Linear combination of XANES for quantitative analysis of Ti–Si binary oxides

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A new method is demonstrated for the quantification of Ti—O—Si and Ti—O—Ti bonds in Ti–Si binary oxides. It is based on the linear combination of two reference X-ray absorption near-edge structure (XANES) spectra at the Ti *K* edge. The proper selection of a Ti—O—Si reference material is most important for the successful application of this method. Three Ti–Si binary oxide systems have been analysed by the new method: Ti–Si mixed oxides, titania supported on silica and Ti-substituted MCM-41 (crystalline mesoporous molecular sieve material invented by Mobil) with various Ti contents.

Keywords: linear combination of XANES; pre-edge fitting; Ti–Si binary oxides.

1. Introduction

The binary oxides of Ti and Si are found in many important materials, such as titanium silicalites, Ti-substituted MCM-41, mixed oxides and TiO_2-coated silica. Most applications take advantage of the properties of the binary oxides, which are better than and often different from those of the individual components. For example, they show remarkable catalytic activities in many selective oxidation reactions. An enormous amount of characterization data has been reported for these interesting materials, obtained with various spectroscopic tools. Structural characterization of titanium has focused on the location of Ti cations (in framework, extraframework or on the surface), the coordination state and the symmetry of Ti with oxygen anions, as well as the bonding modes, such as Ti—O—Si or Ti—O—Ti. The Ti—O—Si bonds represent an atomic dispersion of Ti in a silica matrix, while Ti—O—Ti bonds indicate the presence of a bulk TiO_2 phase. Quantitative analysis of these bonds in a sample is of great importance, since the state of Ti is closely related to catalytic activity. However, a reliable method for the quantification is not yet available.

The coordination state of Ti has often been probed by Ti *K*-edge XANES in a qualitative manner by comparison of the shape or intensity of the pre-edge peak with XANES spectra of reference materials. A number of studies have been devoted to the XANES of the Ti *K* edge by itself, or combined with extended X-ray absorption fine structure (EXAFS) analysis of various Ti-containing oxides. Other X-ray techniques, such as X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), have also been employed to supplement XANES and EXAFS results. In the present work, a new method is proposed to separate, in a quantitative manner, the contributions of the Ti—O—Si and Ti—O—Ti bonds to the total XANES of a Ti–Si binary oxide by fitting the pre-edge peak of the sample with the linear combination of two reference XANES spectra. The method has been applied to three kinds of samples of different nature: Ti–Si mixed oxides, titania supported on silica and Ti-substituted MCM-41. Detailed procedures are discussed together with important assumptions and limitations. Its advantages over conventional techniques are emphasized.

2. XANES of Ti–Si binary oxides

2.1. *Conventional methods of quantification*

The characteristic feature of the Ti *K*-edge spectra is the pre-edge caused by the excitation of a 1*s* electron into an empty bound state derived from the *d* and *p* states of Ti and O (Bordiga *et al.*, 1994). In the tetrahedral symmetry of Ti^{IV}, transitions occur from A_1 into the final states of T_2 and E. As the A_1 to T_2 transition is allowed and overwhelms the weaker A_1 to E transition, tetrahedral Ti^{IV} is represented by a strong single peak in the pre-edge region. In the case of octahedral symmetry, three weak peaks are observed: two of them are associated with A_{1g} to T_{2g} and A_{1g} to E_g, which are both Laporte-forbidden, and the third peak at the lowest energy is of uncertain origin. Thus, the pre-edge peak intensity and shape are the most important features related to the Ti coordination state (Vayssilov, 1997).

The pre-edge intensity of the Ti *K* edge was initially used as an indication of Ti coordination. In the case of Ti–Si mixed oxides and TiO_2 supported on SiO_2, Gao & Wachs (1999) considered the molecular structure of Ti species and the pre-edge intensity was used to determine roughly the coordination geometry of Ti in fourfold, fivefold and sixfold coordination. However, this comparison of pre-edge peak intensity is not adequate to obtain the amount of a specific Ti coordination mode. Problems arise from the fact that there is no universal standard for tetrahedral symmetry of Ti in Ti—O—Si bonding environments and the pre-edge peak intensity varies with the nature of the sample, the preparation method and the X-ray absorption measurement conditions (Mountjoy, Pickup, Wallidge, Anderson *et al.*, 1999; Mountjoy, Pickup, Wallidge, Cole *et al.*, 1999). Both pre-edge position and pre-edge height have also been used to derive information on the Ti coordination chemistry of titanosilicate glasses and melts (Farges *et al.*, 1997; Farges, 1997). However, the obtained information was still qualitative.

There has been an attempt to quantify fourfold and sixfold coordinated Ti in a series of TiO_2–SiO_2 glasses with XANES and EXAFS spectra collected in a fluorescence mode (Greegor *et al.*, 1983). A series of Ti–Si binary oxides having well defined structural regularity of Ti—O—Si were prepared by the flame hydrolysis method, with relatively low Ti contents of up to 14.7 wt% TiO_2. To find the fraction of Ti—O—Si, Greegor *et al.* (1983) divided the pre-edge peak area of a sample by that of the sample having the largest pre-edge peak area (2 wt% TiO_2). The latter sample, employed as a reference representing pure tetrahedral Ti^{IV}, had one of the highest pre-edge peak intensities (87% of the main edge jump) among the series of Ti–Si binary oxides reported in the literature, justifying the assumption of the pure tetrahedral symmetry of Ti in the sample. The Ti—O—Ti fraction was then obtained by subtracting the Ti—O—Si fraction from unity. This method of quantification, based on a single reference, is applicable only for samples with a low Ti loading, for which the peak intensity caused by Ti—O—Ti bonds is negligible. When two types of titanium are present in comparable quantities for intermediate and high Ti loadings, it is difficult to quantify each fraction by just considering the total pre-edge peak intensity.

Another problem in the quantification of tetrahedral Ti species is the effect of water adsorption. When a XANES spectrum is obtained for samples exposed to atmosphere, ambient water adsorbs and preferentially hydrolyses the surface Ti—O—Si bonds to form five-coordinate Ti—OH hydroxyls (Bordiga *et al.*, 1994; Gao *et al.*, 1998). In this case, the intensity and position of the pre-edge peak of tetrahedral Ti change significantly (Gao *et al.*, 1998; Liu & Davis, 1994).

2.2. *A proposed new method: linear combination of XANES spectra*

Our objective in this work is the quantification of two different Ti species in Ti—O—Si and Ti—O—Ti bonding modes *via* pre-edge fitting by the linear combination of two reference XANES spectra. It is assumed that the XANES of our Ti–Si binary oxides could be constructed by a linear combination of the Ti—O—Si and Ti—O—Ti contributions, like the two-site model employed by Greegor *et al.* (1983), and, therefore, their contents could be obtained by the deconvolution of the pre-edge peak into the fractions representing each Ti coordination mode. This linear-combination model can be justified because the two basis functions employed for references do not interact with each other. They have different shapes, positions and numbers of peaks. Due consideration must be made to the choice of reference spectra. Crystalline TiO_2 is the ideal reference material for pure Ti—O—Ti bonds with octahedral symmetry of the Ti cation surrounded by six O anions. The reference for Ti—O—Si bonds is more difficult to select. As a practical procedure, a series of Ti–Si binary oxide samples can be prepared with different Ti loadings. The sample that shows the maximum intensity of pre-edge XANES peak without any indication of the presence of Ti—O—Ti bonding can then be chosen as a first candidate for the Ti—O—Si reference material. If such a sample is not available, the material chosen as the reference in an analogous system could be tried.

The fitting range should be chosen to cover both the single and the triplet pre-edge peaks. Two parameters concerned with the goodness of fitting are defined as

$$\chi_\nu^2 = [1/(N - \mathrm{np})\sigma^2] \sum_{i=1}^{N} [y_{\mathrm{exp}}(i) - y_{\mathrm{theo}}(i)]^2$$

and

$$r = 100 \sum_{i=1}^{N} |y_{\mathrm{exp}}(i) - y_{\mathrm{theo}}(i)| \Big/ \sum_{i=1}^{N} |y_{\mathrm{exp}}(i)|,$$

where N is the number of data points, np is the number of free parameters in the fit, σ is an estimate for the experimental error, and y_{exp} and y_{theo} are experimental and fitted values, respectively. There are four parameters to be fitted in this case using two references: two are partial concentrations and the others are energy shift corrections for each reference XANES spectrum. The fitting was achieved by a least-square minimization of the χ_ν^2 term in the pre-edge region of 4965–4973 eV.

We introduce another term, SOPC, to check the validity of quantification procedure as well as the choice of references. SOPC refers to 'summation of the partial concentrations' of Ti—O—Si and Ti—O—Ti before normalization. This value should be unity if each step of the quantification procedure is correct, including the choice of the reference materials.

3. Experimental details

3.1. *Material preparation*

Three types of Ti–Si binary oxide were studied. $(Ti_xSi_{1-x})O_2$ mixed oxides were prepared by hydrolysis of tetraethyl orthosilicate and titanium tetraisopropoxide *via* a conventional sol–gel method. The total numbers of moles of the two alkoxide precursors were fixed at 0.22 mol and the molar ratio of Ti/Si was changed from 0.01 to 0.50. The aged gel was completely dried under a reduced pressure in a rotary evaporator and calcined at 773 K in an air stream. The detailed procedure has been described elsewhere (Kim *et al.*, 2000). For TiO_2/SiO_2, silica was impregnated to incipient wetness with a solution of titanium tetrabutoxide and toluene. Samples of titania supported on silica were prepared with loadings of 1–20 wt% Ti metal and calcined at 773 K in an air stream (Kim & Lee, 1999). As the third material, Ti-substituted MCM-41 samples were obtained from hydrothermal synthesis by using tetraethyl orthosilicate, titanium tetrabutoxide and an alkyl trimethylammonium bromide $[C_6H_{13}(CH_3)_3NBr]$ as a template (Rhee & Lee, 1997).

3.2. *X-ray absorption measurements*

X-ray absorption measurements were conducted on beamline 7C of the Photon Factory (KEK) in Tsukuba, Japan, and beamline 3C1 of the Pohang Accelerator Laboratory (PAL), Pohang, Korea. The Ti *K*-edge spectra were recorded at room temperature in a transmission mode under ambient conditions. The intensity of the X-rays was monitored using ionization chambers purged with a gas mixture of 30 vol.% N_2 and He for the incident beam, and pure N_2 for the transmitted beam. The XANES spectra were analysed with the *WINXAS97* program (Ressler, 1997). Background correction and normalization of the spectrum were processed by a least-squares fit. The pre-edge background was removed by fitting a pre-edge region of 4740–4940 eV with a straight line and subtracting the extrapolated values from the entire spectrum. The resulting elemental absorption $\mu(E)$ was then normalized by using atom-like absorption $\mu_0(E)$ at the edge. $\mu_0(E)$ was calculated with a cubic spline fit in the post-edge region of 5160–5940 eV.

4. Results and discussion

Fig. 1 shows the Ti *K*-edge XANES spectra of the $(Ti_xSi_{1-x})O_2$ mixed oxides with Ti/Si molar ratios of 0.01–0.5. For the samples with Ti/Si ratios between 0.2 and 0.5, a weak but clear shoulder peak appears next to the main pre-edge peak, indicating the formation of some Ti—O—Ti bonds having octahedral symmetry of Ti, as explained above. Therefore, in the mixed oxide, as the Ti/Si molar ratio increased, the Ti—O—Si network, having tetrahedral symmetry of Ti, was gradually replaced by species containing Ti—O—Ti bonding. Below Ti/Si = 0.04, the quality of the XANES spectra was much worse and the intensities were much less than that of the sample with Ti/Si = 0.04. The spectra were similar to that of crystalline TiO_2. This result

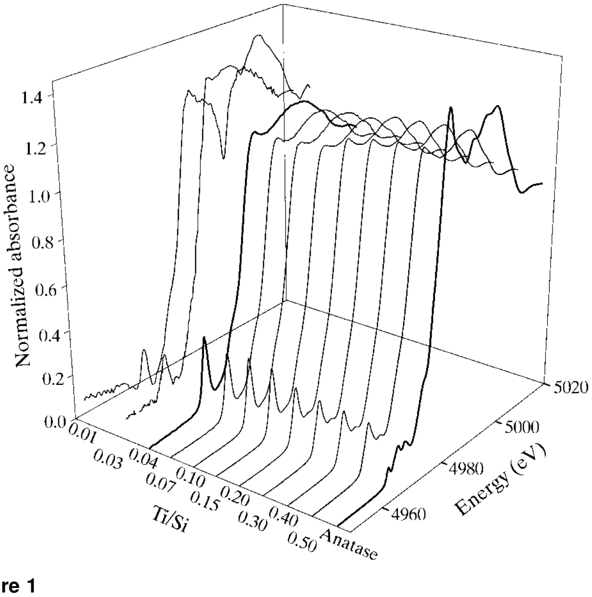

Figure 1
Ti *K*-edge XANES spectra of $(Ti_xSi_{1-x})O_2$ mixed oxides prepared by the sol–gel method with different Ti/Si ratios.

Table 1
Pre-edge fitting parameters and error analysis for $(Ti_xSi_{1-x})O_2$ materials.

c_{TOS} and c_{TOT} are the normalized concentrations (±0.02 mole fraction, at maximum) of Ti—O—Si and Ti—O—Ti, respectively. ΔE_{TOS} and ΔE_{TOT} are the energy shift corrections (±0.02 eV at maximum) for Ti—O—Si and Ti—O—Ti, respectively. χ^2_ν is the reduced χ^2. r is the residual. σ is the experimental uncertainty. SOPC is the sum of partial concentrations.

Ti/Si	c_{TOS}	c_{TOT}	ΔE_{TOS}	ΔE_{TOT}	χ^2_ν	r (%)	σ ($\times10^{-3}$)	SOPC
0.07	0.969	0.031	0.165	−0.898	23.20	2.43	1.00	0.906
0.10	0.990	0.010	0.034	−0.215	0.13	1.78	9.58	0.955
0.15	0.913	0.087	0.095	0.240	0.42	2.42	7.37	0.944
0.20	0.658	0.342	0.161	0.020	1.65	2.90	4.26	1.025
0.30	0.552	0.448	0.146	0.034	2.31	3.49	4.52	1.070
0.40	0.499	0.501	0.173	0.013	1.80	3.82	5.50	1.086
0.50	0.453	0.547	0.168	0.021	1.45	3.56	5.73	1.101

agrees with that of Greegor *et al.* (1983), who postulated the formation of a small number of octahedral holes when a very small amount of TiO_2 was introduced into an SiO_2 glass matrix. Thus, at Ti/Si = 0.04 in our series of $(Ti_xSi_{1-x})O_2$ oxides, the formation of Ti—O—Si connectivity was maximized without any indication of octahedral Ti—O—Ti.

Anatase TiO_2 is the natural choice for the standard local structure of Ti—O—Ti bonding because XRD patterns of samples with high Ti loading indicated the presence of anatase TiO_2 crystallites and post-edge XANES features matched only those of anatase, but not those of rutile. In order to find a reference for Ti—O—Si bonding, a series of materials were prepared with varying Ti contents; we chose the sample with Ti/Si = 0.04 as the standard. The effects of the ambient humidity (water) on our samples could be a major reason for the smaller pre-edge peak intensity found for our samples compared to the highest intensity (87% of main edge jump) reported previously for similar samples (Greegor *et al.*, 1983). It was assumed that the formation of five-coordinate Ti–hydroxyl surface species by strong adsorption of ambient water produced an equivalent effect on the XANES features for our samples as for the Ti—O—Si reference under the same XAS measurement conditions. Since the octahedral Ti—O—Ti bonds, like those in anatase titania, are hardly affected by water adsorption, the validity of the estimation for Ti—O—Si could be checked by summing each fraction and seeing if the sum is unity. The fraction of Ti—O—Si in this case is the sum of the Ti–hydroxyl species and the tetrahedral Ti. The combined fraction of these two species is what we look for since the surface Ti–hydroxyl species originate from Ti—O—Si by hydrolysis. Of course, this concern for surface hydroxyls is unnecessary when all XANES measurements are made under anhydrous conditions, in spite of the difficulties involved in carrying out the experiment under completely water-free conditions.

The results for three different materials analysed by the linear combination of XANES are presented below. Some examples of the pre-edge fitting procedure are also illustrated in Fig. 2. The reference spectra are denoted TOS for Ti—O—Si in the Ti/Si = 0.04 mixed oxide and TOT for the Ti—O—Ti bonds in anatase TiO_2.

4.1. *Ti/Si mixed oxides*

In Table 1, the normalized fractions of TOS and TOT in our mixed oxides obtained by fitting pre-edge peaks are shown as a function of Ti/Si ratios. The SOPC value varied between 0.9 and 1.1, as expected for a valid analysis with a 'good' reference. The greatest change occurred at Ti/Si ratios of 0.15–0.2, suggesting a drastic structural change in Ti species. The great increase in TOT fraction at Ti/Si = 0.2 is accompanied by an important change in the XRD pattern (Kim *et al.*, 2000). Thus, when Ti/Si reached 0.2, the main XRD peak of anatase titania appeared and it became stronger with further increase in Ti/Si.

At intermediate and higher Ti contents, the pre-edge peak area should be insensitive to the fraction of TOS as a result of the increased contribution of TOT. The total pre-edge peak areas decreased only very slowly with increasing Ti/Si at high Ti/Si ratios of above 0.2, because the pre-edge peak became broadened as a result of the contribution of the broad pre-edges of TOT. However, XRD of

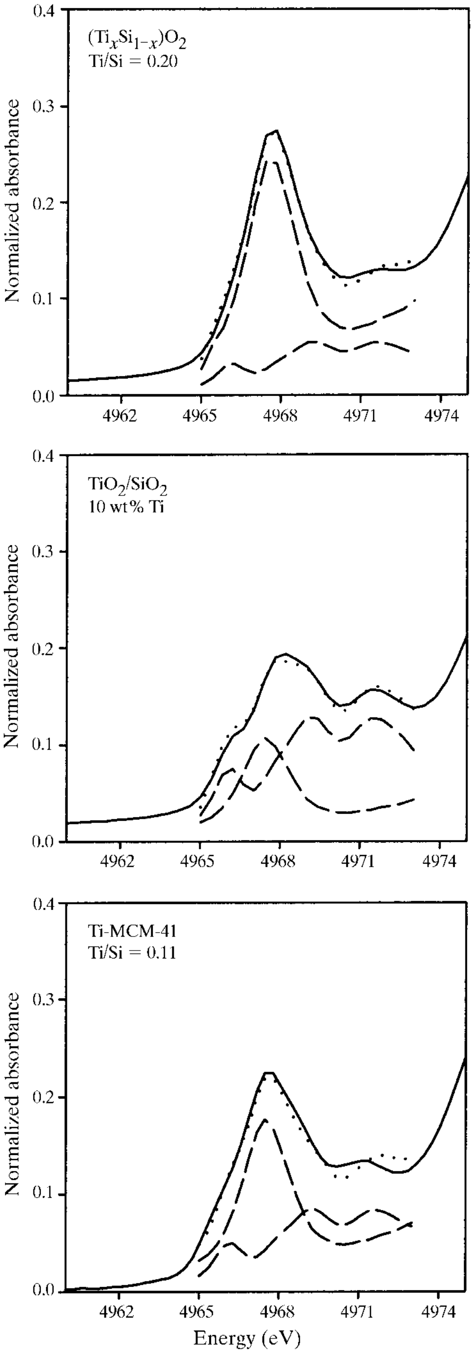

Figure 2
Some examples of pre-edge fitting of XANES spectra of Ti–Si binary oxides by the linear combination of reference XANES spectra. Solid lines are experimental XANES spectra in the pre-edge region and dotted lines are the fitting results. Deconvoluted reference spectra are also included (dashed lines).

Table 2
Pre-edge fitting parameters and error analysis for TiO_2/SiO_2 materials.

c_{TOS} and c_{TOT} are the normalized concentrations (±0.02 mole fraction, at maximum) of Ti—O—Si and Ti—O—Ti, respectively. ΔE_{TOS} and ΔE_{TOT} are the energy shift corrections (±0.02 eV at maximum) for Ti—O—Si and Ti—O—Ti, respectively. χ_ν^2 is the reduced χ^2. r is the residual. σ is the experimental uncertainty. SOPC is the sum of partial concentrations.

Ti (wt%)	c_{TOS}	c_{TOT}	ΔE_{TOS}	ΔE_{TOT}	χ_ν^2	r (%)	σ ($\times10^{-3}$)	SOPC
1	0.463	0.537	0.144	−0.320	6.59	4.35	3.05	1.102
3	0.394	0.606	0.076	−0.135	1.50	4.55	8.56	1.317
5	0.358	0.642	0.141	−0.073	2.87	3.63	4.57	1.268
7	0.380	0.620	0.146	−0.068	2.64	3.24	3.88	1.176
10	0.261	0.739	0.165	−0.063	0.68	2.87	6.20	1.116
13	0.244	0.756	0.142	−0.207	0.52	2.30	6.19	1.128
20	0.218	0.782	0.166	−0.144	0.63	2.90	6.72	1.136

Table 3
Pre-edge fitting parameters and error analysis for Ti-substituted MCM-41 with $(Ti_xSi_{1-x})O_2$, Ti/Si = 004, as the reference for TOS.

c_{TOS} and c_{TOT} are the normalized concentrations (±0.02 mole fraction, at maximum) of Ti—O—Si and Ti—O—Ti, respectively. ΔE_{TOS} and ΔE_{TOT} are the energy shift corrections (±0.02 eV at maximum) for Ti—O—Si and Ti—O—Ti, respectively. χ_ν^2 is the reduced χ^2. r is the residual. σ is the experimental uncertainty. SOPC is the sum of partial concentrations.

Ti/Si	c_{TOS}	c_{TOT}	ΔE_{TOS}	ΔE_{TOT}	χ_ν^2	r (%)	σ ($\times10^{-3}$)	SOPC
0.010	0.574	0.426	−0.184	−0.221	0.54	2.69	5.42	0.796
0.014	0.479	0.521	−0.207	−0.345	1.32	2.86	4.31	0.876
0.026	0.782	0.218	−0.055	−0.122	0.17	2.05	8.10	0.769
0.042	0.814	0.186	−0.129	−0.180	0.17	2.03	8.37	0.780
0.059	0.709	0.291	−0.042	−0.150	0.30	1.92	5.40	0.793
0.083	0.706	0.294	−0.070	−0.214	0.48	2.34	5.14	0.818
0.111	0.471	0.529	0.045	−0.294	2.89	3.80	3.91	1.020

these materials suggested continuous growth of anatase-type bulk titania above this Ti/Si ratio. The application of the proposed method covers a broad range of Ti contents, up to 0.5 Ti/Si (40 wt% TiO_2), and produces a result consistent with XRD which could detect the change in bulk phase.

4.2. *TiO_2/SiO_2 prepared by impregnation*

Unlike $(Ti_xSi_{1-x})O_2$ mixed oxides, TiO_2/SiO_2 prepared by impregnation contains a significant amount of TOT even for the sample with the lowest Ti loading (1 wt%). This presents difficulties when selecting the reference for TOS from the series of materials. When a potential TOS reference is not available among the same series of materials, we have to rely on the transferability of the reference and look for a reference material which might have similar properties. We chose $(Ti_xSi_{1-x})O_2$ with Ti/Si = 0.04 for the TOS reference, which had been employed in the analysis of the mixed oxides. Unlike $(Ti_xSi_{1-x})O_2$ mixed oxides, TiO_2/SiO_2 samples showed SOPC values that were all greater than 1.1. This consistent deviation in one direction (overestimation of all TOS fractions) indicates that the chosen reference for TOS has a smaller intensity than that which a hypothetically good reference material for TiO_2/SiO_2 might have. The structural change at around 10 wt% Ti in Table 2 could be identified as the formation of anatase titania, as indicated by XRD patterns (Kim & Lee, 1999). Thus, even without a proper Ti—O—Si reference, the analysis still provides useful quantitative information.

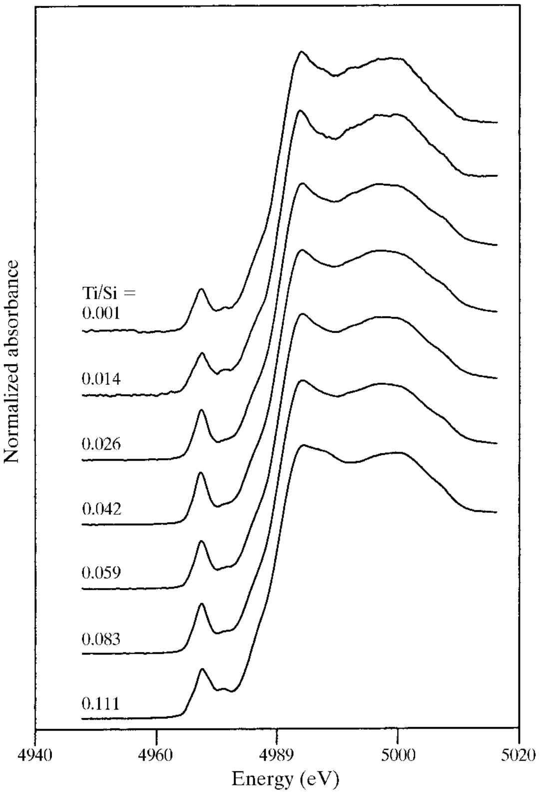

Figure 3
Ti *K*-edge XANES spectra of Ti-substituted MCM-41 with different Ti/Si ratios.

4.3. *Ti-substituted MCM-41*

Fig. 3 shows XANES spectra of Ti-substituted MCM-41 with different Ti loadings and Table 3 presents the pre-edge fitting results. For the whole range of Ti contents, XANES spectra showed a noticeable contamination by octahedral Ti species, as indicated by the presence of a shoulder peak next to the main pre-edge peak. Therefore, the same reference materials, $(Ti_xSi_{1-x})O_2$ (Ti/Si = 0.04) and anatase, were used as in the two previous cases. All the samples except one (Ti/Si = 0.111) had SOPC values less than 0.9, indicating that the chosen reference for TOS had now a larger intensity than a hypothetically good reference material in this case. This result led us to the conclusion that a part of Ti always exists on the extraframework of MCM-41 without being substituted into the MCM-41 structure. Also, a severe effect of water enclosed in the framework during hydrothermal synthesis could be another reason for the overall underestimation of TOS fractions. Small-angle XRD data showed that introduction of Ti into the Si framework without destruction of a well defined MCM-41 structure was possible below Ti/Si = 0.042 (Rhee & Lee, 1997). It is coincident with the maximum fraction of TOS occurring at this Ti/Si ratio as observed in this study.

Another analysis was tried with Ti-MCM-41, Ti/Si = 0.042, as a reference for TOS, although the sample contains a small amount of octahedral Ti species. Table 4 shows the pre-edge fitting results that show SOPC values near unity except for Ti/Si = 0.111. Thus, the chosen reference of TOS was a better one, suggesting that it gives better results when the reference is selected among the same type of samples prepared by the same procedure.

5. Conclusions

Quantification of Ti—O—Si and Ti—O—Ti bonds in Ti–Si binary oxides is possible by pre-edge fitting with the linear combination of two reference XANES spectra. The method represents an advance-

Table 4

Pre-edge fitting parameters and error analysis for Ti-substituted MCM-41 with Ti-MCM-41, Ti/Si = 0042, as the reference for TOS.

$c_{\rm TOS}$ and $c_{\rm TOT}$ are the normalized concentrations (±0.02 mole fraction, at maximum) of Ti—O—Si and Ti—O—Ti, respectively. $\Delta E_{\rm TOS}$ and $\Delta E_{\rm TOT}$ are the energy shift corrections (±0.02 eV at maximum) for Ti—O—Si and Ti—O—Ti, respectively. χ_ν^2 is the reduced χ^2. r is the residual. σ is the experimental uncertainty. SOPC is the sum of partial concentrations.

Ti/Si	$c_{\rm TOS}$	$c_{\rm TOT}$	$\Delta E_{\rm TOS}$	$\Delta E_{\rm TOT}$	χ_ν^2	r (%)	σ ($\times10^{-3}$)	SOPC
0.010	0.754	0.246	−0.058	−0.215	0.31	2.01	5.42	0.954
0.014	0.644	0.356	−0.096	−0.390	0.96	2.44	4.31	1.022
0.026	0.967	0.033	0.068	−0.275	0.05	1.27	8.10	0.978
0.059	0.891	0.109	0.083	−0.394	0.06	0.82	5.40	0.990
0.083	0.888	0.112	0.054	−0.471	0.13	1.20	5.14	1.018
0.111	0.623	0.377	0.172	−0.487	2.32	3.37	3.91	1.186

ment compared to previous techniques based only on the total intensity of the pre-edge peak relative to a Ti—O—Si reference. These conventional methods are applicable only for samples with low Ti loadings, for which the peak intensity arising from the Ti—O—Ti bonds is negligible. A potential difficulty in the new method is the choice of a proper Ti—O—Si reference. In most cases, a series of samples can be prepared with different Ti loadings. The sample that shows the maximum intensity of the pre-edge XANES peak without any indication of Ti—O—Ti bonding is chosen as the Ti—O—Si reference. If such a sample is not available in a system under study, the material chosen for an analogous system can be tried. The validity of the reference selection can then be checked by seeing if the SOPC term becomes unity. Better results are obtained when the Ti—O—Si reference is chosen among a series of samples prepared by the same method, with different Ti loadings. This may be due to the similar degree of structural disorder of these samples, which is known to have a significant effect on XANES (Farges *et al.*, 1997).

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Received 26 July 2000 • Accepted 15 December 2000