifted to low binding energy side with increase in titanium content. Vetter et al. [17] observed the Ti $2p_{3/2}$ spectrum with peak maxima at 458.6 and 460.6 eV on TS-1. They related the first one to extraframework titanium ions in species and the second was assigned as Ti^{4+} in tetrahedral position in silicalite framework. The presence of Ti $2p_{3/2}$ spectrum with lower binding energy was also recognized by Reddy and Sayari [18], who stated that most of titanium was in isolated tetrahedral species, but that a small fraction of octahedrally coordinated Ti^{4+} was present. These results indicate that it is possible to separate the framework and extraframework Ti^{4+} in the TS-1 samples and to estimate the Ti/Si ratio for only TS-1 with MFI structure from deconvolution data of Ti 2p spectrum.

In the present work, the oxidation states of titanium in TS-1 samples prepared under various conditions were determined by XPS, in order to clarify correlations among the intensity of XRD peak due to TiO_2, x_f of TS-1 framework, x_{ex} of extraframework Ti^{4+}, and x_g of the precursor gel, where x_i ($i = f, ex, g$) was defined by $Ti/(Ti + Si)$.

2. Experimental

In the synthesis of TS-1 samples according to the method of Thangaraj et al. [4], tetrabutylorthotitanate (TBOT, 99.999%; Tokyo Kasei Kogyo), tetraethoxysilane (TEOS, 99.9%; Kanto Chem.), 2-propanol (IPA, 99.5% up; Kanto Chem.), and both of tetra-*n*-propylammonium hydroxide (TPAOH, 20%, Na < 42 ppm, K undetected; SACHEM) and that (25%, Na < 26 ppm, K undetected; Kanto Chem.) were used. Mixture of TBOT (0–4.82 g) and IPA (8.5 ml) was slowly dropped to the mixture of TEOS (28.0 g) and TPAOH (33.3 g) for 1–5 h, followed by addition of remaining TPAOH (6.7 g; about 17% of a given amount). After the obtained gel-like solution was aged at 333 K for 5 h, about 20 g of de-ionized and then distilled water, which was warmed at 333 K, was added. The $Ti/(Ti + Si)$ atomic ratio of the precursor gel, which was represented by x_g, was determined from the amounts of the starting materials used. The final precursor gel was transferred into a Teflon bottle, which was settled in an autoclave, and hydrothermal synthesis was carried out at 438 K for 7 days. The precipitate formed was centrifuged after washing by de-ionized-distilled water, and dried at 353 K for 12 h. The dried precipitate was calcined at 50 K intervals for 0.5 h after keeping it at 373 K for 2 h, and finally at 823 K for 5 h. The calcined samples were powdered to grains smaller than 53 μm ϕ. Other reaction conditions used in the synthesis are summarized in Table 1.

H.TS-1 was the sample prepared by the procedure mentioned above in atmosphere. In the preparation of all other samples, a glove box purged with Ar gas stream and carefully vacuum distilled TBOT and IPA were used, and the TEOS and TPAOH mixture was cooled to 273 K to depress vaporization of water. Especially, for Y.TS-1 samples, the precursor gel before hydrothermal synthesis was well shaken or mixed using an ultrasonic wave vibrator.

XRD patterns were determined by powder method employing Rigaku MJ201 (Cu Kα, 40 kV) and Al sample holder. IR spectra for the presence of TS-1 framework Ti^{4+} were recorded on Jasco FT-IR 7000 spectrometer using thin film of TS-1 powder pressed on polyethylene film (3 M IR card), and DRUV–Vis spectra for extraframework Ti^{4+} (i.e., TiO_2) were taken on Shimazu UV-3100 spectrometer using silicalite-1 as a reference sample. In the case of XPS measurement using Perkin Elmer ESCA 5100 (Mg Kα, 300 W), the TS-1 powder was pressed to self-supporting 13 mm ϕ disc 0.6 mm thick, which was pretreated at 823 K for 5 h in a stream of oxygen. Photoelectron energy scale of the XPS was calibrated

Table 1
Reaction conditions used in the synthesis of TS-1 sample

Condition	Sample						
	H.TS-1	S.TS-1	V.TS-1	W.TS-1	X.TS-1	U.TS-1	Y.TS-1
Use of purge box	×	○	○	○	○	○	○
Distillation of TBOT and IPA	×	○	○	○	○	○	○
Temperature of TEOS and TPAOH (K)	303	273	273	273	273	273	273
TPAOH/TEOS ratio	0.29	0.29	0.37	0.29	0.29	0.29	0.29
Temperature of aging for 5 h (K)	333	333	333	333	353	333	333
Temperature of hydrothermal synthesis for 7 days (K)	438	438	438	438	438	458	438
Remarks				[a]			[b]

[a] The mixture of TEOS and TPAOH was kept at 303 K for 30 min with mixing by a magnetic stirrer, and then cooled to 273 K.
[b] The gel-like mixture at the aging stage was shaken or mixed using an ultrasonic wave vibrator.

using Cu $2p_{3/2}$ = 932.4, Ag $3d_{5/2}$ = 368.1, and Au $4f_{7/2}$ = 83.8 eV. In charge-up correction, the spectrum line of C 1s = 284.6 eV was employed. Spectrum deconvolution was carried out using the spectra of X-ray satellite peak subtraction and Shirley background correction. In calculation of surface atom concentration, atomic sensitivity factors based on peak area, recommended by Perkin Elmer were used [19].

3. Results and discussion

3.1. XRD

XRD patterns of the synthesized TS-1 were first measured. All the samples showed quite similar diffraction pattern to that of orthorhombic TS-1 by Millini et al. [7], but new peaks appeared at 2θ = 25.5° and 48.18° when x_g of the precursor gel was larger than about 0.02; as examples, XRD patterns for Y.TS-1 samples are shown in Fig. 1. The two new diffraction peaks agreed with those for TiO_2 anatase. The peak height intensity ratio of 2θ = 25.5° to 23.24° peak ($I_{25.5}$) increased almost linearly with x_g, as shown in Fig. 2 and Table 3. The M.TS-1 in the figure was a sample prepared by Omori [20] at different place in a similar way to H.TS-1. From these results, it was certified that at least over x_g = 0.02 the extraframework TiO_2 forms during the course of synthesis. The larger $I_{25.5}$ of H.TS-1 series and M.TS-1 than other samples might indicate that the crystallization of TiO_2 particle proceeded faster than other samples.

3.2. FT-IR

In the O–H stretching vibration range, very small two peaks at 3600–3800 cm^{-1} and a week and broad peak at around 3400 cm^{-1} due to hydrogen bonding OH species were observed. However, it was very difficult to discuss their behavior in relation to x_g and x_f (defined later). In the region 400–1400 cm^{-1}, a distinct adsorption band at 960 cm^{-1} except for peaks due to silicalite structure was present. The band was assigned to the stretching vibration of Si–O perturbed by Ti^{4+} in a neighboring position [12,13,21]. The intensity ratio of the band to 550 cm^{-1} peak (I_{960}) is shown in Table 3, in comparison with other parameters. The linear correlation between I_{960} and titanium content, which was reported by van der Pol and van Hooff [22], was not obtained, but there was a tendency for the intensity of the band to increase with x_f.

3.3. DRUV–Vis

Fig. 3 shows DRUV–Vis spectra for mechanical mixture of SiO_2 and TiO_2 (x_g corresponds to 0.025) and Y.TS-1 samples with x_g = 0.023, 0.044, and 0.070, when as a reference sample the silicalite-1 prepared in the same manner as described above was used. The absorption band at about 200–260 nm are due to electron excitation from ligand oxygen to an unoccupied orbital of the framework Ti^{4+} and the maximum at 300–380 nm are assigned to the absorption band of Ti^{4+} species in the extraframework TiO_2 particles [11,14,15]. The intensity of the absorption band at 300–380 nm increased evidently with that of

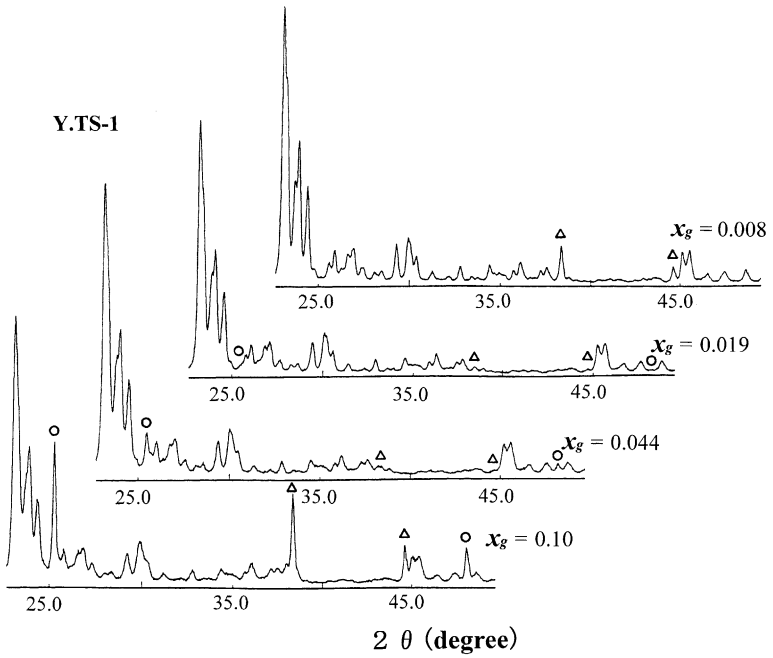

Fig. 1. XRD patterns of orthorhombic Y.TS-1 samples with $x_g = 0.008$, 0.019, 0.044, and 0.10. (○) TiO_2 (anatase); (△) Al metal used as a sample holder.

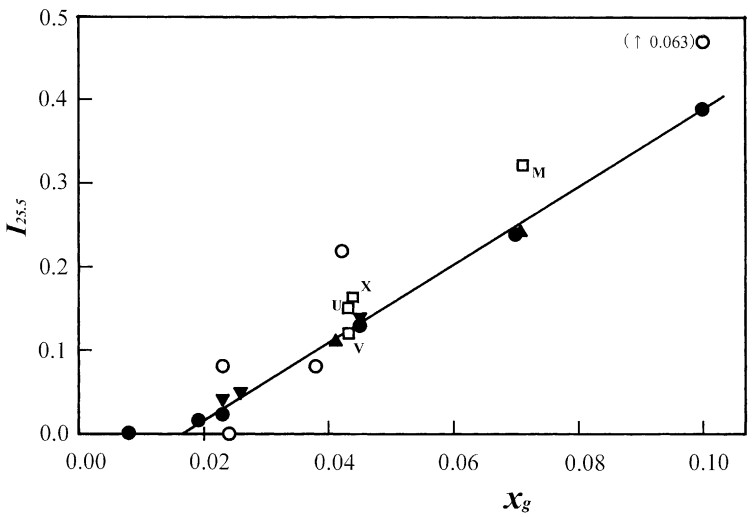

Fig. 2. Correlation between $I_{25.5}$ and x_g: (●) Y.TS-1 series; (▲) S.TS-1 series; (▼) W.TS-1 series; (○) H.TS-1 series; (□) M.TS-1, V.TS-1, X.TS-1, or U.TS-1.

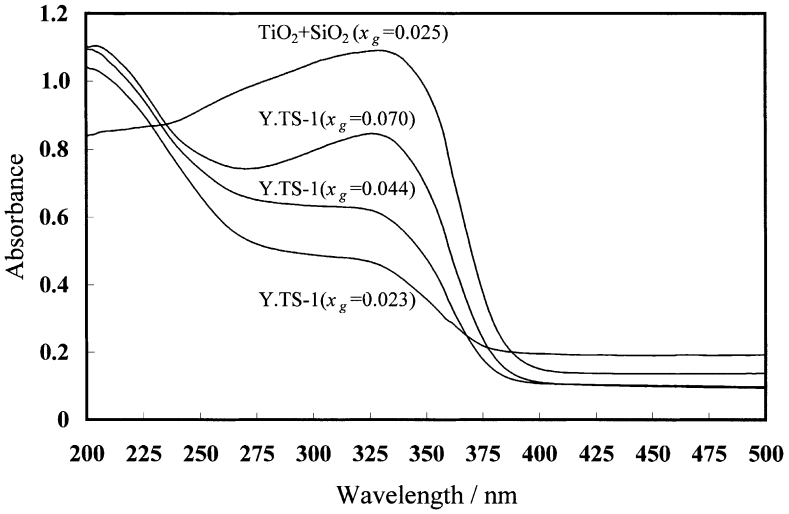

Fig. 3. DRUV–Vis spectra of mechanical mixture of SiO_2 and TiO_2 (x_g corresponds to 0.025) and Y.TS-1 samples with $x_g = 0.023$, 0.044, and 0.070. As a reference sample the silicalite-1 was used.

$2\theta = 25.5^\circ$ peak in XRD ($I_{25.5}$) shown in Fig. 2 and Table 3.

3.4. XPS

Spectra of Si 2p, O 1s, Ti 2p, and C 1s were measured by multiplex mode for each sample. Binding energy (BE) of Si 2p was 103.7±0.1 eV. O 1s was single spectrum with peak maximum at 532.9 ± 0.3 eV, but over $x_g = 0.07$ a peak with a center at 529.3 ± 0.2 eV appeared. Fig. 4 shows Ti 2p spectra for Y.TS-1 series. The two Ti $2p_{3/2}$ peaks at 460.0 and 457.8 eV fundamentally coincided with those reported by Vetter et al. [17], Reddy and Sayari [18], and Bittar et al. [10]. Relatively, the first spectrum decreased and the second increased with increasing x_g. All other samples with $x_g \geqq 0.019$ resulted in similar spectra too. Deconvolution of the Ti 2p spectrum for Y.TS-1 with $x_g = 0.044$ resulted in two core spectra of Ti 2p (α) and Ti 2p (β) having 460.0 eV (FWHM 2.3 eV) and 457.9 eV (FWHM 1.7 eV) as BE of Ti $2p_{3/2}$, respectively, as shown in Fig. 5. In the same manner, it was possible to deconvolute the Ti 2p spectra for all samples except for H.TS-1 ($x_g = 0.024$) and Y.TS-1 ($x_g = 0.008$). Table 2 indicates BE values of Si 2p and the core spectra of Ti $2p_{3/2}$ and O 1s and also those for silicalite-1, mechanical mixture of SiO_2 and TiO_2

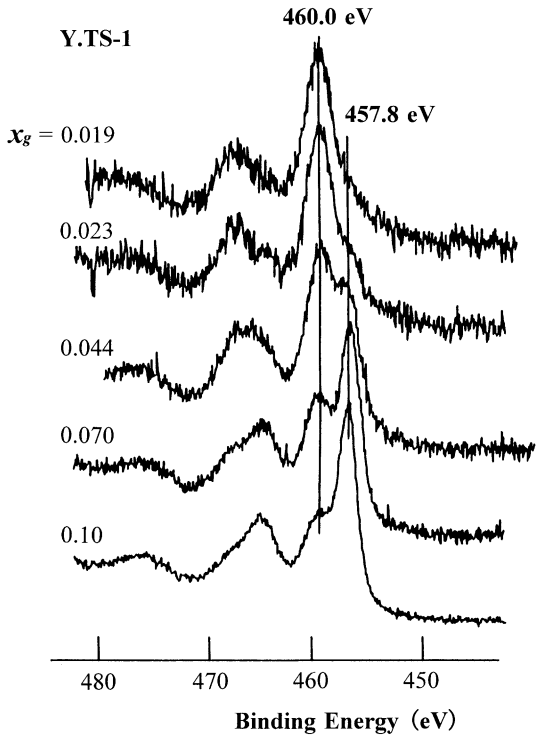

Fig. 4. Ti 2p photoelectron spectra for Y.TS-1 samples with $x_g = 0.019$, 0.023, 0.044, 0.070, and 0.10.

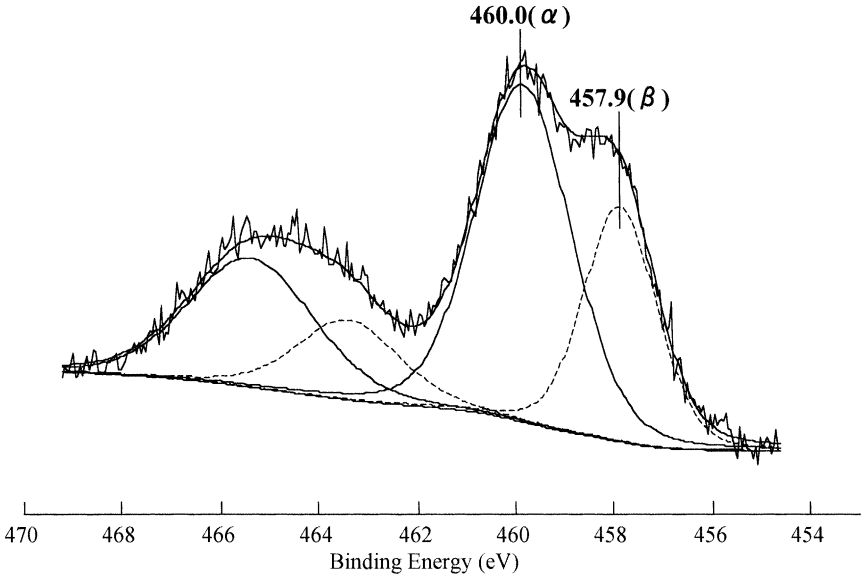

Fig. 5. Deconvolution of the Ti 2p spectrum for Y.TS-1 with $x_g = 0.044$.

corresponding to $x_g = 0.025$, and TiO_2 anatase which were determined in the same way as TS-1 samples.

The BE of Si 2p for all the TS-1 samples agreed with those for silicalite-1 and the mechanical mixture. The agreement between 457.9 ± 0.2 eV of the core spectrum Ti $2p_{3/2}$ (β) and that for the mechanical mixture evidently indicates that the extraframework TiO_2 of anatase structure are present in the TS-1 samples, because the samples producing the spectrum Ti $2p_{3/2}$ (β) result in the strong absorption band at 300–380 nm in DRUV–Vis spectra and the Ti^{3+} and Ti^{2+} species on TiO_2 surface have more low BE [23]. From these results, the core spectrum of Ti $2p_{3/2}$ (α) with 460.0 ± 0.2 eV in BE was concluded to be attributable to Ti^{4+} of TS-1 framework. The shift of Ti $2p_{3/2}$ line from 458.8 eV of TiO_2 to 460.0 eV of the α spectrum is caused by the difference in electronegativities of Ti^{4+} and Si^{4+} and corresponds to the lowering in electron density of the Ti^{4+} isomorphously displaced with Si^{4+} of silicalite structure in comparison with that of TiO_2. On the other hand, the shift of Ti $2p_{3/2}$ line from 458.8 to 457.8 eV of the core spectrum β would be explained by considering that TiO_2 particle surrounded by TS-1 particles is subjected to electron donating effect of oxygen atoms of them which have unshared electron pairs and the largest ionic radius.

In addition, the photoelectron energy line of O 1s at 532.9 ± 0.3 eV (spectrum a) was almost compatible with those for silicalite-1 and SiO_2, and the line at 529.3 ± 0.2 eV (spectrum b) coincided in position with O 1s of TiO_2 in the mechanical mixture. The appearance of the spectrum b distinctly suggests also the existence of anatase-type TiO_2 particles, i.e., extraframework Ti^{4+}, in the TS-1 samples. The slight shift of O 1s spectrum line from 533.2 eV of silicalite-1 to 532.9 eV of the TS-1 samples is due to partial electron transfer from Ti^{4+} to adjacent O^{2-} in the TS-1 framework, which also results from the difference in electronegativities of Si^{4+} and Ti^{4+}. The shift of O 1s line of TiO_2 from 530.1 to 529.3 eV in the TS-1 samples would be attributable to electron donating effect of oxygen atoms of the neighboring TS-1 particles, in analogy with the shift of the core spectrum Ti $2p_{3/2}$ (β) to the low BE side.

The presence of octahedrally coordinated Ti^{4+} in the TS-1 has been frequently suggested and discussed [15,18,24,27]. Since the FWHM (1.6 eV) of Ti $2p_{3/2}$ for the mechanical mixture of SiO_2 and TiO_2 agrees with 1.5–1.7 eV for Ti $2p_{3/2}$ (β) spectrum, the larger FWHM (2.2–2.4 eV) of the Ti $2p_{3/2}$ (α) core spectrum seems likely to indicate a possibility to be deconvoluted into two core spectra corresponding to

Table 2
Binding energies of Si 2p, Ti $2p_{3/2}$, and O 1s spectra of TS-1 samples

Sample	x_g[a]	Si 2p (eV)	Ti $2p_{3/2}$ (eV)[b]		O 1s (eV)	
			α	β	a	b
H.TS-1	0.024	103.5	460.2	n.d.[c]	533.1	
	0.023	103.6	460.4	458.0	533.0	
	0.038	103.7	460.3	457.9	533.2	
	0.042	103.6	460.2	457.9	533.1	
	0.10	103.7	460.3	458.3	533.1	529.5
M.TS-1	0.071	103.9	460.5	458.0	533.3	
S.TS-1	0.041	103.5	460.2	458.0	533.0	
	0.071	103.6	460.2	458.2	533.1	
U.TS-1	0.043	103.6	459.8	457.9	532.5	
V.TS-1	0.043	103.6	459.8	457.9	532.6	
W.TS-1	0.023	103.8	460.1	457.8	532.8	
	0.026	103.6	459.9	457.5	532.6	
	0.045	103.7	460.0	457.8	532.8	
X.TS-1	0.044	103.8	460.0	457.8	532.9	
Y.TS-1	0.008	103.6	460.2	n.d.	532.8	
	0.019	103.4	459.8	457.6	532.6	
	0.023	103.6	460.0	457.7	532.7	
	0.044	103.6	460.0	457.9	532.7	
	0.070	103.6	460.0	457.9	532.7	529.0
	0.10	103.6	460.0	457.9	532.7	529.3
Silicalite-1		103.7			533.2	
$(SiO_2 + TiO_2)$-mixture	0.025	103.6		458.0	533.0	529.4
TiO_2 (anatase)				458.8		530.1
Ti^{3+} (by Ar^+-sputtering of TiO_2)[d]				457.1		531.2
Ti^{2+} (by Ar^+-sputtering of TiO_2)[d]				455.2		532.3

[a] Mole ratio of Ti/(Ti + Si).
[b] The full widths at half maximum (FWHM) of the α and β spectra of Ti $2p_{3/2}$ for TS-1 samples were 2.2–2.4 and 1.5–1.7 eV, respectively. Also the FWHM of $(SiO_2 + TiO_2)$ mixture and TiO_2 (anatase) were 1.6 and 1.3 eV, respectively.
[c] No detectable intensity.
[d] Ref. [23].

tetrahedral and octahedral coordination of Ti^{4+} in the TS-1 structure. However, the deconvolution was impossible, because any evidence for the presence of octahedrally coordinated Ti^{4+} was not found in the original XPS spectra, and in the measurements of anatase and rutile types of TiO_2 prepared at 773 and 1373 K for 5 h in atmosphere respectively, the BE difference in the two Ti $2p_{3/2}$ spectrum lines with 1.3–1.4 eV in FWHM was only 0.2–0.3 eV (this difference was too small to deconvolute XPS spectra effectively). For spreading in FWHM of XPS spectrum, Takasu et al. [25] reported that the decrease in the amount of palladium deposited on amorphous silica enlarged the FWHM of Pd $3d_{5/2}$ spectrum, and such an effect has been frequently observed for metal/carrier samples [26]. Considering that the dispersion of framework Ti^{4+} in TS-1 matrix is very large, the large FWHM of the spectrum Ti $2p_{3/2}$ (α) might be quite reasonable.

Using the photoelectron spectrum areas and atomic sensitivity factors, surface atomic concentration can be calculated. The ratios of Ti/(Ti + Si), x_f, of TS-1 framework and x_{ex} of extraframework Ti can be estimated by the following equations:

$$x_{tl} = x_f + x_{ex}, \qquad x_f = \frac{C_{Ti(\alpha)}}{C_{Si} + C_{Ti(\alpha)} + C_{Ti(\beta)}},$$

$$x_{ex} = \frac{C_{Ti(\beta)}}{C_{Si} + C_{Ti(\alpha)} + C_{Ti(\beta)}}$$

where C_i is the surface atom concentration of core spectrum i (i=Si, Ti (α), Ti (β)), and x_{tl} the Ti/(Ti+Si) ratio of calculated from total area of Ti 2p. The x_f, x_{ex},

Table 3
The x_i values as atomic ratio of Ti/(Ti + Si) determined by XPS spectra and the relative intensities of XRD peak at $2\theta = 25.5^\circ$ and IR peak at 960 cm^{-1}

Sample	Gel composition x_g	Values determined by XPS			$I_{25.5}$[a] ratio	I_{960}[b] ratio
		x_f	x_{ex}	x_{tl}		
H.TS-1	0.024	0.018	n.d.[c]	0.018	n.d.	0.25
	0.023	0.015	0.004	0.019	0.078	0.20
	0.038	0.017	0.005	0.023	0.082	0.17
	0.042	0.016	0.014	0.030	0.22	0.22
	0.10	0.018	0.069	0.087	0.63	0.26
M.TS-1	0.071	0.020	0.015	0.035	0.32	0.41
S.TS-1	0.041	0.020	0.009	0.029	0.11	0.32
	0.071	0.028	0.012	0.040	0.24	0.36
U.TS-1	0.043	0.025	0.012	0.037	0.15	0.26
V.TS-1	0.043	0.018	0.011	0.029	0.12	0.27
W.TS-1	0.023	0.016	0.003	0.019	0.04	0.22
	0.026	0.016	0.004	0.020	0.05	0.23
	0.045	0.018	0.008	0.026	0.15	0.31
X.TS-1	0.044	0.012	0.011	0.023	0.16	0.21
Y.TS-1	0.008	0.005	n.d.	0.005	n.d.	
	0.019	0.016	0.002	0.018	0.016	0.22
	0.023	0.017	0.003	0.020	0.023	0.20
	0.044	0.030	0.015	0.044	0.13	0.27
	0.070	0.024	0.030	0.054	0.24	0.32
	0.10	0.030	0.045	0.075	0.39	0.32
$(SiO_2 + TiO_2)$-mixture	0.025	0.0	0.024	0.024	–	–

[a] Relative peak intensity of the $2\theta = 25.5^\circ$ peak referred to the 23.3° peak in XRD patterns.
[b] Relative peak intensity of the 960 cm^{-1} peak referred to the 550 cm^{-1} peak in FT-IR spectra.
[c] No detectable intensity.

and x_{tl} obtained are given in Table 3. The x_{ex} was not zero except for two cases. The x_{tl} was always smaller than x_g. These facts indicate that all of Ti^{4+} used in the synthesis was not always incorporated into TS-1 framework and also extraframework TiO_2.

For the H.TS-1 series prepared, first the increase in x_f with x_g was not observed and the reproducibilities of $I_{25.5}$ and x_{ex} values were very poor. In order to improve these shortcomings, i.e., to purify TBOT and to depress hydrolysis of TBOT with trace amount of water before reaction, TBOT and IPA were previously vacuum distilled and the mixture was added dropwise to the solution of TEOS and TPAOH cooled to 273 K in a glove box purged with Ar gas stream (S.TS-1, W.TS-1, V.TS-1). From these improvements, the x_f slightly increased and the formation of TiO_2 was fairly retarded ($I_{25.5}$, x_{ex}, and x_{tl} decreased), but the incorporation of Ti^{4+} into TS-1 framework was yet insufficient. When the aging temperature of the precursor gel was elevated by 20 K, the x_f inversely decreased and the $I_{25.5}$ increased (X.TS-1). Furthermore, when the hydrothermal synthesis was carried out at 458 K, the x_f increased remarkedly, but the $I_{25.5}$ also increased. Since even by the improved methods mentioned above satisfactory results were not obtained, a doubt occurred to our mind that the dispersion of Ti^{4+} in the precursor gel might be insufficient or heterogeneous. To facilitate the dispersion of Ti^{4+}, at the aging stage of the gel-like reactant mixture an ultrasonic wave vibrator was applied. Among $I_{25.5}$, x_f, x_{ex}, and x_g for Y.TS-1 sample series synthesized using the proposed method, some good relationships were found.

Fig. 6 shows relationship between x_f and x_g. In the Y.TS-1 series, the x_f increased linearly up to 0.03 with x_g and over $x_g = 0.04$ showed a plateau. This result indicates that Si^{4+} of silicalite-1 can be replaced by Ti^{4+} up to Ti/Si = 0.03, which is larger than 0.025 reported by Perego et al. [6] and Millini et al. [7]. The H.TS-1 and W.TS-1 samples with $x_g < 0.025$ resulted in a similar x_f values to Y.TS-1, but all other samples

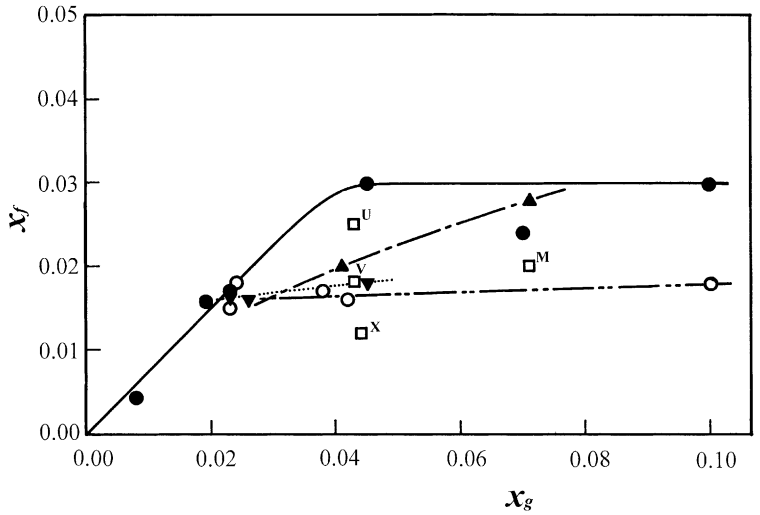

Fig. 6. Relationship between x_f and x_g: (●) Y.TS-1 series; (▲) S.TS-1 series; (▼) W.TS-1 series; (○) H.TS-1 series; (□) M.TS-1, V.TS-1, X.TS-1, or U.TS-1.

showed smaller x_f values compared to Y.TS-1 series. Fig. 7 indicates correlation between x_{ex} and x_g. The x_{ex} for Y.TS-1 series was directly proportional to x_g at $x_g \geqq 0.017$. The x_{ex} values of two W.TS-1 with $x_g = 0.023$ and 0.026 and of two H.TS-1 with $x_g = 0.023$ and 0.042 coincided with the straight line for Y.TS-1, but other three H.TS-1 was scattered and the S, V, X, and M.TS-1 samples of $x_g > 0.025$ lay in the lower area of the line. Furthermore, Y.TS-1 series indicated a good linear correlation between $I_{25.5}$ and x_{ex}, but the $I_{25.5}$ values for all other samples lay in the upper area of the line, as shown in Fig. 8. In depth profile measurement of Y.TS-1 with $x_g = 0.023$ by Ar^+-sputtering (3 kV, raster 7, 10^{-5} Pa), the Ti

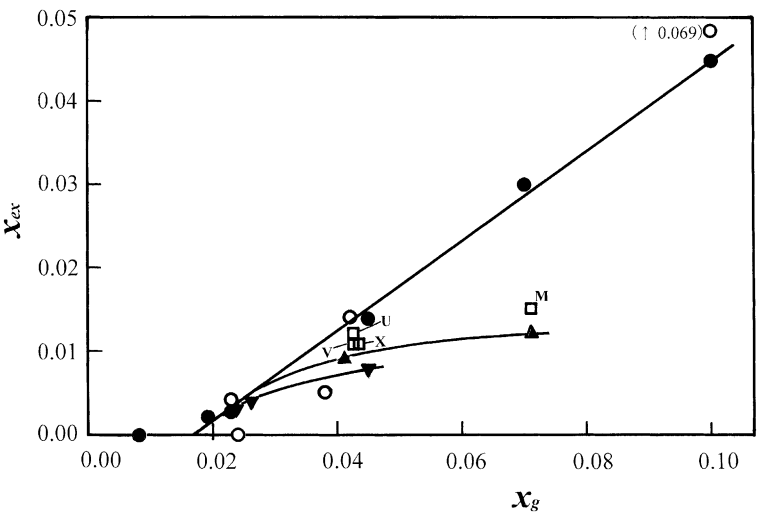

Fig. 7. Correlation between x_{ex} and x_g: (●) Y.TS-1 series; (▲) S.TS-1 series; (▼) W.TS-1 series; (○) H.TS-1 series; (□) M.TS-1, V.TS-1, X.TS-1, or U.TS-1.

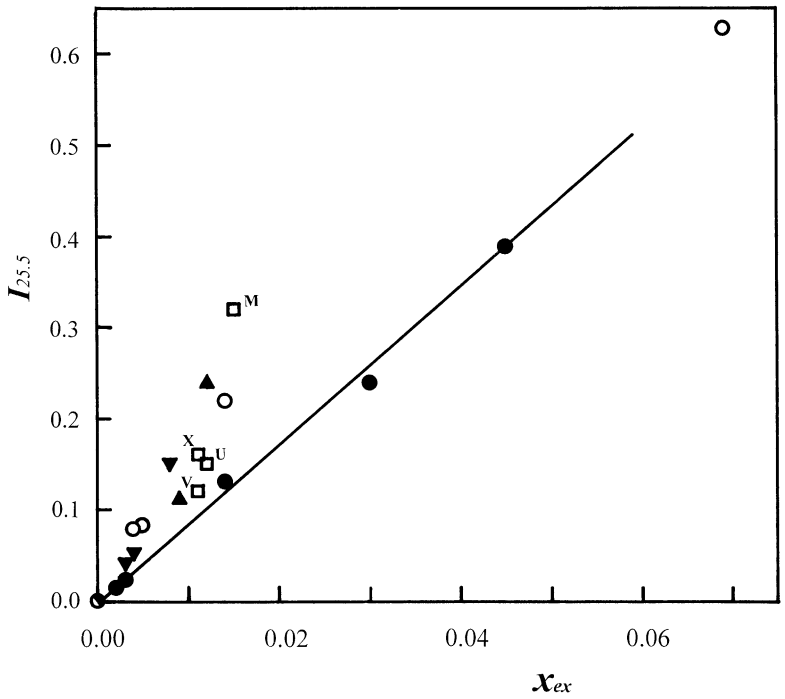

Fig. 8. Correlation between $I_{25.5}$ and x_{ex}: (●) Y.TS-1 series; (▲) S.TS-1 series; (▼) W.TS-1 series; (○) H.TS-1 series; (□) M.TS-1, V.TS-1, X.TS-1, or U.TS-1.

concentration was almost unchangeable, while for H.TS-1 with $x_g = 0.042$ it increased gradually with sputtering time and after 240 min by a factor of about 20% of the original surface one (16% as x_{tl}). These results imply that the surface Ti concentration of the samples other than Y.TS-1 series may be different from the bulk. As another reason, it is considered that the $I_{25.5}$ given by the ratio of peak height intensity depends on the degree of crystallization of TiO_2, since the peak height intensity of XRD peak becomes large with the size of crystalline. Consequently, the results that the samples except for Y.TS-1 series offered large $I_{25.5}$ would be explained by the heterogeneity in Ti concentration and the difference in crystalline size of extraframework TiO_2. For the results in Fig. 2, similar explanation might also be possible.

Finally, in Fig. 2 the extrapolation of the $I_{25.5}$ vs. x_g plot to $I_{25.5} = 0.0$ gave $x_g = 0.017$. The same x_g value was also obtained in the x_{ex} vs. x_g plot shown in Fig. 7. The x_f at $x_g = 0.017$ is estimated to be about 0.013 from Fig. 6. This means that pure TS-1 sample without extraframework TiO_2 is obtained only at $x_f \leqq 0.013$. However, since the H.TS-1 with $x_g = 0.024$ included no extraframework TiO_2, other factors undiscovered in the present work may be present. The surface atom concentrations of Si and Ti were calculated with atomic sensitivity factors used in general, but the degree of confidence of x_i value ($i = \mathrm{tl}, \mathrm{f}, \mathrm{ex}$) obtained was fairly excellent, because the x_{tl} of Y.TS-1 samples with $x_g < 0.044$ was very near to the x_g and the x_g of the mechanical mixture almost agreed with $x_{tl} = 0.024$ (Table 3).

4. Conclusion

In the XPS measurements of the TS-1 samples with $Ti/(Ti + Si) \geqq 0.02$, the Ti 2p core spectra corresponding to two kinds of oxidation states of titanium were observed. The spectra with BE of about 460.0 eV and those of about 457.9 eV were assigned to framework Ti^{4+} of TS-1 structure and extraframework Ti^{4+}, respectively. The former was confirmed by the measurements of XRD pattern and IR spectrum.

The presence of extraframework Ti^{4+} (TiO_2) was also ascertained by the observation of the absorption band at 300–380 nm in DRUV–Vis spectra and the peaks at $2\theta = 25.5^\circ$ and 48.18° in XRD patterns. The amount of Ti incorporated into TS-1 framework, when the samples were prepared in atmosphere, was smaller compared to x_g of the precursor gel and the reproducibilities of $I_{25.5}$ and x_{ex} were poor. The use of vacuum distilled TBOT and IPA, TEOS and TPAOH cooled to 273 K, and a glove box purged with Ar gas increased slightly x_f and retarded the formation of TiO_2, but the incorporated amount of Ti^{4+} was yet insufficient. If the temperature at the aging stage of the precursor gel or at the hydrothermal synthesis was elevated by 20 K, no remarkable improvement was obtained. To facilitate the dispersion of Ti^{4+}, the precursor gel prepared in the glove box using the mixture of distilled TBOT and IPA and the solution of TEOS and TPAOH cooled to 273 K was well shaken by an ultrasonic wave vibrator. In the Y.TS-1 series, synthesized by this method, a linear relationship between the x_f and x_g and a plateau of $x_f = 0.03$ at $x_g > 0.044$ were obtained, and the linear correlations between $I_{25.5}$ and x_g and between x_{ex} and x_g were established in the range of $0.017 \leqq x_g < 0.10$. That is, these results indicate that the use of ultrasonic wave vibrator is very effective and valid to facilitate the incorporation of Ti^{4+} into the TS-1 framework and to retard the crystallization of extraframework TiO_2. From the extrapolation of the $I_{25.5}$ vs. x_g plot and the x_{ex} vs. x_g plot, the $x_g = 0.017$ was obtained at $I_{25.5} = 0.0$ and $x_{ex} = 0.0$, respectively. This corresponded to $x_f = 0.013$. Consequently, pure TS-1 with no extraframework TiO_2 might be obtained only at $x_f \leqq 0.013$.

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