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Re-investigation of titanium silicalite by X-ray absorption spectroscopy: are the novel titanium sites real?

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EXAFS studies have been carried out on titanium silicalite-1 (TS-1). The titanium atom is coordinated to four oxygen atoms at the distance of 1.80(1) Å. There is no evidence for the presence of 5- and 6-coordinated titanium species or the novel 4-coordinated titanium species involving [TiO_x] units sharing edges with [SiO_4] units. The EXAFS spectrum of TS-1 appears to be consistent with the model that titanium resides at the tetrahedral sites of the framework.

Keywords: EXAFS; zeolite; titanium silicalite

1. Introduction

Although much of the catalytic activity of titanium silicalite has been attributed to the presence of Ti–O–Si [1–3] and titanyl groups [4], the coordination of titanium atoms in this material is still being debated. Earlier X-ray diffraction work by Perego et al. showed that the unit cell of titanium silicalite-1 (TS-1, zeolite structure-type MFI) expanded linearly with titanium content [5]. Such a result has been interpreted as evidence for the replacement of silicon by titanium at the tetrahedral sites of the framework [5]. However, recent X-ray absorption results disagree with this interpretation. The work by Behrens et al. [6] and by Lopez et al. [7] indicated that a large portion of the titanium atoms in TS-1 resided in octahedrally-coordinated environments. Recently, a detailed analysis of the extended X-ray absorption fine structure (EXAFS) spectra by Trong On et al. [8] suggested that novel titanium sites were present in titanium silicalite-2 (TS-2, zeolite structure-type MEL), involving [TiO_x] units sharing edges with [SiO_4] tetrahedral units. The objective of the present work is to resolve the controversial issues on titanium coordination and, in particular, to determine if the novel titanium sites, as proposed for TS-2, could also exist in the TS-1 counterpart.

2. Experimental and data reduction

The TS-1 sample for this study was kindly supplied by Professor M. Davis of California Institute of Technology. This sample was prepared using a procedure similar to that described by Taramasso et al. [9]. X-ray fluorescence measurements showed that the sample contained 1.4 wt% titanium. The sample was stored at ambient conditions before all the measurements.

Powder XRD data were collected on a Scintag PAD V diffractometer using Cu Kα radiation. Silicon powder was used as an internal standard.

EXAFS measurements were made in fluorescence mode at room temperature on beamline X-11A at NSLS with electron beam energy of 2.583 GeV and stored current between 110 and 200 mA. Data were collected with a fixed exit monochromator using two flat Si(111) crystals. Harmonics were rejected by detuning 15% from the maximum intensity. The incident beam intensity was monitored with a 6 in. (14.70 cm) ion chamber continuously flushed with a 17 : 83 mixture of nitrogen and helium gases at 67 cm^3/min. The fluorescence signal was detected with a Lyttle detector [10] flushed with nitrogen gas at 60 cm^3/min. Energy resolution was estimated to be at least 3 eV by the Cu foil 3d near-edge feature. The samples were 1 in. wafers made of either pure titanium silicalite, or reference compounds (anatase and fresnoite), diluted to 2 wt% titanium by mixing with ZSM-5 sieve. Five scans were taken and averaged for each sample to improve statistics and ensure reproducibility of the data. The EXAFS data were Fourier-filtered using the Macintosh edition of the University of Washington EXAFS analysis package [11]. Two to three spline knots were used in the background subtraction and fill gas [12] and McMaster [13] corrections were performed on the experimental spectra. Forward and inverse Fourier transform ranges are given in table 1 and 0.5 Å^{-1} Hanning windows were used in the forward transform. Ab initio EXAFS calculations were carried out with FEFF 4.0 [14].

Structural information was extracted from the EXAFS data through non-linear least-squares fitting to the standard EXAFS equation [15],

Table 1
Ranges of the forward and inverse Fourier transform and the fitting of the first coordination shell of Ti

Sample	FT (Å^{-1})	IFT (Å)	Fitting (Å^{-1})
TiO_2 (anatase)	4.1–12.7	1.0–1.9	4.7–12.0
TS-1 (well-behaved)	4.5–12.2	0.9–1.8	5.1–11.8
TS-1 (anomalous)	4.4–12.2	1.0–1.9	5.1–11.8

$$\chi(k) = \sum_j (N_j/kR_j^2)F_j(k)\,\exp(-2k^2\sigma_j^2)\sin[2kR_j + \varphi_j(k)]\,.$$

Here N_j is the number of identical atoms at an average distance R_j to the absorbing atom, σ_j is the EXAFS Debye–Waller factor, $F_j(k)$ and $\varphi_j(k)$ are the backscattering amplitude and total phase shift (note that mean-free path and many-body effects have been lumped into $F_j(k)$) and $k = \sqrt{[2m(E - E_0)/h^2]}$ is the electron wave number, where m is the electron mass, h is Planck's constant, and E_0 is the edge energy. The fitting procedure was a modification of the Levenberg–Marquardt algorithm as implemented in MINPACK-1 [16] and minimized the quantity

$$\Delta = \sum_{i=1}^{M} k^w(\chi_i^{\text{exp}} - \chi_i^{\text{fit}})^2\,,$$

where w is the weight of the fit and M is the number of points in the fitting range. The edge energy E_0, number of near neighbors N, radial distance R and Debye–Waller factor σ^2 were used as fitting parameters. The confidence limits for the fitting parameters were calculated as square roots of the diagonal elements of the covariance matrix of the fit multiplied by the minimum value of Δ [17].

3. Results

We suspect that the controversies over the coordination of titanium may arise partly from the sample preparation. In this work, efforts have been made to ensure that the sample exhibited the characteristics of a TS-1 material as defined by the catalysis community. Catalytic testing showed that the sample of this study had consistent activity for all major reactions that the TS-1 was reported to catalyze [18]. The X-ray diffraction pattern of the sample (fig. 1) was similar to that reported by Perego et al. [5]. Furthermore, the lattice parameters, $a = 20.125(2)$ Å, $b = 19.932(2)$ Å, $c = 13.411(1)$ Å, matched excellently with the reported values for TS-1 having 1.5 wt% titanium [5]. In addition, the infrared spectrum of the sample (fig. 2) showed a sharp band at 961 cm^{-1} with a relative peak height comparable to that in the literature [5]. We are therefore confident that the sample of this study is consistent with a well-behaved TS-1 material in the literature.

The normalized absorption spectrum of TS-1 near the titanium K-edge is shown in fig. 3, along with the spectra of two references, anatase (TiO_2 with 6-coordinated titanium) and fresnoite ($Ba_2TiSi_2O_8$ with 5-coordinated titanium). We note that the pre-edge feature (near 4968 eV) of TS-1 is qualitatively different from that of anatase. As a result, the sample of this study should contain no appreciable titanium species with regular oxygen octahedra as occurs in anatase. Unfortunately, the near-edge features alone do not permit the unambiguous determination of the titanium coordination in TS-1. Earlier work by Behrens et al. [6] showed that simi-

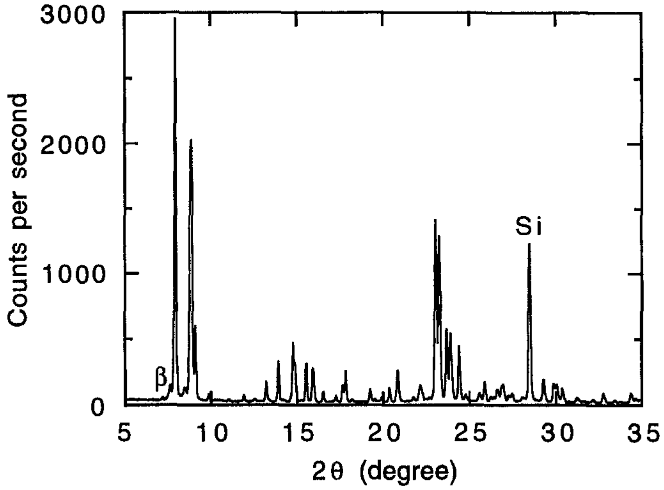

Fig. 1. Powder X-ray diffraction pattern of the TS-1 sample of this study. Some weak peaks are due to the tungsten Lα and copper Kβ radiation.

lar pre-edge peaks (at 4968 eV) can arise from 4- and 5-coordinated titanium as well as 6-coordinated titanium with severely distorted oxygen octahedra.

The k-weighted EXAFS spectrum $k\chi(k)$ for TS-1 is shown in fig. 4. Comparing to the data reported by Trong On et al. [8], we note that the data of the present work had a much better signal-to-noise ratio. The previously reported data was very noisy above 6 Å^{-1}. In contrast, our data has acceptable signal-to-noise ratio even at

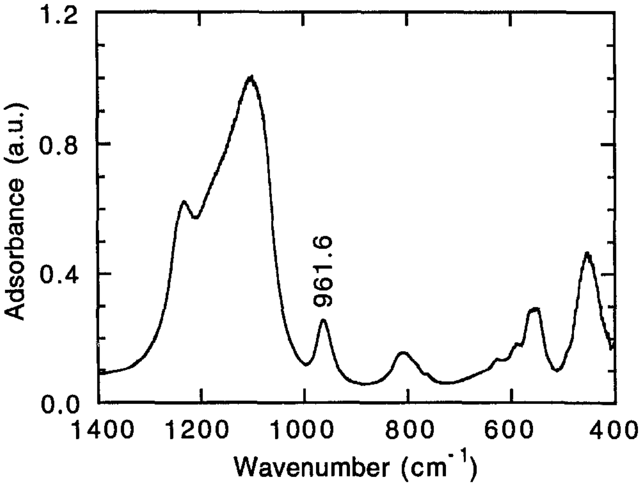

Fig. 2. Infrared spectrum for the TS-1 sample of this study. Note that the peak at 961 cm^{-1} is characteristic of TS-1.

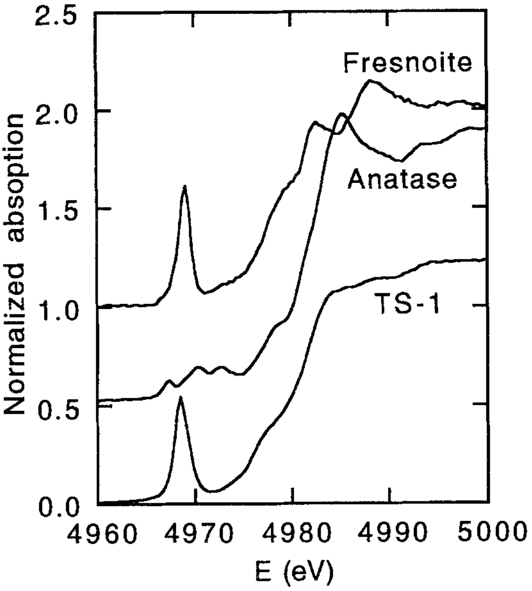

Fig. 3. X-ray absorption spectra near Ti edge for TS-1, anatase and fresnoite. The spectra of anatase and fresnoite are shifted upwards by 0.5 and 1.0, respectively.

12 Å^{-1}. This extended k-range is of critical importance for extracting structural information beyond the first shell.

To determine the titanium coordination, we have carried out a Fourier trans-

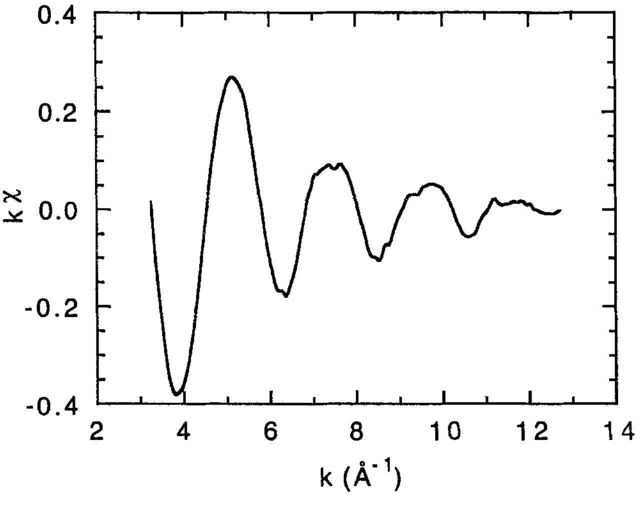

Fig. 4. Experimental $k\chi(k)$ for TS-1.

form (FT) of $k^3\chi(k)$. The magnitude of this FT, as shown in fig. 5, exhibits three distinct features: two peaks at 1.5 and 2.1 Å respectively, and a broad hump centered at 3.0 Å. The origin of each feature and its implication concerning the titanium coordination are discussed below.

3.1. THE FIRST PEAK

We have analyzed the first peak in the FT using both theoretical and experimental backscattering amplitude and phase-shift functions. The experimental functions were obtained through an inverse Fourier transform of the well-isolated first peak in the FT of the anatase data. The theoretical functions were calculated with FEFF for a titanium atom tetrahedrally coordinated to four oxygen atoms at the distance of 1.90 Å. The theoretical amplitude functions were Fourier-filtered in data ranges similar to those used for TS-1 and TiO_2 (anatase), and were calibrated by fitting the inverse FT of the first shell of TiO_2, which is known to contain six oxygen atoms at an average distance of 1.95 Å. The fitted distance in TiO_2 is 1.94(1) Å, in agreement with the known value.

The first peak in the FT of TS-1 corresponds to the first coordination shell of titanium, which is expected to consist of oxygen atoms only. Fig. 6 shows the back Fourier transform of the first shell and the fitted curves. The theoretical and experimental fits gave the same results (within the confidence limits). The refined structural parameters are: $N_{\text{Ti-O}} = 4.1(5)$, $R_{\text{Ti-O}} = 1.80(1)$ Å, $\sigma^2 = 0.0026(10)$ Å^2,

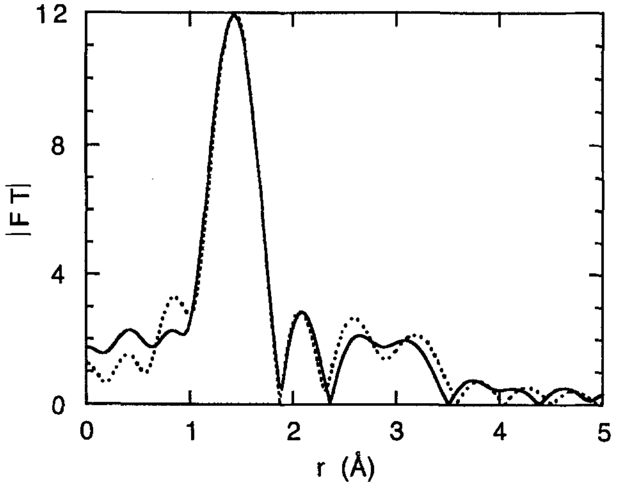

Fig. 5. Magnitude of the first shell Fourier transform for TS-1 (full line) and the corresponding result from a FEFF simulation (dotted line). The simulation was based on the structural model that contains four oxygen atoms at 1.80 Å, two silicon atoms at 3.18 Å, four oxygen atoms at 3.29 Å, and four oxygen atoms at 3.56 Å.

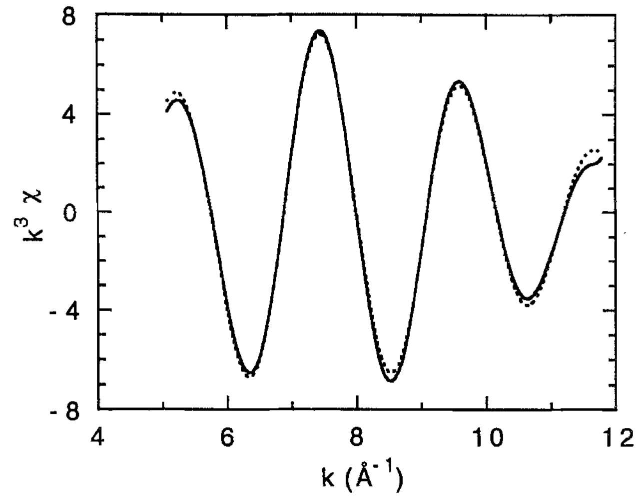

Fig. 6. $k^3\chi(k)$ of the first shell for TS-1: experimental (full line) and fitting (dotted line).

which are, respectively, the number of oxygen atoms surrounding a titanium atom, the titanium–oxygen distance and the Debye–Waller (DW) factor.

Although the fitted value of $N_{\mathrm{Ti-O}}$ (4.1 ± 0.5) suggested the presence of 4-coordinated titanium, the large uncertainty associated with the fitting makes this result less convincing. Furthermore, we found that the obtained coordination number can vary from 3.5 to 4.5 depending on the details of the background subtraction. Therefore, this result alone may not be sufficient to determine titanium coordination definitely.

Evidence for the presence of 4-coordinated titanium comes from the analysis of the titanium–oxygen distance. In table 2, we list the titanium–oxygen bond length data for all the structurally characterized 4-coordinated titanium(IV) compounds [19], along with several representative 5- and 6-coordinated compounds [20–28]. We observed a correlation between the titanium environment and the titanium–oxygen distance as summarized below:

(i) The average titanium–oxygen distances in the 4-coordinated compounds lie only in a narrow window between 1.76 and 1.81 Å. For a given compound, the length differences, ΔR, between the individual bonds are small ($\Delta R < 0.07$ Å).

(ii) The average titanium–oxygen distance in the 5-coordinated compounds is greater than 1.90 Å. The apical oxygen atom is much closer to the central titanium atom than the four basal oxygen atoms ($\Delta R = 0.27$ Å).

(iii) The average titanium–oxygen distances in 6-coordinated compounds vary from 1.85 to 1.96 Å. For compounds having nearly regular oxygen octahedra ($\Delta R < 0.05$ Å), the titanium–oxygen distances are around 1.94 Å. In the case of severely distorted octahedra ($\Delta R = 0.22$ Å), titanium–oxygen distances are as low as 1.85 Å.

The titanium–oxygen distance obtained by fitting of the first shell of TS-1 is

Table 2
Individual Ti–O distances, averaged Ti–O distances (R), and differences in Ti–O distances (ΔR) for the selected Ti compounds

Ti(IV) compound	Ti–O distance (Å)	R (Å)	ΔR (Å)	Ref.
6-coordinated				
TiO_2 (anatase)	1.934 × 4, 1.980 × 2	1.957	0.046	
TiO_2 (rutile)	1.949 × 4, 1.980 × 2	1.964	0.031	
$SrTiO_3$	1.952 × 6	1.952	0.000	[20]
$MgTiO_3$	1.735 × 3, 1.956 × 3	1.846	0.221	[21]
5-coordinated				
$Ba_2TiSi_2O_8$ (fresnoite)	1.698, 1.970 × 4	1.916	0.270	[22]
4-coordinated				
Ba_2TiO_4	1.766, 1.812, 1.817, 1.836	1.808	0.070	[23]
$CsAlTiO_4$	1.751, 1.757, 1.773 × 2	1.764	0.022	[24]
$C_{48}H_{68}O_4Ti$	1.780 × 2, 1.781 × 2	1.781	0.001	[25]
$C_{40}H_{52}O_4Ti$	1.778 × 4	1.778	0.000	[26]
$C_{40}H_{52}O_4Ti$	1.760, 1.761, 1.776, 1.793	1.773	0.033	[26]
$C_{96}H_{80}O_{10}Si_8Ti$	1.777, 1.778, 1.781, 1.791	1.782	0.014	[27]
$C_{88}H_{104}O_8Ti_2 \cdot 6C_7H_8$	1.782, 1.797, 1.813, 1.845	1.809	0.063	[28]

1.80 Å. No broadening and/or distortions in the shape of the FT peak were observed, allowing us to rule out the possibility of large static disorder. The refined DW factor is 0.0026 Å^2, suggesting that the variation of titanium–oxygen bond distances, ΔR, is not greater than 0.05 Å. Evidently, these results are consistent only with the case of 4-coordinated titanium. The cases of other coordination can be eliminated based on the large mismatches in the titanium–oxygen distance and/or the DW factor.

Additional evidence came from the result on the DW factor. We consistently obtained a smaller DW factor for the first shell of TS-1 ($\sigma^2 = 0.0026(10)$ Å$_2$) than that for crystalline anatase ($\sigma^2 = 0.0049(8)$ Å^2). This result may seem to be puzzling since it implies that titanium–oxygen distances in TS-1 are better defined than those in crystalline TiO_2. We later found that such behavior is common in the 4-coordinated titanium compounds, and has been attributed to the strengthening of the titanium–oxygen bond due to the reduction in length [25–27]. We therefore conclude that the titanium in TS-1 is 4-coordinated and the titanium–oxygen distances of four bonds are very similar.

3.2. THE SECOND PEAK

The occurrence of a peak at 2.1 Å in the FT (2.4 Å by fitting) was first reported by Trong On et al. [8]. Since this distance was not consistent with the known MFI framework, the observation of this peak led the authors to conclude that titanium is not incorporated in the MFI framework. Several structural models containing such a distance were proposed.

The FT of our data confirms the existence of this peak, but our interpretation for its origin is totally different. We have simulated the $\chi(k)$ of TS-1 based on a simple model which contained a single oxygen shell at 1.80 Å. The theoretical $\chi(k)$ was then Fourier transformed in the same way as was done for the experimental data. Although no atoms were present in the vicinity of 2.4 Å, a peak was present at 2.1 Å in the simulated FT, with amplitude just slightly (~ 20%) smaller than that of the experimental one. When a few higher shells were included in the simulation to model the possible atoms in the distance range 3.1–3.6 Å, we found that the simulated peak near 2.1 Å resembles very well the experimental one both in position and in size (fig. 5). It thus appears that this second peak arises as an artifact of the Fourier transform. This result emphasizes that TS-1 does not have any atomic shells at 2.2–2.8 Å from titanium. Consequently, all models that contain such distances can be eliminated, including the models that involve the novel Ti sites [8].

3.3. THE BROAD HUMP

Our simulations suggest that the broad hump centered at 3.0 Å represents a real structural feature of the material. This result suggests that the titanium species in TS-1 are bonded to the framework. However, analysis of this region of the FT for the detailed atomic structure is difficult due to the limited k-range and the presence of at least two distances in the spectrum. Although it is not possible for us to make definite conclusions about the structure of this shell, the following picture emerges:

- The hump must consist of at least two subshells of atoms with different radial distances to the central titanium atom. We found it impossible to fit this hump using a single shell of atoms.
- The hump appears to consist of oxygen and silicon. However, we were not able to determine if only oxygen or silicon, or a mixture of the two were involved. Assuming that the second shell has two subshells, we found that the data could be fitted equally well using either oxygen or silicon. On the other hand, we found it impossible to fit the hump with any subshells involving titanium. This led us to the conclusion that very few Ti–O–Ti bonds are present in TS-1.
- When it consists of only oxygen and/or silicon, we found that the hump covers radial distances from 3.1 Å to 3.8 Å. Hence, any realistic models of TS-1 should contain oxygen and/or silicon atoms located 3.1–3.8 Å away from the titanium atoms.

In the pure ZSM-5 silicalite, we note that there is a nearly continuous distribution of oxygen and silicon starting from 3.4 Å. This feature is consistent with the location of the broad hump. In the case that titanium replaces silicon in the MFI framework, we expect that a similar atomic distribution would also exist above

3.4 Å [29]. To test this model, we have carried out ab initio calculations assuming that the titanium–oxygen bond length was 1.80 Å and the higher shell distances were unchanged from those in the MFI structure. We found that the calculated FT contained a broad hump in the region between 2.4 and 3.5 Å. Although the detailed shape of the simulated hump differed from that of the experimental one, this was not surprising, since in reality atoms in the higher shells also relax as a result of titanium substitution. The important result of this calculation is that the seemingly continuous silicon and oxygen distribution can produce a broad hump centered around 3.0 Å in the FT with comparable amplitude. We therefore conclude that our EXAFS results (all three features in the Fourier transform) are consistent with the model that titanium replaces the silicon in the MFI framework.

4. Discussion and conclusions

To elucidate the cause for the discrepancies of titanium coordination in titanium silicalite, it is useful to show additional data that we obtain from an anomalous TS-1 sample (1.3 wt% titanium, prepared elsewhere). Instead of a sharp infrared peak at 961 cm^{-1}, this sample gave a shoulder at a slightly higher wavenumber (985 cm^{-1}) in the infrared spectrum. For this material, we found that the pre-edge peak at 4968 eV was considerably smaller than that of the well-behaved TS-1 (fig. 7). In addition, a phase difference was observed between the EXAFS oscillations of this sample and the well-behaved TS-1, indicating a different titanium–oxygen distance. Fits of the first FT peak of this sample gave titanium–oxygen distance of

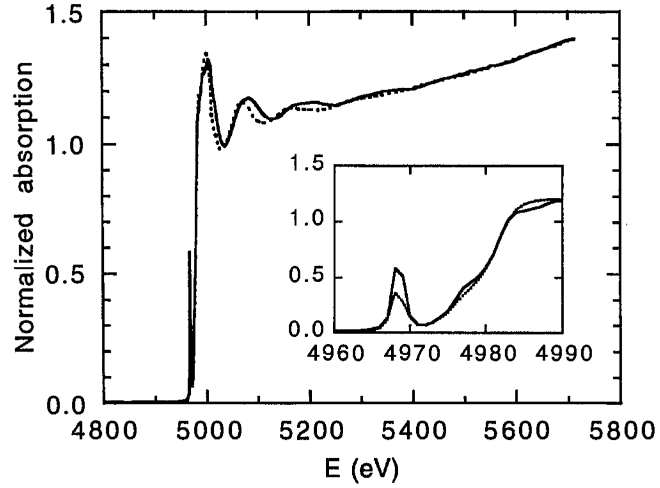

Fig. 7. Comparison of X-ray absorption spectra for well-behaved TS-1 (full line) and an anomalous sample with a suppressed 961 cm^{-1} infrared band (dotted line). The inserted curves are the enlargement of the spectra in the near-edge region.

1.87(1) Å and coordination number of 4.8(5), in agreement with earlier results [7]. Our interpretation for such results is that the majority of the titanium in the anomalous sample resided at the 5- or 6-coordinated sites, probably outside the framework.

We would like to discuss the reasons for the disagreements between the present work and the earlier EXAFS work. The difference between our work and that of Trong On et al. [8] is largely due to the interpretation of a Fourier-transform peak at 2.1 Å. Although Ti coordination in TS-2 may differ from that in TS-1, it is our feel that the signal-to-noise ratios of the earlier TS-2 data were not up to the level to allow statistically meaningful fits involving multiple atomic shells and 17 fitting parameters [8]. On the other hand, the disagreement with the work by Behrens et al. [6] is probably due to differences in material. We note that their sample exhibits a pre-edge peak (at 4968 eV) much smaller in size than our samples, either the well-behaved TS-1 or the anomalous sample. Furthermore, the lattice parameters of their sample appear to correspond to the pure silicalite with no titanium content [5]. These observations point to the possibility that the majority of the titanium in their sample reside at non-framework sites (largely 6-coordinated according to their analysis), similar to the anomalous TS-1 sample in our study. It appears that the samples used in the earlier X-ray absorption work [6] may contain appreciable non-framework titanium species, which are not present in a properly synthesized TS-1 material.

In conclusion, we found that the titanium atom in TS-1 is coordinated with four oxygen atoms at the distance of 1.80 Å. There is no evidence for the presence of 5- and 6-coordinated titanium species as well as the 4-coordinated titanium species, involving [TiO] units sharing edges with [SiO_4] units. The EXAFS results for TS-1 appear to be consistent with the model that titanium resides at the tetrahedral silicon sites of the framework.

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