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A structural study of $(TiO_2)_x(SiO_2)_{1-x}$ ($x=0.18$, 0.30 and 0.41) xerogels prepared using acetylacetone

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A combination of ^{29}Si and ^{17}O MAS NMR, EXAFS and FTIR spectroscopy have been used to study the atomic structure of $(TiO_2)_x(SiO_2)_{1-x}$ ($x=0.18$, 0.30 and 0.41) xerogels prepared using an acetylacetone stabilised $Ti(OPr^i)_4$ precursor. In the as-prepared materials, Ti is present in a distorted octahedral coordination with a significant proportion still complexed by acetylacetone. For the first time in such an amorphous solid, a ^{17}O NMR resonance has been observed at 110 ppm which is attributed to $(O_5)Ti–O–Si$ groups. Heat treatment of these xerogels tends to convert TiO_6 into TiO_4 where the Ti is substituted into the silica network. Our results are in accord with previous work which suggests that the upper limit for solubility of TiO_2 in SiO_2 is *ca.* 15 mol%. Clear evidence of some phase separation in the $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample after heat treatment to 750 °C is presented, although the ^{17}O MAS NMR results show that the use of acetylacetone significantly increases the amount of Ti–O–Si bonding at this composition compared to samples prepared without it.

Introduction

Titania–silica mixed oxide materials, $(TiO_2)_x(SiO_2)_{1-x}$, are of significant technological importance. Silica glasses with a few mol% TiO_2 exhibit ultra-low thermal expansion[1] and mixed silicon–titanium oxides are important as catalysts and catalytic support materials.[2] In the optical industry, they can be produced as anti-reflective thin films with tailored refractive indices.[3] The properties of titania–silica binaries are strongly dependent on their chemical composition, homogeneity, and texture which in turn depend on synthesis conditions. Homogeneity at the atomic level is especially important. Sol–gel synthesis, based on the hydrolysis and subsequent condensation of metal alkoxide precursors, provides a low temperature route to materials with a high level of atomic mixing and a high degree of porosity.[1] When the sol–gel route is used to prepare $(TiO_2)_x(SiO_2)_{1-x}$ materials, the different rates of hydrolysis of the silicon and titanium alkoxides can cause phase separation, producing Ti- and Si-rich regions, which reduces the usefulness of the material.

In our previous work, the above problem has been circumvented by using the method of Yoldas[4] which involves partially hydrolysing the Si alkoxide prior to mixing it with the Ti alkoxide. Solid state ^{17}O and ^{29}Si magic angle spinning (MAS) NMR spectroscopy has been applied to the study of the atomic level structure of two mixed Ti–Si oxides prepared this way.[5] The ^{17}O NMR revealed directly phase separation in high titanium samples, $(TiO_2)_{0.41}(SiO_2)_{0.59}$ calcined at various temperatures, through the presence of signals for OTi_3 and OTi_4 sites. This phase separation became more apparent with increasing temperature of the heat treatment. The results for a much lower titanium sample, $(TiO_2)_{0.07}(SiO_2)_{0.93}$, indicated atomic mixing of titania and silica by the presence of a signal for Ti–O–Si linkages and the absence of Ti–O–Ti bonds. This sample remained atomically homogeneous after heating to 600 °C. An extended X-ray absorption fine structure (EXAFS) study on samples prepared the same way produced similar results.[6] The Ti–O distances of *ca.* 1.82 Å and coordination numbers of *ca.* four derived from this study for $(TiO_2)_{0.08}(SiO_2)_{0.92}$ samples, preheated to various temperatures, were consistent with titanium occupying tetrahedral sites within the silica network and showed the samples to be atomically mixed. These structural results are consistent with those from the industrial catalyst TS-1 (a zeolite from the pentasil family containing a few mol% Ti) in which titanium is known to directly substitute for Si atoms in tetrahedral sites.[7] The EXAFS derived structural parameters from $(TiO_2)_{0.41}(SiO_2)_{0.59}$ samples were very different.[6] The Ti–O bond distances of *ca.* 1.90 Å and coordination numbers of *ca.* 5.5 were significantly higher than for the low titanium sample. These parameters were much closer to those expected for pure TiO_2 (anatase or rutile), which has an average Ti–O distance of 1.95 Å and coordination number of six,[8] and indicated a high degree of phase separation in samples of this composition. Samples of composition $(TiO_2)_{0.18}(SiO_2)_{0.82}$ were also studied. Interestingly, the unheated xerogel of this composition contained mostly octahedrally coordinated Ti which, with heat treatment up to 750 °C, converted to predominantly tetrahedral coordination.

In this study, the effect of modifying the Ti alkoxide used in the synthesis of the $(TiO_2)_x(SiO_2)_{1-x}$ materials is investigated. Titanium isopropoxide is reacted with acetylacetone in order to produce a less reactive precursor which is in turn reacted with a prehydrolysed solution of tetraethyl orthosilicate (TEOS).[9] The resulting samples are heat treated and studied using ^{29}Si and ^{17}O MAS NMR, EXAFS and Fourier transform infrared spectroscopy (FTIR).

Experimental

Sample preparation

Samples were prepared using the following precursors: tetraethyl orthosilicate (TEOS, Aldrich, 98%), titanium(IV) isopropoxide ($Ti(OPr^i)_4$, Aldrich, 97%) and acetylacetone (acac, Fluka, 99.5%). HCl was used as a catalyst to promote the hydrolysis and condensation reactions and isopropyl alcohol (IPA, Fluka, 99.5%) was used as a mutual solvent. All reagents were loaded in a dry box and transferred using syringes to avoid absorption of moisture from the atmosphere. The dry box used was a single port type, connected to a vacuum pump and a cylinder of dry nitrogen. The alkoxide precursors were checked for hydrolysis using FTIR spectroscopy.

As mentioned previously, the first stage of the synthesis involved stabilising the $Ti(OPr^i)_4$ by reacting it with acetylacetone. $Ti(OPr^i)_4$ was slowly added to 2 mol equivalents of acac while stirring. After the evolution of heat had ceased and the resulting solution had cooled, the formation of the Ti–acac complex, $Ti(acac)_2(OPr^i)_2$, was confirmed using FTIR.[10] The Ti–acac complex was then mixed with a prehydrolysed solution of TEOS.[4] The chosen prehydrolysis conditions were TEOS : IPA : H_2O in a 1 : 1 : 1 molar ratio in the presence of HCl (pH 1), stirring for 2 h. The resulting sol was stirred for a few min before water was added slowly such that the overall water : alkoxide molar ratio (R) was 2. Stirring was continued until the sol had gelled which typically took a few days depending on composition. Samples for ^{17}O MAS NMR were prepared using 20 mol% ^{17}O water (D-chem) in the hydrolysis.

All samples were air-dried for several days, finely ground and then pumped under vacuum for 24 h to remove any excess solvent. Heat treatments were performed at a heating rate of 5 °C min^{-1} and each temperature maintained for 2 h. Samples were prepared with nominal compositions of $(TiO_2)_x(SiO_2)_{1-x}$ (x=0.18, 0.30 and 0.41). Each sample was heated to 750 °C. Samples enriched with ^{17}O were prepared for the compositions x=0.18 and 0.41.

FTIR spectroscopy

IR spectra were recorded in diffuse reflectance mode on a Biorad FTS175C spectrometer controlled by Win-IR software. Samples were diluted (1 : 10 by weight) in dry KBr and scanned in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was the result of summing 64 scans.

MAS NMR

The MAS NMR spectra were acquired on a Chemagnetics CMX300 Infinity spectrometer. The ^{29}Si spectra were collected at 59.6 MHz using MAS at typically 6 kHz with a 2.0 μs (*ca.* 30° tip angle) pulse and a 20 s recycle delay. A 7.5 mm Chemagnetics double-bearing probe was used. The pulse delay was sufficient to prevent saturation. The spectra were referenced externally to Zeolite A (−89.7 ppm). Each spectrum was the result of summing *ca.* 3000 scans.

The ^{17}O NMR spectra were collected at 40.7 MHz under MAS at typically 15 kHz with a recycle delay of 1–2.5 s using a Chemagnetics 4 mm double-bearing probe. The delay was sufficient to prevent saturation. A 90°–τ–180° echo sequence was applied with a short τ delay of 71.4 μs to overcome problems of probe ringing, thereby allowing the spectra to be phased correctly. The spectra were referenced externally to H_2O (0 ppm). Typically each spectrum was the result of 50 000–100 000 co-added scans and took *ca.* 24 h to collect.

EXAFS spectroscopy

Ti K-edge EXAFS data were collected in transmission mode on station 8.1 at the Daresbury Laboratory SRS using a Si[111] crystal monochromator and 50% harmonic rejection. Ionisation chambers, filled with a mixture of Ar–He or Kr–He at appropriate partial pressures to optimise detector sensitivities, were placed in the beam path before and after the sample. Finely ground samples were diluted in boron nitride to give a satisfactory edge jump and absorption. Typically, each EXAFS spectrum was the sum of three 45 min scans.

Results and data analysis

FTIR spectroscopy

Fig. 1(a) and (b) show the IR spectra of the $(TiO_2)_x(SiO_2)_{1-x}$ xerogels unheated and after heating to 750 °C, respectively. The peaks in these spectra have been assigned according to the literature. The broad band in the region 3600–3000 cm^{-1} corresponds to the fundamental stretching vibrations of different hydroxy groups.[11] The band at 3590 cm^{-1} is mainly due to stretching vibrations involving Si–OH groups and the band at 3350 cm^{-1} corresponds to adsorbed water. The band at 1610 cm^{-1} is assigned to the H–O–H bending vibration of water. The peaks at 1160, 1070 and 800 cm^{-1} are characteristic of a silica network: the bands at 1160 and 1070 cm^{-1} are ascribed to the LO and TO components of the asymmetric stretch of the SiO_4 unit, respectively, and the feature at 800 cm^{-1} is due to the symmetric stretch of the SiO_4 unit.[12] The shoulder at 980 cm^{-1} is made up of contributions from Si–(OH) stretches and a Si–O–Ti vibration.[13] The sharp bands at 2970, 2930, 1580, 1430, 1360, 1280, 1190, 1020, 930 and 660 cm^{-1} in the room temperature spectra are due to acetylacetone ligands remaining in the samples.[10]

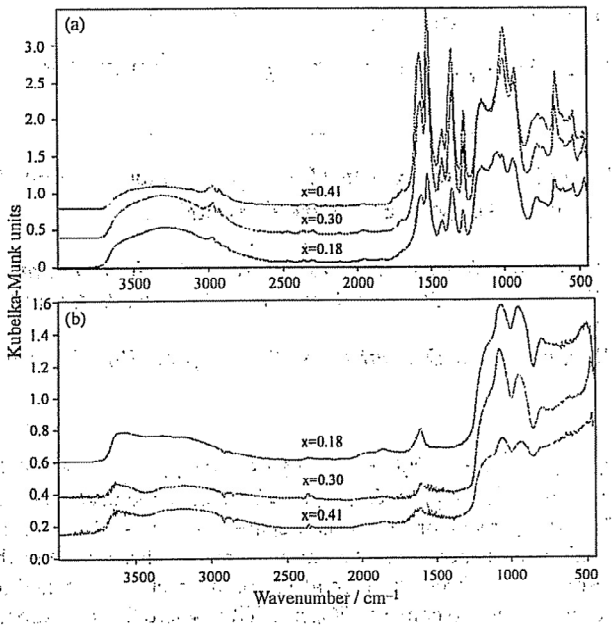

Fig. 1 (a) FTIR spectra of unheated xerogels [x refers to $(TiO_2)_x(SiO_2)_{1-x}$] and (b) FTIR spectra of xerogels heated to 750 °C.

MAS NMR

The ^{29}Si MAS NMR spectra were deconvolved by Gaussian fitting using Spinsight 3.02 software; three signals could be distinguished at −92, −101 and −110 ppm with varying intensities. Each resonance represents a specific degree of Si–O–Si polymerisation. The −92 ppm signal arises from Si sites in a Q^2 configuration, and the −101 and −110 ppm signal arise from Q^3 and Q^4 configurations, respectively (Q^n denotes a SiO_4 unit with n bridging oxygens[14]). The results of the Gaussian fitting are summarised in Table 1. Fig. 2 shows the ^{29}Si NMR data and peak deconvolution for the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample and clearly illustrates a shift to higher average Q species with heat treatment.

The ^{17}O MAS NMR spectra of enriched $(TiO_2)_{0.18}(SiO_2)_{0.82}$ and $(TiO_2)_{0.41}(SiO_2)_{0.59}$ samples are shown in Fig. 3 and 4, respectively. The spectra are dominated by a resonance which peaks at 0 ppm and shows structure at negative shift due to the quadrupole interaction.[15] This resonance has spinning sidebands from the MAS process at −325 and 350 ppm. There is a second distinct resonance at 250 ppm and at the lower temperatures there is clearly intensity between the 0 and 250 ppm peaks. In the unheated samples this shows up as a clear peak at 110 ppm. These signals at 110 and 250 ppm represent oxygens located in Ti–O–Si bridges.[16] By comparison with the ^{17}O signal from Ti–O–Si linkages at 190 ppm in the mineral fresnoite ($Ba_2TiSi_2O_8$)[5] and at 160 ppm in titanite ($CaTiSi_2O_5$);[17] the signals at 110 and 250 ppm have been

Table 1 ^{29}Si NMR data[a] for $(TiO_2)_x(SiO_2)_{1-x}$ samples

		Q^2			Q^3			Q^4		
Sample	Heat treatment (T/°C)	fwhm/Hz	δ(ppm)	I (%)	fwhm/Hz	δ(ppm)	I (%)	fwhm/Hz	δ(ppm)	I (%)
$x=0.18$	None	727	−93.4	16	400	−100.8	30	635	−109.5	54
	750	—	—	—	550	−101.9	7	675	−112.3	93
$x=0.30$	None	465	−93.0	9	425	−101.4	38	600	−110.5	53
	750	—	—	—	740	−101.0	19	715	−110.0	81
$x=0.41$	None	585	−91.4	12	440	−100.3	36	555	−109.6	52
	750	615	−92.1	6	615	−101.6	23	685	−110.5	71

[a]fwhm, δ and I represent the line width, ^{29}Si chemical shift and relative intensity, respectively. Errors: fwhm ±25–50 Hz, δ ±1 ppm, I ±5%.

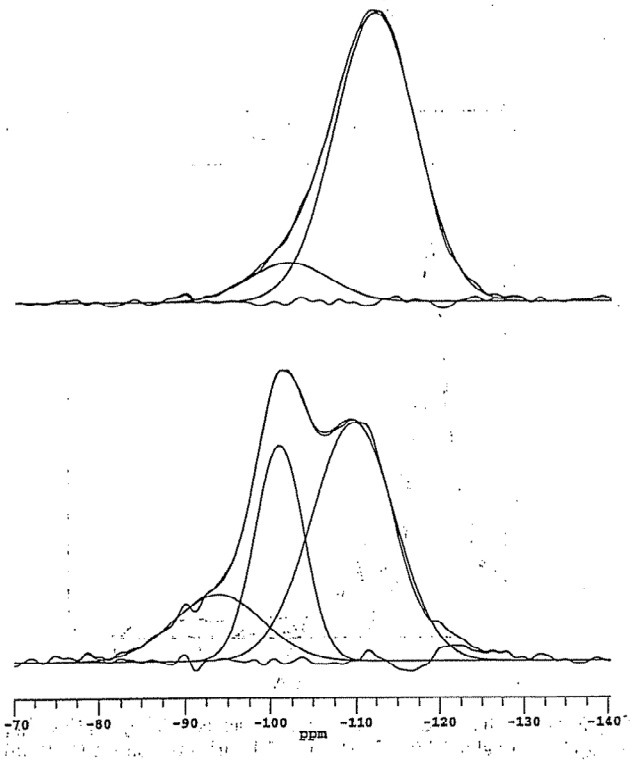

Fig. 2 ^{29}Si MAS NMR spectra with peak deconvolution and curve fitting for a $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample in the unheated xerogel form (bottom) and after heat treatment at 750 °C for 2 h (top).

assigned to Ti–O–Si linkages with Ti coordinated to six and four oxygens, respectively. The Ti atoms are coordinated to five oxygens in fresnoite and to six oxygens in titanite. The trend in ^{17}O chemical shift from 110 to 250 ppm probably corresponds to the Ti–O coordination number changing from six to four. The resonance at 0 ppm is due to Si–O–Si linkages[16] with a contribution from Si–OH groups.[18] The spectrum for the $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample heated to 750 °C exhibits two additional resonances at 360 and 530 ppm. These have been assigned to oxygens in OTi_4 and OTi_3 groups, respectively,[16] and provide evidence of phase separation within this sample.

EXAFS spectroscopy

The equation for the interpretation of EXAFS data is

$$\chi(k)=AFAC\sum_j \frac{N_j}{kR_j^2}|f(\pi, k, R_j)|$$
$$e^{-2R_j/\lambda(k)}\, e^{-2\sigma_j^2k^2}\sin(2kR_j+2\delta(k)+\psi(k, R_j))$$

where $\chi(k)$ is the magnitude of the X-ray absorption fine structure as a function of the photoelectron wave vector k. $AFAC$ is the proportion of electrons that perform an EXAFS-type scatter and has been fixed at 0.8 for this analysis. N_j is the coordination number and R_j is the interatomic distance for the jth shell. $\delta(k)$ and $\psi(k, R_j)$ are the phase shifts experienced by the photoelectron, $f(\pi, k, R_j)$ is the amplitude of the photoelectron backscattering and $\lambda(k)$ is the electron mean free path; these are calculated within EXCURV97.[19] The Debye–Waller factor is $A=2\sigma^2$ in EXCURV97.

The programs EXCALIB, EXBACK and EXCURV97[19] were used to extract the EXAFS signal and analyse the data. Least squares refinements of the structural parameters of our samples were carried out against the k^3 weighted EXAFS signal to minimise the fit index, FI,

$$FI=\sum_i (k^3(\chi_i^T-\chi_i^E))^2$$

where χ_i^T and χ_i^E are the theoretical and experimental EXAFS, respectively. The results of the refinements are reported in

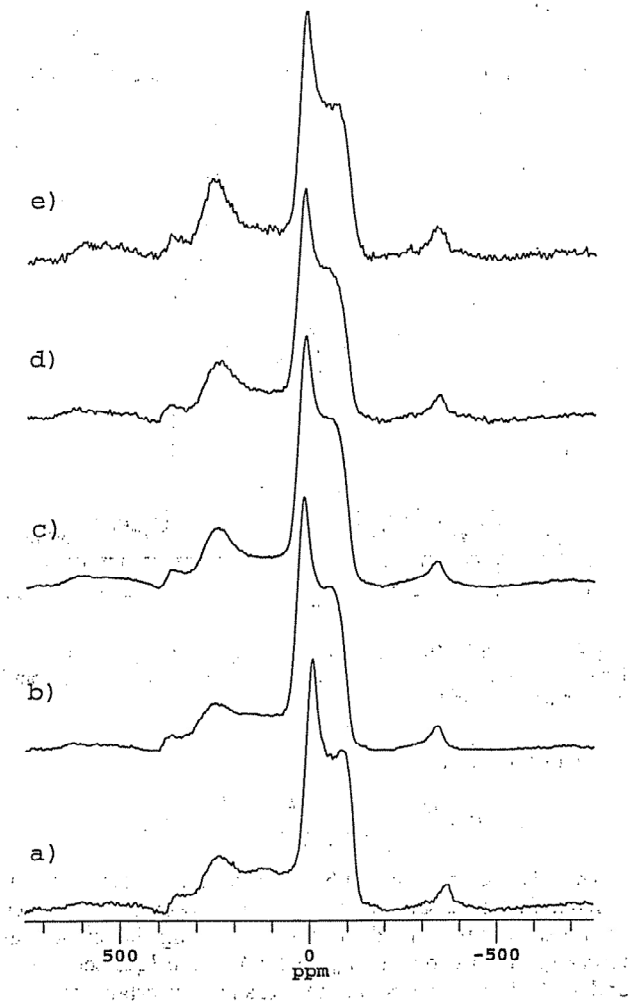

Fig. 3 ^{17}O MAS NMR spectra of a $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample after various heat treatments: (a) no heat treatment, (b) 250 °C, (c) 350 °C, (d) 500 °C and (e) 750 °C (peaks at −325 and 350 ppm are spinning side bands).

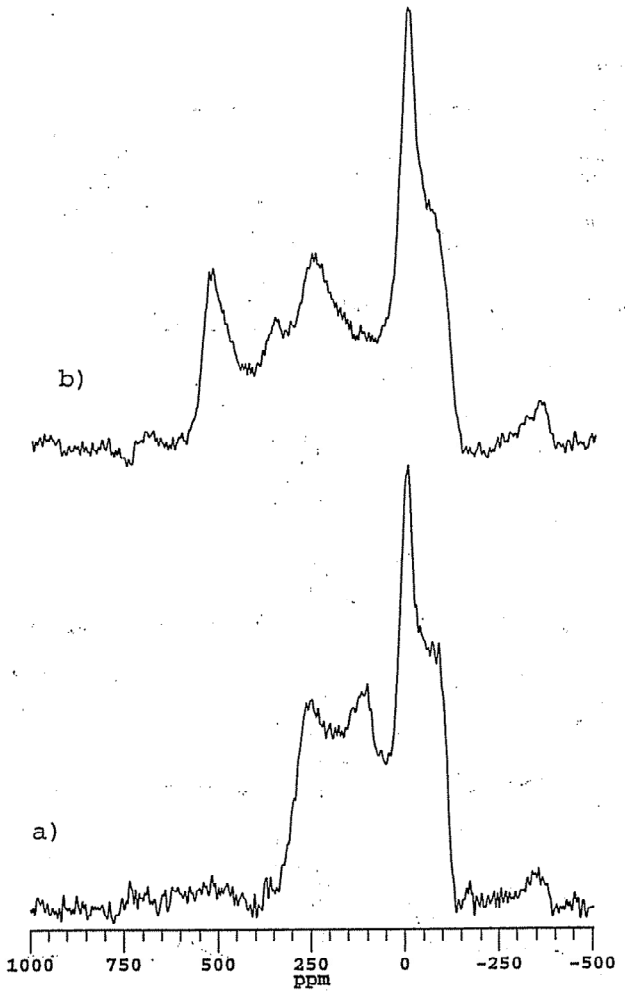

Fig. 4 ^{17}O MAS NMR spectra of a $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample: (a) no heat treatment, (b) after heating to 750 °C (the peak at −325 ppm is a spinning side band).

terms of the discrepancy index,

$$R = \frac{\int|(\chi^T(k) - \chi^E(k))|k^3 dk}{\int|\chi^E(k)|k^3 dk} \times 100\%$$

The Ti K-edge EXAFS derived parameters of our $(TiO_2)_x(SiO_2)_{1-x}$ samples are shown in Table 2. These were obtained by fitting the data in k-space using the single scattering approximation with $k_{min} = 3.0$ Å^{-1} and k_{max} between 10 and 13 Å^{-1}. The errors are the statistical uncertainties calculated by EXCURV97. The overall uncertainties of the structural parameters are likely to be larger due to other sources of inaccuracies such as data collection and background subtraction. Reasonable estimates of the total errors are ±0.02 Å

Table 2 EXAFS derived structural parameters for $(TiO_2)_x(SiO_2)_{1-x}$ sol–gel samples prepared with acetylacetone

Sample	Heat treatment (T/°C)	Shell	N	R/Å	A/Å^2	R (%)
$x=0.18$	None	Ti–O	7.3(4)	1.88(1)	0.039(3)	17.0
		Ti–C	6.1(12)	3.72(2)	0.016(9)	
	750	Ti–O	3.3(2)	1.82(1)	0.009(1)	29.7
$x=0.30$	None	Ti–O	7.0(3)	1.89(1)	0.040(3)	16.1
		Ti–C	6.0(11)	3.73(2)	0.019(9)	
	750	Ti–O	3.2(2)	1.84(1)	0.012(2)	27.0
$x=0.41$	None	Ti–O	7.0(4)	1.91(1)	0.046(4)	17.5
		Ti–C	6.1(17)	3.73(3)	0.037(14)	
	750	Ti–O	5.2(5)	1.86(1)	0.021(3)	29.1
		Ti–Ti	0.9(5)	3.03(2)	0.008(5)	

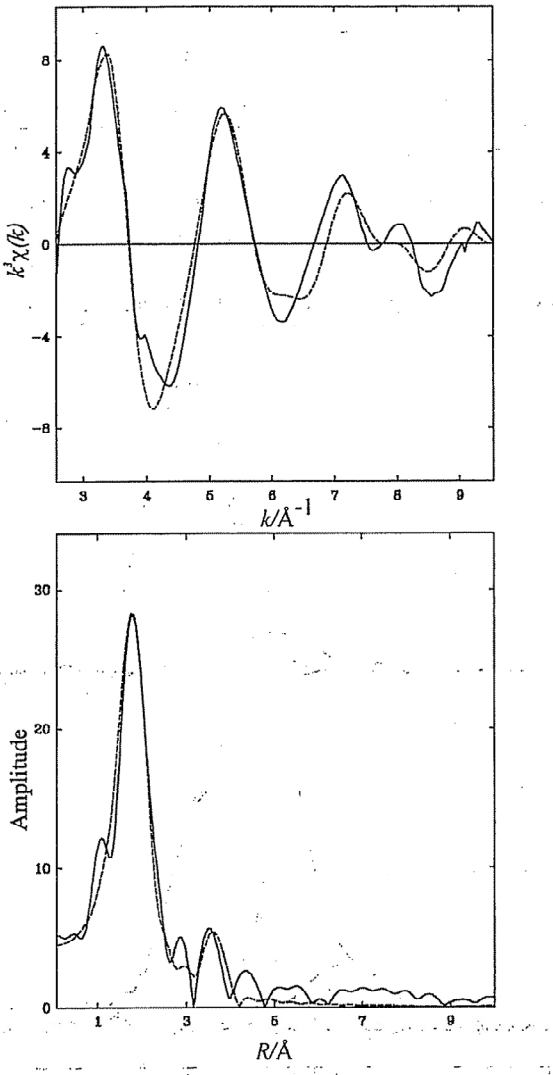

Fig. 5 Ti K-edge EXAFS data for unheated $(TiO_2)_{0.18}(SiO_2)_{0.82}$ xerogel: k^3 weighted EXAFS (top) and Fourier transform (bottom). Experimental data, solid line, and theoretical fit, dotted line.

for nearest neighbour separations and ±20% for nearest neighbour coordination numbers. The levels of uncertainty become greater beyond the nearest neighbour shell. Fig. 5 and 6 show the EXAFS data and their Fourier transforms together with the calculated fits for the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample before heat treatment and after heating to 750 °C. These data illustrate a clear structural change: for the unheated xerogel two peaks, at *ca.* 1.9 and 3.5 Å, can be observed in the Fourier transform, whereas for the heat treated sample only one peak, at *ca.* 1.8 Å is present. Similar behaviour is shown by the results of fitting to the data from the $(TiO_2)_{0.30}(SiO_2)_{0.70}$ and $(TiO_2)_{0.41}(SiO_2)_{0.59}$ samples. The peak at 1.8–1.9 Å can be ascribed to Ti–O bonding whereas the peak at 3.5 Å is due to a Ti–C correlation. The basis for the latter assignment is that the FTIR results show that there are still acac ligands present in the unheated gels, and hence it can be assumed that a significant proportion of Ti remains complexed by acac even after gellation. This assignment is supported by previous work which suggests that the $Ti(acac)_2(OPr^i)_2$ complex hydrolyses rapidly in water to form $Ti(acac)_2(OH)_2$ which in turn reacts with prehydrolysed TEOS.[20] These authors conclude that the acac ligands are stable to hydrolyis and as a consequence formation of Ti–O–Si bridges is favoured over the formation of Ti–O–Ti bonding due to the steric hindrance provided by the large chelated acac ligands. The Ti–O shell for all the unheated xerogels exhibits a large Debye–Waller factor of *ca.* 0.04 Å^2 which reflects the large spread of Ti–O distances

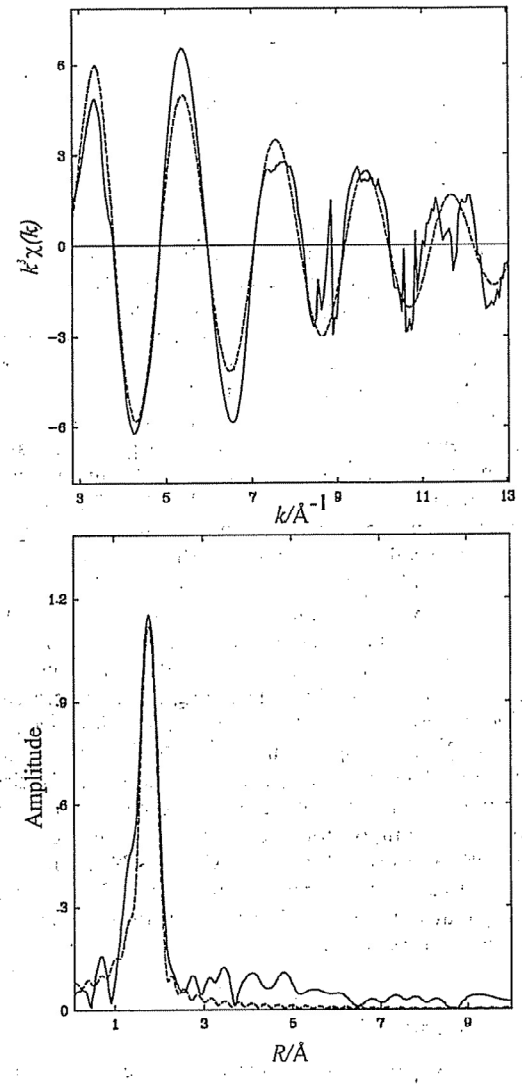

Fig. 6 Ti K-edge EXAFS data for $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample preheated to 750 °C: k^3 weighted EXAFS (top) and Fourier transform (bottom). Experimental data, solid line, and theoretical fit, dotted line.

present: terminal Ti–OR (R = Et or Pr^i) bonds and Ti–(OSi) bridges where the Ti is four coordinated with respect to oxygen have distances *ca.* 1.8 Å, whereas Ti–acac bonds and Ti–(OSi) bridges where the Ti is octahedrally coordinated are closer to 2.0 Å.[21–23] It should be noted that the structural parameters obtained for the Ti–C distances are only rough guides. The atomic arrangement of the chelating acac ligands where the M–O–C angle is close to linear means that the component of the EXAFS signal corresponding to Ti–C correlations also includes multiple scattering contributions.[24] The result is an increase in intensity at *ca.* 3.5 Å in *r*-space for the unheated xerogels. Analysis of the Ti–C correlations including modelling the possible multiple scattering effects is beyond the scope of this paper. For the heat treated samples the situation is much simpler. The $(TiO_2)_{0.18}(SiO_2)_{0.82}$ and $(TiO_2)_{0.30}(SiO_2)_{0.70}$ samples show only one Ti–O correlation at *ca.* 1.83 Å whereas, the $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample also exhibits a Ti–Ti distance at 3.03 Å.

Discussion

The ^{29}Si MAS NMR results for the unheated xerogels all exhibit around 50% Q^2 and Q^3 species which are due to the presence of a high concentration of terminal –OH and –OEt groups bonded to Si and represent incomplete condensation of the network. There may also be a small contribution to the Q^2 and Q^3 species from TiO_6 network modifying groups. The fact that all the unheated xerogels have similar Q distributions illustrates that the Ti content does not have a large effect on the number of non-bridging oxygens at the gel stage. The effect of heat treatment for all three samples is an increase in more polymerised Q^n species as the temperature increases. It is well known that for SiO_2 sol gels heat treatment leads to the loss of organic groups and to further condensation, which strengthens the silica network and eventually leads to the presence of only Q^4 species (*i.e.* virtually all the SiO_4 tetrahedra are connected to four other SiO_4 units). The interesting feature of our results is that for the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample after heat treatment to 750 °C, *ca.* 93% of the silicon is present in Q^4 units. Similar ^{29}Si NMR results were observed for a heat treated $(TiO_2)_{0.08}(SiO_2)_{0.92}$ sample prepared without acac which was known to contain only TiO_4 tetrahedra within the silica network.[5] This implies that virtually all the TiO_2 is dissolving in the silica network in the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample. Previous results by Walther *et al.* on $(TiO_2)_x(SiO_2)_{1-x}$ sol–gels showed the presence of significant percentage of Q^2 and Q^3 species even after heat treatment to 600 °C[25] which indicated that some titanium in their samples was acting as a network modifier, *i.e.* in TiO_6 octahedra. In our case, the $(TiO_2)_{0.30}(SiO_2)_{0.70}$ and $(TiO_2)_{0.41}(SiO_2)_{0.59}$ samples show significant proportions of Q^2 and Q^3 linkages after heat treatment, which suggests that these samples contain network modifying Ti.

The FTIR results illustrate well the change in structure and composition of the sol–gels after heating to 750 °C. The spectra from the unheated xerogels are all dominated by vibrations from hydroxy groups and acac ligands. The acac vibrations are strongest in the $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample simply because this sample contained more of the Ti–acac complex when it was prepared. The presence of a broad band centred at *ca.* 3300 cm^{-1} corresponding to –OH vibrations is consistent with the ^{29}Si MAS NMR results and again reflects incomplete condensation of the gel network. The FTIR spectra from the preheated gels yield more information on the role of titanium in the silica network. The bands involving vibrations of the SiO_2 network, *i.e.* the two components of the SiO_4 asymmetric stretch at 1160 and 1070 cm^{-1} and the symmetric stretch of the same moieties at 800 cm^{-1}, become much stronger and sharper for the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ and $(TiO_2)_{0.30}(SiO_2)_{0.70}$ samples. The reason for this is that increasing the amount of Ti doping has a disruptive effect on the SiO_2 network, thus making the SiO_2 vibrations less well defined. This conclusion is supported by the ^{29}Si NMR results. The band at *ca.* 980 cm^{-1} for the heated samples also becomes much stronger as the amount of Ti is reduced. This peak has contributions from Si–(OH) stretches and from an Si–O–Ti vibration, where the Ti is substituted in the silica network. Since all three samples contain similar amounts of hydroxy groups, it is likely that the increase in intensity of the 980 cm^{-1} band is due to an increase of network substituted Ti. The broad hydroxy band is split into two components in the spectra of the heated samples, indicating that the locations of the hydroxy groups have become better defined. These components correspond to isolated surface Si–OH groups (*ca.* 3600 cm^{-1})[26] and adsorbed water (*ca.* 3350 cm^{-1}).

The Ti K-edge EXAFS derived parameters in Table 2 give insight into the local environment of the titanium atoms in these samples. The results from the three unheated xerogels are all similar: a significant proportion of the Ti is still complexed by acac ligands. The Ti–O coordination numbers of around seven and the large Debye–Waller factor for this shell suggest distorted octahedral geometry. The most likely distortion is two short Ti–(OSi) bonds and four longer Ti–acac bonds. This type of distorted six-fold coordination has recently been observed in similar titania–silica sol–gel samples using XANES (X-ray absorption near edge structure).[27] The XANES study revealed that for samples prepared with acac

most of the Ti had a highly distorted octahedral coordination. Samples prepared without acac were also studied but did not exhibit such distorted coordination. It is after heat treatment that the clearest differences between the samples can be observed. In the case of the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample, the Ti–O bond distance of 1.82 Å and coordination number of 3.3 are consistent with Ti being four coordinated with respect to oxygen and, hence, most of the titanium being substituted in the silica network. The coordination number is a little low but this is most probably due to the EXAFS technique being unable to determine accurate coordination numbers. The relatively low Debye–Waller factor of 0.009 Å^2 is also an indication that nearly all the Ti is located in one environment. The results for the $(TiO_2)_{0.30}(SiO_2)_{0.70}$ sample are similar. The fact that the Ti–O bond distance and Debye–Waller factor are slightly larger indicates that some of the Ti is present as TiO_6, agreeing well with the ^{29}Si NMR results. For the $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample the Ti–O coordination number of 5.2 and bond distance of 1.86 Å are much closer to the values expected for octahedrally coordinated Ti, and suggest the presence of significant number of TiO_6 groups. The large Debye–Waller factor for the Ti–O first neighbour shell in this sample is due to the presence of both TiO_4 and TiO_6 groups in this sample. The Ti–Ti correlation at 3.03 Å is close to the value of 3.04 Å found in anatase, one form of crystalline TiO_2, and is direct evidence of phase separation within this sample. These results are in agreement with those of our previous studies which found evidence of phase separation within samples of the composition $(TiO_2)_{0.41}(SiO_2)_{0.59}$.[5,6]

The ^{17}O MAS NMR results for a $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample shown in Fig. 3 illustrate in more detail the structural changes during the xerogel to glass transition which occurs with heat treatment. In the unheated xerogel, three distinct environments of oxygen are observed: Si–O–Si bridges (0 ppm), Ti–O–Si bridges where the Ti is present as TiO_6 (110 ppm) and Ti–O–Si bridges where the Ti is present as TiO_4 (250 ppm). This is the first time that O_5Ti–O–Si moieties have been observed directly and unequivocally in a disordered material using ^{17}O MAS NMR. The 250 ppm signal must arise from Ti that has entered the silica network, whereas the 110 ppm signal arises from Ti which has octahedral coordination due to the presence of acac ligands. The fact that both peaks are present in the spectrum from the unheated gel indicates that some of the Ti–acac complex has been hydrolysed during gelation. Preheating the sample to 250 °C has little effect on the ^{17}O NMR spectrum, indicating little structural change. Between 350 and 750 °C the 250 ppm resonance grows in intensity while the 110 ppm peak shrinks and has all but disappeared by 750 °C. These changes are caused by titanium initially present as TiO_6 entering the silica network and becoming tetrahedrally coordinated as the sample is heat treated to progressively higher temperatures.

Fig. 4 shows the ^{17}O MAS NMR spectra for a $(TiO_2)_{0.41}(SiO_2)_{0.59}$ xerogel, unheated and heated to 750 °C. The spectrum for the unheated gel is similar to that of the $(TiO_2)_{0.18}(SiO_2)_{0.82}$ sample showing the presence of both tetrahedral and octahedral Ti. After heat treatment, two new peaks are observed due to OTi_4 and OTi_3 moieties at 360 and 530 ppm, respectively. These peaks represent direct evidence of phase separation within this sample. Despite phase separation, the 750 °C spectrum exhibits a large peak at 250 ppm due tetrahedrally substituted Ti. In a previous study of samples prepared without the use of acac,[5] a $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample heat treated to 600 °C displayed an absence of resonances due to Ti–O–Si bridges and a presence of resonances associated with Ti–O–Ti linkages at 370 and 560 ppm, indicating extensive phase separation. Thus, although the heat treated $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample is partly phase separated, the use of acac has increased the level of atomic mixing.

These NMR results are important because they yield information on the local environment of the Ti atoms within the glass structure, as do XANES and EXAFS data, but have been obtained using a technique that is much more widely accessible.

Conclusions

Our results have enabled us to determine the role of titanium in $(TiO_2)_x(SiO_2)_{1-x}$ sol–gels prepared using acetylacetone as a stabilising agent. The unheated xerogels all contain Ti in a distorted octahedral coordination with respect to oxygen which is consistent with previous XANES results.[27] For the $(TiO_2)_{0.18}(SiO_2)_{0.82}$, sample heating to 750 °C converts virtually all the TiO_6 to TiO_4 which can exist within the silica network. Previous studies on titania–silica glass, prepared by flame hydrolysis and sintering, have put the upper limit for solubility of TiO_2 in SiO_2 at *ca.* 15 mol%.[28,29] Thus our results show that the use of acetylacetone in our preparation has allowed us to produce homogeneous $(TiO_2)_x(SiO_2)_{1-x}$ materials with a titanium doping close to the stable upper limit. The $(TiO_2)_{0.30}(SiO_2)_{0.70}$ sample also appears to remain homogeneous after heating to 750 °C. However, the EXAFS results show a slightly longer Ti–O bond distance and higher Debye–Waller factor for this shell, suggesting the presence of a significant proportion of network modifying TiO_6. The presence of Q^2 and Q^3 species in the ^{29}Si NMR signal supports these findings. The $(TiO_2)_{0.41}(SiO_2)_{0.59}$ sample clearly displays phase separation after heating, a phenomenon observed in samples of this composition prepared without using acac in a previous NMR study.[5] However, ^{17}O MAS NMR has shown this sample to contain a significant number of Ti–O–Si bridges indicating that there is a higher level of atomic mixing than in samples prepared without acac.

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