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XANES Study of Ti Coordination in Heat-Treated $(TiO_2)_x(SiO_2)_{1-x}$ Xerogels

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Accurate measurements of the height and position of the preedge peak in Ti K-edge XANES (X-ray absorption near-edge structure) can distinguish 4-, 5-, and 6-fold coordination of Ti by O ($^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti, respectively), and mixtures thereof. This approach has been applied to titania−silica xerogels, $(TiO_2)_x(SiO_2)_{1-x}$, prepared from Si and Ti alkoxides using a prehydrolysis step and acid catalyst, with $0.18 < x < 0.75$. As expected, samples with $x = 0.75$ contain phase-segregated, amorphous, pre-anatase $^{[6]}$Ti, which is converted to anatase after heating at 500 °C. Samples with $x = 0.18$ contain a majority of isolated, distorted $^{[6]}$Ti before heating, which is converted to $^{[4]}$Ti substituted for Si after heating at 750 °C. This is the first time that the changes in the coordination of isolated Ti have been unambiguously described. Xerogels with $0.25 < x < 0.35$ and heat treatment at 750 °C showed concentration limits of $^{[4]}$Ti substitution for Si of 10−15mol %. Slightly higher values were obtained for xerogels prepared using acetylacetone, but the main difference was that the latter had a significantly larger content of distorted $^{[6]}$Ti before heat treatment. There is no evidence of significant amounts of $^{[5]}$Ti.

1. Introduction

Titania−silica oxide materials, $(TiO_2)_x(SiO_2)_{1-x}$, with low TiO_2 content $x \ll 1$, are useful for technological applications,[1] such as ultralow expansion glasses, antireflective thin film coatings, and catalytic materials.[2] Their structure is interesting because Si has tetrahedral coordination, with Si−O bond length of 1.61 Å,[3] whereas Ti prefers octahedral coordination. Although in minerals and alkali silicate glasses, Ti can have tetrahedral, square pyramidal, or octahedral coordination[4−6] (hereafter, $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti), with bond lengths of 1.81, 1.70/1.99, and 1.96 Å respectively.[4,7]

The effect of Ti concentration has previously been seen in titania−silica glasses, the properties of which have different behaviors in the stable and metastable regions.[1] Phase-segregation of TiO_2 occurred with $x > 0.13$ in titania−silica glasses prepared by flame hydrolysis and sintering.[8,9] Stable glasses formed with $x < 0.09$, and these crystallized into cristobalite with Ti substituting for Si. An EXAFS (extended X-ray absorption fine structure) study found only $^{[4]}$Ti for $x < 0.08$, but a mixture of $^{[4]}$Ti and $^{[6]}$Ti for $x = 0.115$.[9] The limited ability of an SiO_2 network to incorporate $^{[4]}$Ti has been explained as due to the unfavorable nature of Ti−O−Ti bonds between large, coordinately unsaturated, Ti^{4+} ions. Ions which can be substituted into an SiO_2 network generally have a suitable combination of small size and/or small charge.[10] From this point of view Ti^{4+} is less favorable than Al^{3+}, for example.

The sol−gel process is a relatively recent method of preparation,[11] with the advantages that it involves liquid precursors and occurs at low temperature. The structure of a xerogel, i.e., dried gel, tends to be porous with excess hydroxyl groups. This becomes more similar to a melt-quenched glass through the effects of heat treatment (at roughly 1000 °C). The structure of titania−silica xerogels has been studied using many techniques. IR, Raman, and ^{29}Si NMR spectroscopies[12,13] most readily give information about Ti−O−Si, Si−O−Si, and Si−O−H groups. UV spectroscopy[13] is sensitive to the coordination of Ti. EXAFS[14] is a direct structural probe of the Ti environment. Diffraction[14] is less direct due to overlapping peaks from Si−O and Ti−O bonds. However, the structure of xerogels is strongly dependent on the details of preparation and heat treatment.

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Table 1. Single Ti−O Shell Fits from EXAFS of Samples with Similar Preparation to Those in This Study (without acac)[18]

x	heat treatment	distance ± 0.01 (Å)	coordination number	Debye−Waller term $2\sigma^2$ (Å)^2
0.08[a]	none	NA	NA	NA
0.08[a]	250 °C	1.85	3.0 ± 0.5	0.016 ± 0.007
0.08[a]	500 °C	1.84	3.2 ± 0.5	0.014 ± 0.004
0.08[a]	750 °C	1.82	3.2 ± 0.4	0.010 ± 0.003
0.18	none	1.84	5.5 ± 1.0	0.033 ± 0.011
0.18	250 °C	1.85	5.3 ± 0.7	0.028 ± 0.007
0.18	500 °C	1.84	5.0 ± 0.5	0.024 ± 0.004
0.18	750 °C	1.81	4.4 ± 0.4	0.016 ± 0.003
0.41	none	1.87	6.2 ± 1.0	0.045 ± 0.012
0.41	250 °C	1.88	5.3 ± 0.7	0.032 ± 0.008
0.41	500 °C	1.88	5.2 ± 0.7	0.029 ± 0.007
0.41	750 °C	1.90	5.0 ± 0.6	0.022 ± 0.005

[a] Denotes measurements performed in fluorescence mode.

Our group has used several techniques to study one set of titania−silica xerogel samples. X-ray[15] and neutron diffraction[16] confirmed Ti substitution for unheated samples with $x \leq 0.18$. ^{29}Si NMR spectroscopy[17] showed an average of ∼0.8 nonbridging oxygens per Si in unheated samples. ^{17}O NMR spectroscopy[17] showed the presence of Ti−O−Si bonds for samples with $x \leq 0.18$, and O−Ti$_n$ bonds for $x = 0.41$. EXAFS[18] results were consistent with a predominance of $^{[4]}$Ti for samples with $x = 0.08$, and $^{[6]}$Ti for $x = 0.41$, after heat treatment at 750 °C (see Table 1). The results for unheated samples with $x = 0.18$ were similar to those for $x = 0.41$, but after heat treatment were similar to those for $x = 0.08$. This interesting observation was supported by a preliminary XANES study.[18]

Here we report the results of a XANES study of xerogels with similar preparation to those previously studied by our group, and also with a modified preparation involving acetylacetone. Following the approach of Farges et al.,[4] and using results from previous studies of titania−silica materials, we have been able to obtain quantitative information about Ti coordination in titania−silica xerogels, which provide a clear picture of changing Ti coordination due to composition and heat treatment. We consider the implications of this work for interpretation of EXAFS results, and for previous XANES studies of xerogels and zeolites containing Ti. XANES was first used to study titania−silica glass by Sandstrom et al.,[19] and we refer to their subsequent work[9] below.

2. Methods

2.1. Sample Preparation. Our samples were prepared using the sol−gel process with precursors of tetraethoxyorthosilicate, TEOS (Aldrich 98%), and titanium isopropoxide, Ti(i-PrO)$_4$ (Aldrich 97%). The method of Yoldas[20] was used to encourage homogeneity. Before mixing with the Ti alkoxide, the TEOS was prehydrolyzed for 2 h using TEOS/IPA/H$_2$O in a 1:1:1 ratio (where IPA is isopropyl alcohol), in the presence of an acid catalyst (pH of 1). Ti(i-PrO)$_4$ and water were then added, such that the ratio of water to alkoxide equals 2. With this ratio, complete hydrolysis can only occur by utilizing water released from initial condensation. The mixtures were stirred while gelling and typical times to gelation were ∼100 h. Further samples were prepared using a Ti alkoxide with some ligands of acetylacetone, acac (Fluka 99.5%), i.e., Ti(i-PrO)$_2$(acac)$_2$. This was made by slowly stirring acac and Ti(i-PrO)$_4$ in the ratio 2:1.

The resulting gels were dried under vacuum to produce xerogels. The xerogel samples were subjected to different heat treatments, consisting of heating at 5 °C/min followed by 2 h at constant temperature. The samples have been labeled according to their composition x, preparation method, and heat treatment. For example, the xerogel sample with $x = 0.18$ prepared using acac and heat treated at 750 °C is referred to as “18acac750”. We also examined reference compounds of anatase (Aldrich 99.9%), rutile (anatase heated to 1000 °C), ZrTiO$_4$,[21] Na$_2$TiSiO$_5$,[22] and Ba$_2$TiO$_4$[23] (solid-state reaction of oxides heated to 1000 °C). The structures of these samples were checked using X-ray diffraction (the ZrTiO$_4$ was found to contain a small amount of rutile).

2.2. Experimental Section. The XANES experiments were carried out on station 8.1 of the SRS, Daresbury Laboratory, U.K. Suitable XANES samples were prepared from powders diluted with BN. Spectra were collected at the Ti K-edge, at 4966 eV,[24] at room temperature. We used a Si (111) monochromator with a harmonic rejection rate of 50%, and a resolution of approximately 1 eV[25] (the lifetime broadening at the Ti K-edge is 0.8 eV[4]). Ion chambers before and after the sample were used to measure the incident and transmitted beam intensities, I_0 and I_t, respectively. Absorption was measured in the near-edge region, from 10 eV below to 30 eV above the edge, with intervals 0.1 eV. The XANES spectra were processed in the usual way[26] to obtain the absorbance, $\mu t = \ln(I_t/I_0)$, and then pre- and postedge backgrounds were fitted to obtain normalized absorbance, $\chi(E) = (\mu t(E)\text{-}\mu t_{\text{pre}})/(\mu t_{\text{post}} - \mu t_{\text{pre}})$, as shown in Figures 1 and 2.

We have interpreted the Ti K-edge XANES data using a method that is based on accurate calibration of the energy scale. This was done by placing a Ti foil after the transmission ion chamber, and placing a third ion chamber after the Ti foil. The absorption through a Ti metal foil was therefore measured simultaneously with the measurement associated with the xerogel samples. Despite its importance, details of energy calibration are often not reported (see Table 2). The monochromator drifted by approximately 0.1 eV between each sample change, which is not negligible in this context.

2.3. Data Analysis. We refer the reader to Bianconi[26] for general information about the XANES technique.

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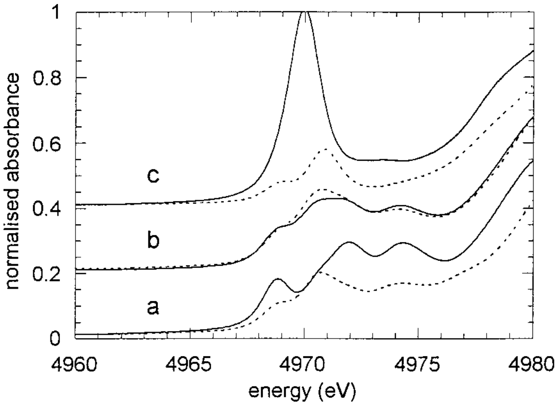

Figure 1. Preedge features in XANES spectra of (a) 6-fold-coordinated reference compounds $ZrTiO_4$ (dotted) and anatase (solid), and xerogel samples; (b) 75IPA120 (dotted), 75IPA500 (solid); and (c) 18acac0 (dotted), and 18acac750 (solid).

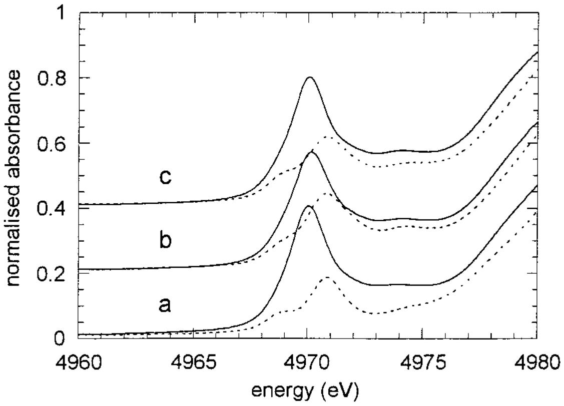

Figure 2. Preedge features in XANES spectra of xerogel samples (a) 30acac0 (dotted), 30acac750 (solid); (b) 30IPA0 (dotted), 30IPA750 (solid); and (c) simulated XANES spectra for 50/50 mixtures of 18acac0 and 75IPA120 (dotted), and 18acac750 and 75IPA500 (solid).

Table 2. Studies of Reference Compounds, Titania–Silica Glasses, and Zeolites Containing Ti Which Report Preedge Peak Position and Height, and Details of Energy Calibration

author	ref	standard for energy (eV) (±0.1)	correction to energy (eV)	energy calibration
Farges	4	$BaTiO_4 = +3.4$ to $+3.5$	none	Ti metal foil
Greegor	9	$BaTiO_4 = +3.4$	none	no details
Behrens	30	$BaTiO_4 = -4.5$ and Ramsayite $= -3.0$	+8.0	no details
Lopez	31	$BaTiO_4 = +3.5$	none	no details
Bordiga	32	first maximum of Ti foil	+0.95	no details
Blasco	35	Ramsayite $= +4.8$	+0.2	no details

The work of Waychunas[27] and Farges et al.[4] has demonstrated that the preedge peak which occurs at the Ti K-edge gives information about Ti coordination. In brief, a preedge peak occurs due to *pd* mixing.[28] The dominant preedge peak is assigned to T_{2g} states.[29] Its intensity decreases, and energy increases, as the degree of centrosymmetry increases. In octahedral coordination, there is sometimes a second peak at higher energy which is assigned to E_g states, and a shoulder at lower energy, the origin of which is unclear.

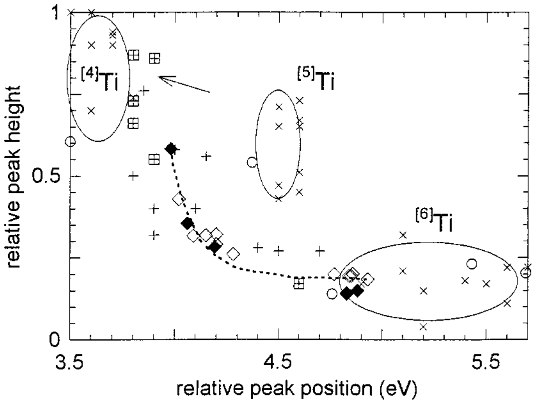

Figure 3. Position and height of preedge peak in minerals[4] (×), zeolites containing Ti[30–32,35] (+), silica–titania glasses[9] (squares), reference compounds in this study (circles), and xerogels (empty and solid diamonds for IPA and acac respectively). Ellipses are a guide to the eye. Arrow indicates (pure) TiO_2-SiO_2 reference compounds containing $^{[4]}$Ti.[9,32] Dotted line represents results for simulated XANES spectra of xerogels with mixtures of $^{[4]}$Ti and $^{[6]}$Ti.

Farges et al.[4] made an extensive study of minerals containing Ti, and their results, reproduced in Figure 3, show that $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti are distinguishable according to the position and height of the preedge peak. The most variation occurs for reference compounds with $^{[6]}$Ti, which can be subdivided into those with distorted and regular octahedra[27,30] (with lower and higher preedge peak energies, respectively). The XANES of a xerogel will be the same as a concentration-weighted average of the XANES for each of the Ti coordinations present in the xerogel (as characterized in the reference compounds). This is the basis of a XANES study by Farges et al.[5] of Ti coordination in alkali silicate glasses, the results of which were in agreement with those from an EXAFS study.

Following the method of Farges et al.,[4] quantitative information was extracted from the XANES spectra by least-squares fitting in the interval from 4900 to 4980 eV. The fitting uses Lorentzian peak shapes to reflect the lifetime broadening of excited states. A single Lorentzian was used to model the dominant preedge peak, i.e., the feature of interest, and additional Lorentzians were used to model the beginning of the main edge step, and any remaining preedge features. The latter were <10% of the size of the dominant preedge peak (except for samples with $x \geq 0.75$). The results we report have an uncertainty of 0.06 eV in energy and 0.01 in height (normalized absorbance). The uncertainty in energy is the sum in quadrature of 0.04 eV uncertainty in calibration of the absorption edge for Ti metal foil, and 0.04 eV uncertainty in peak fitting of the preedge peaks for samples.

We stress that results of peak position are only acceptable when reported relative to a directly measured reference sample. We adopt the most common convention of reporting the sample preedge peak positions relative to the midpoint of the first inflection of the Ti metal K-edge. The absolute energy attributed to this point varies in the literature[4,9] but is not important when reporting relative positions. Relative positions

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determined using other reference compounds can only be compared with those using Ti metal if the correct preedge peak positions are assigned to the reference compounds. The most common of these is Ba_2TiO_4 at 3.4 to 3.5 eV.[4,6,9,31]

The measured height of sharp preedge peaks can depend on the monochromator used. As this is usually not reported, the values of preedge peak heights are generally not comparable between different studies. In addition, heights obtained by peak fitting are lower than heights measured directly from the XANES spectra (without peak fitting). This is because the preedge peak is overlapped by a background due to the other components of the near-edge structure.

3. Results

3.1. Reference Samples. Titania−silica xerogels do not contain additional cations, so it is important to consider pure titania−silica reference materials. Two such materials are titania−silica glass prepared by flame hydrolysis[9] and zeolites containing Ti,[32] which EXAFS studies showed to contain predominantly $^{[4]}$Ti. Figure 3 shows that these samples have preedge peaks with significantly higher energies than those of $^{[4]}$Ti in minerals which contain additional cations. (The heights cannot be compared without further details.)

Figure 3 shows our results for reference compounds. These are Ba_2TiO_4, Na_2TiSiO_5, $ZrTiO_4$, rutile, and anatase, in order of increasing energy of the preedge peak. Our heights are lower than those of Farges et al. because we used a monochromator with lower resolution than theirs. The positions for Ba_2TiO_4 and Na_2TiSiO_5 are in good agreement with those of Farges et al.[4] Our values for rutile and anatase are 5.4 and 5.7 eV, whereas Farges et al. report 5.6 and 5.5 eV, respectively. In the literature there is some confusion over the relative positions of these preedge peaks.[4,9,28,30] There is a significant difference between the preedge peak position of $ZrTiO_4$ reported here, 4.76 eV, and that reported by Farges et al., 5.1 eV. The reason for this is not clear, but it may be related to the presence of an order−disorder transition in $ZrTiO_4$ which is known to depend on preparation conditions.[33] The characterization of preedge peaks may be less precise for $^{[6]}$Ti because the preedge peaks are smaller.

3.2. Xerogel Samples. Figures 1 and 2 show representative XANES spectra for our xerogel samples. The sample 75IPA500 contains phase-segregated $^{[6]}$Ti in the form of anatase. As shown in Figure 1, the XANES spectra is slightly different to that for anatase, possibly due to the small crystal size of ∼5 nm (from X-ray diffraction). A different XANES spectra is seen for sample 75IPA120, which we expect to contain amorphous, pre-anatase, phase-segregated $^{[6]}$Ti.[17] There is a large change in preedge features between samples 18acac0 and 18acac750, before and after heat treatment, respectively. Figure 2 shows that the unheated xerogels are different depending on whether acac was used. The spectra for sample 30acac0 is similar to that for sample 18acac0, whereas the spectra for sample 30IPA0 intermediate between that for samples 18acac0 and 75IPA120. However, heat treatment causes the spectra for samples 30acac750 and 30IPA750 to become more similar.

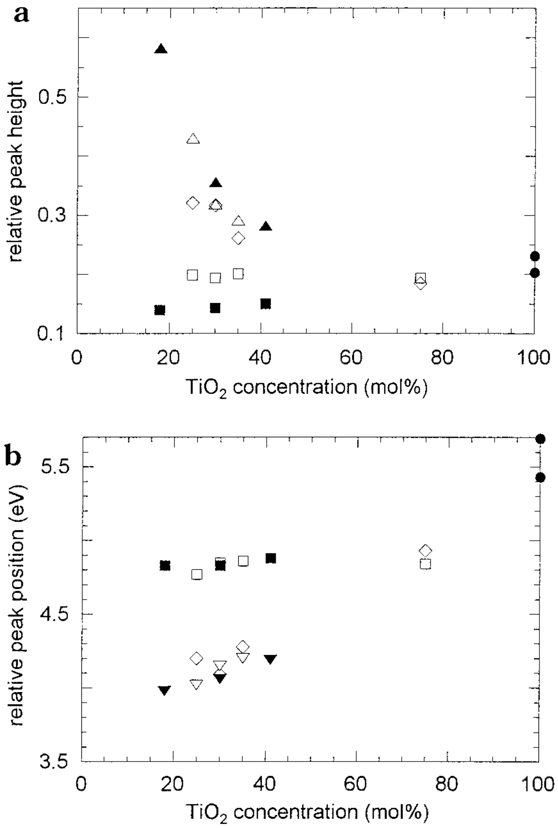

Figure 4. (a) Height and (b) position of preedge peak in xerogel samples prepared with acac (solid symbols) and IPA (empty symbols) with different heat treatments (none, squares; 500 °C, diamonds; 750 °C, triangles) and anatase and rutile (circles).

The positions and heights of preedge peaks in the xerogel samples are presented in Figures 3 and 4. The xerogel samples with higher peak energies have smaller peak heights and are close to those for $ZrTiO_4$, i.e., a distorted $^{[6]}$Ti coordination. This includes all of the unheated samples. Conversely, the heat-treated xerogel samples have significantly greater preedge peak heights and lower peak energies. These features were strongest for sample 18acac750, which has preedge peak energy similar to those for (pure) titania−silica reference materials containing only $^{[4]}$Ti, and height similar to that for Ba_2TiO_4. Figure 4 shows that the effect of heat treatment is to reduce the average Ti coordination, approximately in inverse proportion to TiO_2 content (with the exception of $x = 0.75$). It also clearly shows a difference between samples made with and without acac.

The dominant preedge peaks are characterized by their position and height, and also by their area and width. These are not independent parameters, and in common with Farges et al.[4] we present heights. The intensity or area of the preedge peak depends on the Ti coordination. For $^{[4]}$Ti, $^{[5]}$Ti, and $^{[6]}$Ti respectively, Farges et al. found areas to be roughly proportional to height,

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i.e., areas of 1.0−1.2, 0.8, and 0.1−0.6, whereas widths varied less than heights or areas, i.e., fwhms of 0.8−0.9 eV, 0.8−1.1 eV, and 1.3−1.4 eV. We observed the same trends, with areas of 0.4−0.8 and 0.9−1.5, and fwhm's of 1.9−2.7 eV and 1.6−2.2 eV for unheated and heat-treated xerogel samples, respectively (where fwhm are obtained by peak fitting of the dominant preedge peak). Note that the variation in results we observed for unheated xerogels represents distinct differences between those made with and without acac.

4. Discussion

4.1. Samples with $x = 0.18$. The results for sample 18acac750 are in good correspondence with those for reference materials with [4]Ti in a silica matrix, and the preedge peak height is similar to that for Ba_2TiO_4. On this basis we consider sample 18acac750 to contain a majority of Ti present as [4]Ti. Greegor et al. studied titania−silica glasses prepared by flame hydrolysis, and found that the proportion of [4]Ti decreases from 100% to 70% with an increase from $x = 0.08$ to 0.14. The limit for metastable Ti substitution for Si has been estimated as $x = 0.13$.[8] Hence, we estimate that for sample 18acac750 the proportion of Ti present as [4]Ti is 60−80%, which corresponds to 11−14 mol %.

The XANES spectra for sample 18acac0 is similar to those for reference compounds with highly distorted octahedral coordination, such as ramsayite,[30] and the peak heights and positions are consistent with [6]Ti and not [4]Ti. This is somewhat surprising, given that the majority of the Ti is present as [4]Ti after heat treatment (i.e., sample 18acac750). Hence the [6]Ti present in sample 18acac0 must be isolated rather than phase-segregated. This could explain why it is more distorted than the [6]Ti in sample 75IPA120. We consider the following alternative explanations to be unlikely: (i) [6]Ti is initially phase-segregated but changes into [4]Ti, or (ii) the XANES results actually represent [4]Ti.

This is the first time that the changes in the coordination of isolated Ti have been unambiguously described. However, the proposition of an isolated, distorted [6]Ti coordination in a pure titania−silica material is not unprecedented. In their XANES study of zeolites containing Ti,[30] Behrens et al. reported that Ti substitutes for Si but is present as isolated, distorted [6]Ti similar to that in ramsayite (which has four bond lengths in range 1.82−1.96 Å and two in the range 2.14−2.18 Å). They propose Ti has four shorter Ti−O bonds to bridging oxygens (bonded to Si), and two longer Ti−O bonds to hydroxyl or silanol groups. We consider hydroxyl groups to be the most likely in xerogels, especially those prepared without acac. This is a matter for further investigation, requiring a structural technique capable of distinguishing mixed ligand groups. We doubt that EXAFS has the necessary sensitivity. Although IR is in principle sensitive to Ti−O−Si and Ti−O−H groups, the latter are obscured by overlap with deformation modes of SiO_2.

4.2. Samples with Intermediate TiO_2 Content. As discussed above, the results for samples 75IPA120 and 18acac0 represent amorphous, pre-anatase and isolated, distorted [6]Ti, respectively. It is reasonable to expect that sample 30IPA0 contains a mixture of the two kinds of [6]Ti. Indeed, Figure 2 shows the observed XANES spectra for sample 30IPA0 is similar to a 50/50 mixture of those for samples 18acac0 and 75IPA120. However, the results for sample 30acac0 show greater similarity to those for sample 18acac0, and the observed XANES spectra is similar to a 90/10 mixture of those for samples 18acac0 and 75IPA120 (respectively). This could imply that the use of acac has produced a larger proportion of isolated, distorted [6]Ti. However, the necessary concentration, ~27 mol %, is much greater than previously observed limits of Ti substitution for Si. Alternatively, some of the additional distorted [6]Ti may represent a second form of phase-segregated Ti, which is initially different to the amorphous, pre-anatase form (i.e., sample 75IPA120). This is an issue which warrants further investigation.

Table 3. Estimated Proportions of [4]Ti in Heat-Treated Samples

TiO_2 content (mol %)	prep.	proportion of 18acac (%) (±5)		[4]Ti relative to	
		unheated[a]	750 °C[b]	Ti+Si (%)	[4]Ti+Si (%)
18	acac	100	100	10.8−14.4	11.6−15.0
30	acac	90	50	9.0−12.0	11.4−14.6
41	acac	70	35	8.6−11.5	12.7−16.2
25	IPA	55	65	9.8−13.0	11.5−14.8
30	IPA	50	45	8.1−10.8	10.4−13.3
35	IPA	40	35	7.4−9.8	10.3−13.1

[a] By direct comparison with simulated XANES spectra for mixtures of samples 18acac0 and 75IPA120. [b] By comparison of peak-fitting results for simulated XANES spectra for mixtures of samples 18acac750 and 75IPA500.

The unheated samples with $x \leq 0.41$ contain a mixture of both isolated, distorted [6]Ti and phase-segregated [6]Ti, and heat treatment causes the average coordination to decrease toward 4-fold. It seems clear that heat treatment must convert isolated, distorted [6]Ti into [4]Ti, so that heat-treated samples contain a mixture of [4]Ti and phase-segregated [6]Ti. These coordinations are represented by the results for samples 18acac750 and 75IPA500. Indeed, Figure 2 shows that the XANES spectra for sample 30IPA750 is very similar to a 50/50 mixture of those for samples 18acac750 and 75IPA500 (note this a very similar mixture to that for the unheated samples). Hence we estimate that sample 30IPA750 has approximately 30−40% of Ti present as [4]Ti.

A more quantitative interpretation of the effect of heat treatment at 750 °C is possible by comparing the results for heated xerogel samples with those obtained from simulated XANES spectra representing different mixtures of [4]Ti (i.e., sample 18acac750) and phase-segregated [6]Ti (i.e., sample 75IPA500). The preedge peak positions and heights for simulated spectra were obtained using the same fitting procedures as for the experimental spectra. The results for simulated mixtures of [4]Ti and [6]Ti are shown in Figure 3. Table 3 shows the estimated proportions of [4]Ti, denoted y, and the proportions of Ti substitution for Si, i.e., $xy/(1 - x + xy)$. The latter quantity is in the range 11.4−16.2 mol % for xerogels prepared with acac, which is similar to the range reported for metastable titania−silica glasses.[8] The range is only slightly lower for xerogels prepared without acac.

The results for xerogel samples show a predominance of [4]Ti and [6]Ti, and by comparison with the results for

Na_2TiSiO_5, we can exclude the possibility of a majority of $^{[5]}$Ti in any of the samples. Farges et al.[8] have shown that mixtures of $^{[4]}$Ti and $^{[5]}$Ti, or mixtures of $^{[5]}$Ti and $^{[6]}$Ti, are distinguishable from mixtures of $^{[4]}$Ti and $^{[6]}$Ti, and our results are clearly consistent with the latter. We suggest that $^{[5]}$Ti is less likely to occur in a pure titanium silicon oxide material because there are no additional cations available to provide charge compensation for the nonbridging oxygen anion in the short Ti−O bond. We also note that conversion of distorted $^{[6]}$Ti such as in ramsayite into $^{[4]}$Ti is most likely to occur by breaking the two long (weak) bonds and contracting the four shorter bonds.

4.3. Other Studies of Ti Coordination in Titania−Silica Oxide Materials. Having demonstrated the effectiveness of the current XANES approach, it is worthwhile to reconsider previous reports of XANES data for titania−silica xerogels. Emili et al.[14] report preedge peak heights (without peak fitting) which show the same trends as seen in this study, but the significance was not discussed. What is most interesting is that the peak heights decreased with heat treatment between 1000 °C and 1200 °C. This implies a reduced concentration limit of Ti substitution for Si at high temperatures. Furthermore, a decrease occurred for a sample with only $x = 0.077$, which implies a inhomogeneous distribution of $^{[4]}$Ti in their samples.

It is also worth reconsidering EXAFS results, keeping in mind that xerogel samples will commonly contain a mixture of $^{[4]}$Ti, isolated $^{[6]}$Ti, and phase-segregated $^{[6]}$Ti. Furthermore, distorted $^{[6]}$Ti has an asymmetric distribution of bond lengths,[4] which may give shorter mean bond length than expected (while there is little variation in the mean bond length for $^{[4]}$Ti[4,23,34]). This situation complicates the interpretation of EXAFS bond lengths and coordination numbers obtained by fitting a single Ti−O shell. However, the mean(s) should decrease as the proportion of $^{[4]}$Ti increases with heat treatment. This was observed in our previous EXAFS study[18] for samples with $x = 0.18$ (see Table 1). In addition, the results showed an increase in average Ti−O bond length with heat treatment for samples with $x = 0.41$, which is consistent with reduced distortion in phase-segregated $^{[6]}$Ti as anatase is crystallized.

The results of the present work are also relevant to studies of zeolites containing Ti substituted for Si. In fact, Ti K-edge XANES have been reported as part of EXAFS studies for several such zeolites.[30,31,32,35] On the basis of the EXAFS results, the Ti sites were concluded to be entirely $^{[4]}$Ti, mostly $^{[4]}$Ti or mostly isolated $^{[6]}$Ti, depending on the sample, preparation, and heat treatment. Unfortunately, the studies used different monochromators, the peak heights were measured without peak fitting, and the energy calibration was not reported (as shown in Table 2). Despite these limitations, we show the XANES data in Figure 3. The zeolite results are in qualitative agreement with the simulated results for mixtures of $^{[4]}$Ti and $^{[6]}$Ti. (In only one case was $^{[5]}$Ti reported as dominant, due to the mistaken assignment of a preedge peak position of 4.0 eV to $^{[5]}$Ti when it actually corresponds to $^{[4]}$Ti.[35]) A careful application of the current technique to zeolites may yield more precise information about Ti coordination.

We have shown that the method of Farges et al.[4] is effective in examining Ti coordination in titania−silica xerogels and that at least three different Ti coordinations exist in these materials, i.e., $^{[4]}$Ti and isolated, distorted $^{[6]}$Ti and phase-segregated $^{[6]}$Ti, depending on composition, preparation, and heat treatment. These results are important for studies which attempt to relate the properties of xerogels to the Ti coordination, such as studies of catalytic properties (ref 2). For example, Imamura et al.[36] propose that epoxidation of alkenes occurs due to the presence of $^{[4]}$Ti which act as Lewis acid sites. They show a correlation between the estimated number of Lewis acid sites and the XANES preedge peak height (obtained without peak fitting). The method presented here is promising for obtaining more information about Ti coordination in relation to catalytic properties.

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