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The architecture of catalytically active centers in titanasilicate (TS-1) and related selective-oxidation catalysts

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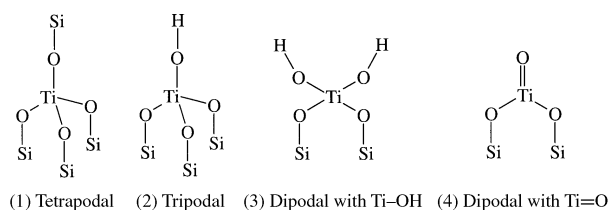
Detailed X-ray spectroscopic studies yield the three-dimensional structure of Ti(IV) centered active sites in a series of TS-1 catalysts, in which titanium ions substitutionally replace a small fraction of the silicon sites in the pentasil structure, Silicalite-1. Advantage has been taken of the atomic structure of $\text{Ti}(\text{OSiPh}_3)_4$, (determined separately by X-ray diffraction). A detailed EXAFS analysis of the X-ray absorption spectra of $\text{Ti}(\text{OSiPh}_3)_4$ which takes advantage of the full cluster multiple scattering methodology leads to the precise nature of the coordination of the Ti ions in a series of TS-1 samples. It proved possible to distinguish between the tetrapodal [i.e., $\text{Ti}(\text{OSi})_4$] and tripodal structure [i.e., $\text{Ti}(\text{OSi})_3\text{OH}$] shown (see T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159; ref. 1) to be present in high performance anchored titanasilicate epoxidation catalysts.

Introduction

The importance of titanium containing silicates as catalysts for a host of reactions² including the epoxidation and ammoxidation reactions, has stimulated widespread investigation of their synthesis and characterisation,³ with TS-1 being perhaps the most commonly studied system.^{3,4} Preparation of this material entails the use of hydrothermal methods and a small percent of Si^{4+} is replaced by Ti^{4+} at this stage; other procedures, such as grafting titanocene dichloride, are also effective in producing a specific concentration of titanium centres in micro- and mesoporous materials.^{1,3} Although the resulting solid is highly crystalline, it has not been possible to determine the structure of Ti^{4+} centres by X-ray diffraction (XRD) methods due to their low concentration and random substitution.⁵ However, Perego *et al.* effectively used X-ray powder diffraction to obtain the correlation between the increase in lattice constants and titanium content.^{6,7} XRD measurements were carried out on hydrated samples with the authors recommending treatment with ammonium acetate to improve the linear correlation of the data.⁷ Lamberti *et al.* have recently reported that a high correlation can also be obtained without pre-treatment of ammonium acetate, provided that the samples are measured after dehydration.⁸ It is worth noting that treatment with ammonium acetate affects the long range order of the samples causing a systematic increment in the cell volume of ca. 15–18 Å³, and in samples of low Ti-content it also induces the orthorhombic to monoclinic solid state phase transformation. Moreover, treated samples exhibit a minor content of internal point defects, as documented by the reduction of the O–H band in the 3100–3800 cm^{−1} region of the FTIR spectra. A strong, local rearrangement of the internal silanol and probably titanol groups is thus hypothesized. These FTIR results are quantitatively confirmed by microcalorimetric experiments of NH_3 adsorption, where a decrease

in the amount of adsorbed NH_3 molecules is observed after treatment.^{9,10} X-ray absorption spectroscopy (XAS) has been used by us and several others, to determine the local structure of the active centres, since XAS is atom-specific and does not depend on the long-range order. Several *in situ* Ti K-edge XAS studies have revealed that titanium in the active catalyst is present in the tetrahedral environment, both in microporous TS-1,^{11–16} $\text{Ti}-\beta$,^{17,18} and mesoporous $\text{Ti} \rightarrow \text{MCM-41}$ or $\text{Ti} \uparrow \text{MCM-41}$ catalysts.^{1,19,20} Although this tetrahedral coordination is a widely accepted model, there is still a considerable debate over the type of species present in the catalysts. Four possible models are shown in Scheme 1. Their stability has been examined using computer modelling methods, which suggest that species (1) or (2) could be interconverted relatively easily by hydrolysis and that species (4), although higher in energy, might play a significant role as an intermediate in catalytic mechanisms.^{21–23} Species (2) and (3) have been postulated to be present from UV-VIS and photoluminescence experiments.^{24,25}

It is generally not possible to differentiate experimentally between the above models [except (4), since $\text{Ti}=\text{O}$ is about 0.1 Å shorter than a $\text{Ti}-\text{O}$ in tetrahedral coordination¹⁸] using conventional Ti K-edge XAS (both XANES and EXAFS) data analysis procedures. In particular, the first three models have similar tetrahedral coordination environment and will have



Scheme 1

very similar XAS spectra. Thus, the majority of the earlier work could not determine the detailed nature of titanium species present in the catalyst although species (4) was immediately discarded.^{15,16,26}

In this paper we describe how a more detailed EXAFS data analysis procedure enables us to differentiate between these species in a series of TS-1 catalysts with different titanium contents. Our approach relies on the detection of silicon neighbours and uses their coordination numbers to provide a unique model for the type of titanium centres present in the catalyst. We also show the importance of the multiple scattering method in determining accurately the various Ti environments using Ti K-edge data recorded *in situ*. Using our new approach, we are able to distinguish between tripodal and tetrapodal environments. In particular, it is shown that when the Ti concentration is *ca.* 1 wt.%, post-synthesis treatment with ammonium acetate changes the nature of the species present from a tetrapodal to a tripodal coordination, whilst at the lower Ti concentration of *ca.* 0.5 wt.%, the tetrapodal coordination dominates even after treatment with ammonium acetate.

Experimental

TS-1 samples were synthesised by EniTecnologie Laboratories, following the patent.⁶ $\text{Ti}(\text{OSiPh}_3)_4$ was prepared using the previously described procedure.^{27,28}

XAFS spectra of the dehydrated TS-1 samples were performed at the EXAFS3 beam line of the DCI storage ring of LURE Laboratories in Orsay, France operating at 1.85 GeV with a typical beam current of 300 mA, using air filled ionisation chambers for the incident and transmitted beams (Proposal CK 029-96). The gas pressure was optimised *ad hoc* for each sample to maximise the measured current within the linear region of the device. The EXAFS spectrum for each sample was acquired eight times under the same experimental conditions, which were averaged prior to background subtraction.

XAFS spectra of $\text{Ti}(\text{OSiPh}_3)_4$ were obtained on Station 8.1 of the SRS at Daresbury, UK, operating at 2 GeV with and average beam current of 150–250 mA, using ion chambers filled with argon–helium mixtures to absorb 20 and 80% of the beam for I_0 and I_t respectively. EXAFS data for this sample were acquired twice under the same experimental conditions, which were averaged prior to background subtraction. The detailed structure of this material is discussed elsewhere.

In both sets of experiments, a double crystal Si(111) monochromator was used, and the crystals de-tuned to give 50% harmonic rejection. The Ti K-edge position was calibrated using a Ti foil.

Dehydration of the TS-1 samples was undertaken in a specially designed *in-situ* cell^{15,16,29} at 400 K under a dynamic vacuum of *ca.* 10^{-3} Pa immediately prior to data collection.¹²

The data were processed using the EXAFS analysis suite of programs at the Daresbury Laboratories comprising EXCALIB (for converting the recorded data to energy *vs.* absorption coefficient), EXBROOK (for pre-edge and post-edge background subtraction), and EXCURV98 (for curve fitting analysis using a least squares procedure). Within the EXCURV98 program, all the non-structural parameters, in particular the phase shifts associated with various atoms are calculated prior to the detailed curve fitting analysis. EXAFS data analysis was undertaken using both the single scattering curved wave approximation³⁰ and using the full multiple scattering calculations using Rehr–Alber small atom theory.^{31,32} *Ab-initio* calculations were used to determine the ground state potential and phase shifts.^{33,34} In the present study, the raw data were processed without using any Fourier filtering techniques.

Results and discussion

First we discuss the analysis of EXAFS data of the model system, $\text{Ti}(\text{O}-\text{Si}-\text{Ph}_3)_4$ in which titanium is surrounded by four Si^{4+} linked via oxygen, and describe the need for the full cluster multiple scattering (MS) approach to derive precisely the coordination environment around titanium. Subsequently we show the results obtained for TS-1 catalyst (some of which have undergone pre-treatment described in a previous publication⁷) with different titanium loading.

EXAFS analysis of $\text{Ti}(\text{OSiPh}_3)_4$ model compound

Recently some of us reported the crystal structure (employing micro-crystal diffraction method) of this material.²⁸ The local structure around titanium consists of four $\text{O}-\text{Si}-\text{Ph}_3$ linkages (see Fig. 1) with three of the $\text{Ti}-\text{O}-\text{Si}$ bond angles being *ca.* 148° and one of them at 180° . The tetrahedral nature of the titanium centre is also reflected in the intense pre-edge intensity in the XANES spectra shown in Fig. 1.

Analysis of the EXAFS data revealed that there are four oxygen atoms in the first coordination sphere at a $\text{Ti}-\text{O}$ distance of 1.806 Å, which is close to that determined by the crystal structure study (see Table 1). Inclusion of silicon neighbours in the analysis of the EXAFS data and using a simple single scattering approximation did not yield a very good fit even after taking multiple scattering into account for the $\text{Ti}-\text{O}-\text{Si}$ shell having the bond angle of 180° [see Fig. 2(a) and 2(b)] (Table 1, method 1). The best fit yielded structural parameters with a large Debye–Waller factor. Furthermore, refinement of all the $\text{Ti}-\text{O}-\text{Si}$ bond angles resulted in a smaller value compared to those determined by crystal structure analysis (Table 1, method 2). We have shown previously the

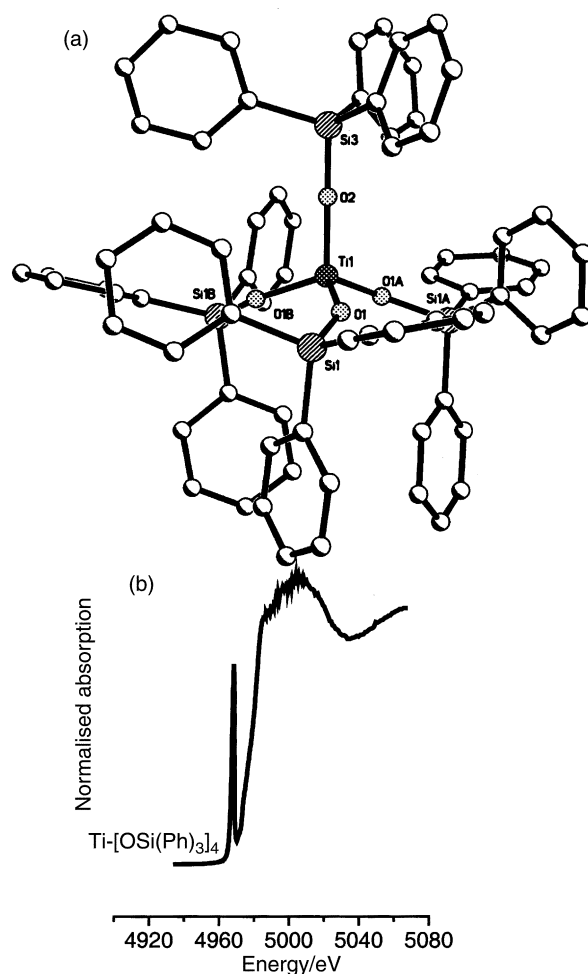


Fig. 1 (a) The structural model (derived from single crystal study) of $\text{Ti}(\text{OSiPh}_3)_4$ used for the EXAFS data analysis; (b) Ti K-edge XANES of the model compound $\text{Ti}(\text{OSiPh}_3)_4$.

Table 1 Refined EXAFS parameters for $\text{Ti}(\text{OSiPh}_3)_4$ using full cluster and partial multiple scattering^a

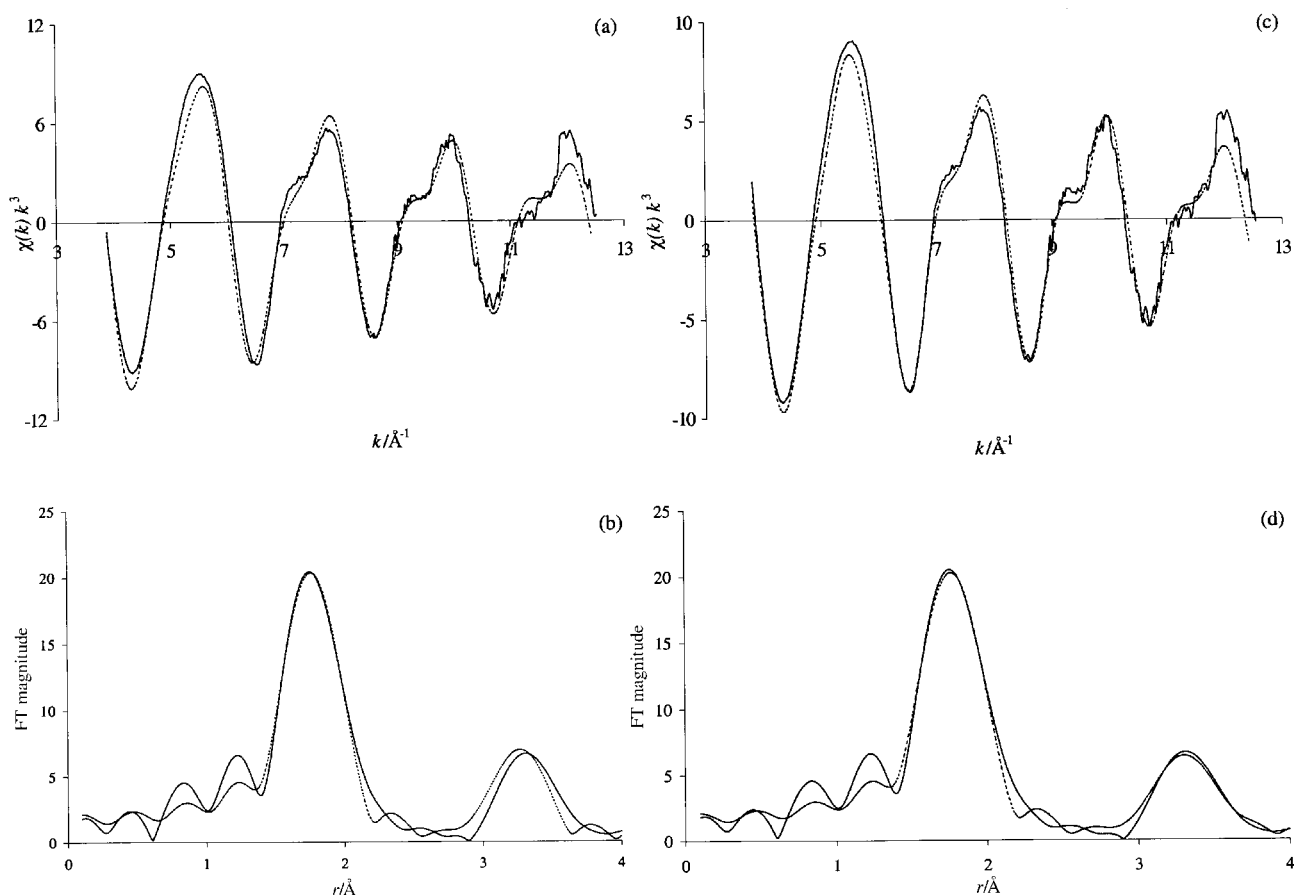
Methodology	CN and atom type	Distance/Å	Debye–Waller factor	Ti–O–Si angle/°
Crystal structure ²⁸	3 × O	1.782		
	1 × O	1.798		
	3 × Si	3.300		148
	1 × Si	3.440		180
Full-MS Method 3	4 × O	1.806	0.007	
	1 × Si	3.410	0.007	179
	1 × Si	3.317	0.005	156
	1 × Si	3.240	0.005	145
	1 × Si	3.164	0.005	137
	$R = 17.93$, $N_{\text{ind}} = 13$			
Part MS (refined 180° Si) Method 2	4 × O	1.808	0.007	
	3 × Si	3.222	0.002	142
	1 × Si	3.367	0.014	163
	$R = 19.78$, $N_{\text{ind}} = 9$			
Part MS (held 180° Si) Method 1	4 × O	1.812	0.007	
	1 × Si	3.427	0.019	180
	1 × Si	3.212	0.015	141
	1 × Si	3.220	0.015	141
	1 × Si	3.215	0.015	142
	$R = 20.01$, $N_{\text{ind}} = 13$			

^a N_{ind} is the number of independent parameters refined. Typical errors: coordination number (CN) $\pm 10\%$; Debye–Waller factor $\pm 10\%$; Ti–O–Si angle $\pm 5^\circ$; distances ± 0.02 Å.

importance of including MS in some of our earlier studies,³⁵ however, this study shows that it is essential to use the new full cluster MS methods to achieve the best description. In order to carry out this analysis we adopted the following procedure.

The starting model used consisted of a geometrically defined cluster containing the first and second co-ordination spheres around the Ti centre derived from the crystal struc-

ture of this material, as shown in Table 1 and Fig. 1. Initially, the EXAFS data were fitted to a model consisting of only the first co-ordination sphere of four oxygens. The values of the Ti–O distances, the Debye–Waller factors and of E_0 were refined to yield the best fit. In this procedure we need to use the C1 symmetry in which all the Ti–O and associated Si linkages were constructed as a single cluster with four individual Ti–O and Ti–Si distances, since other higher symmetries did

**Fig. 2** EXAFS and associated FTs for $\text{Ti}(\text{OSiPh}_3)_4$ model compound with MS included only for the 180° angle (a,b) and using full MS (c,d).

not yield the specific description suited for all possible models. In order to avoid correlation effects, all the Ti–O distances and their respective Debye Waller factors were constrained to be the same. An additional important constraint used in the refinement is to fix the O–Si distances at a typical distance of *ca.* 1.6 Å. For the refinement of the Ti–Si interactions, the individual distances and bond angles were allowed to vary freely whilst the Debye–Waller factors of closely similar bond distances were constrained to be equal. These constraints have been tested for various systems³⁵ and in no cases did they produce unphysical results. They indeed control the refinement in such a way that some of the correlation effects are minimized to yield results that are consistent with crystallographic data (Table 1, method 3).

A detailed MS calculation performed in this way resulted in the best fit shown in Fig. 2(c), (d) and the results are now fully consistent with the crystallographic data which are listed in Table 1 (method 3). Indeed, from calculation for this and other systems it is clearly essential to perform analyses, when the higher shells are included (irrespective of whether the bond angle is 180° or not), using the multiple scattering method to obtain an accurate description of the local structure. Thus, by using the identical procedure we can investigate the local structure of titanium in dehydrated TS-1 catalyst for both systems untreated and treated with ammonium acetate.

EXAFS analysis of TS-1 catalysts

Using the same approach used for the Ti(OSiPh₃)₄ system, a detailed analysis was performed of the Ti K-edge EXAFS of several TS-1 catalysts, which were either treated or untreated with ammonium acetate. Initial analysis of the first shell yielded an average Ti–O distance of *ca.* 1.80 Å and a coordination number of *ca.* 4. This result clearly indicates that we have either species (1) or (2), as shown in Scheme 1, and that there is no evidence for the presence of a Ti=O species similar to that of JDF-L1¹⁸ or the environment given in species (4) of Scheme 1. This finding is consistent with the results reported^{12,15,16} and with the computational studies of Sinclair *et al.*^{21–23} The minor difference between the two experimental results of *ca.* ±0.02 Å, is well within the experimental uncertainty in determining the interatomic distances. It should also be noted that the present analysis procedure employed *ab initio* methods to calculate the phase and amplitude factors as opposed to the use of model compounds by the earlier publication.^{12,14,15,29}

In order to distinguish between the two species (1) and (2), which are termed as tetrapodal and tripodal, respectively, in this paper, we carried out a systematic analysis using full MS cluster methods following the procedure described for the model system, Ti(OSiPh₃)₄. For each catalyst, two types of independent models were constructed, the first representing the tetrapodal and the second the tripodal environment. In each case, several combinations of possible Ti–O–Si bond angles were used as the starting models for further refinement of the experimental data in order to achieve the best possible fits for both the tetrapodal and tripodal systems. In both cases, C1 symmetry was used to achieve the best description (despite the accompanying computational expense). In addition, using this full multiple scattering method, it is not possible, directly, to derive the co-ordination number of the silicon shells of a particular Ti–O–Si linkage having a specific bond angle and distance as the method requires integer values for the occupancies of any given shell. We have therefore fixed the coordination number of each silicon atom to be 1 and refinements were carried out using the various tetrapodal and tripodal starting models. This approach avoids correlation effects between coordination numbers and Debye–Waller factors. We know from the refinement of the first shell that all the catalysts contain 4 oxygen atoms in the first coordination

environment. Thus, by determining the number of silicon atoms needed in the second shell in order to achieve the best fit to the experimental data, it is possible to determine the nature of the species present in the catalyst. To distinguish between the results obtained from various starting models, we used the fit-index as the main criteria and also the Debye–Waller factors of the silicon shell. The fit index *R* is given by:

$$R (\%) = \sum_i^N 1/\varpi_i (|\chi_i^{\text{exp}}(k) - \chi_i^{\text{th}}(k)| \times 100)$$

where $|\chi_i^{\text{exp}}(k) - \chi_i^{\text{th}}(k)|$ is the difference between the experimental and calculated EXAFS spectra at each point. $1/\varpi_i$ is a measure of the experimental statistical errors. For example, since the coordination number is fixed to unity, a high value of the Debye–Waller factor greater than *ca.* 0.025 Å² for $2\sigma^2$ is indicative of the absence of that particular shell. Similarly, a very low value, typically less than 0.001 Å² indicates a higher coordination number for that distance or that the determined Ti–O–Si bond angle is considerably lower.

Using these criteria and the restraints and constraints discussed earlier, we obtained the best fit for the various catalysts. The results for both the tetrapodal and tripodal models (Scheme 1, models 1 and 2, respectively) for all the catalysts studied here are given in Table 2. A typical best fit for the EXAFS data of the 1.2 wt.% TS-1 catalysts and their associated FT's are shown in Fig. 3 (untreated) and 4 (after treatment with ammonium acetate).

It is clear from Table 2, that the majority of the catalysts contains tetrapodally coordinated species (model 1, Scheme 1). Although a four silicon second shell environment is the best description in majority of the cases, it should be noted that their geometries are not identical. In order to simplify the description of the local geometry, we combined closely related Ti–Si distances and their respective bond angles (the error involved in the determination of bond angle is *ca.* ±10°) and found that two average bond angles with a value of 140 and 160° are adequate to describe the distorted environment. For

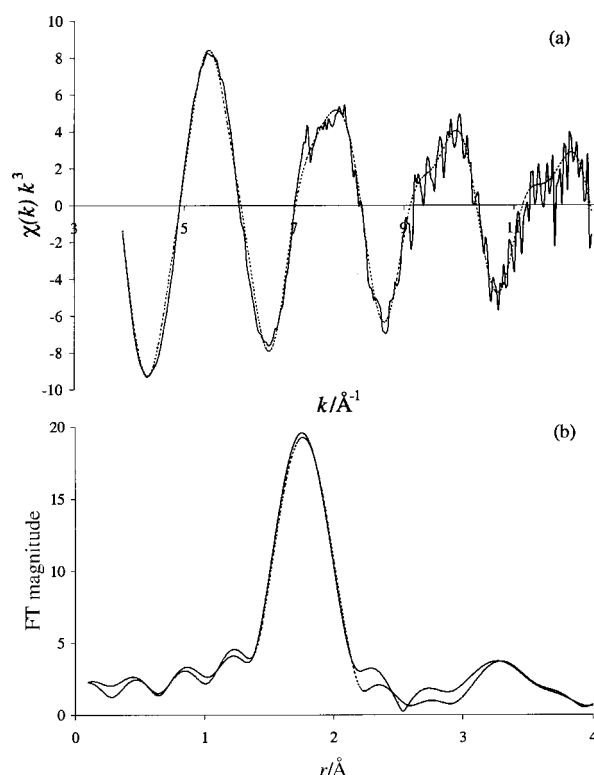


Fig. 3 Typical EXAFS fit (a) and the associated FT (b) for dehydrated 1.2% Ti containing TS-1 catalyst *before* treatment with ammonium acetate.

Table 2 Refined EXAFS parameters for TS-1 samples with or without ammonium acetate treatment^a

Material	Tetrapodal (model 1, Scheme 1)				Tripodal (model 2, Scheme 1)			
	Distance/Å	Debye–Waller factor	Ti–O–Si angle/°	R factor	Distance/Å	Debye–Waller factor	Ti–O–Si angle/°	R factor
0.58% Ti NH ₄ Ac Treated	(Ti–O) 1.798	0.008		31.07	(Ti–O) 1.798	0.009		31.90
	(Ti–Si) 3.370	0.008	163		(Ti–Si) 3.363	0.009	163	
	(Ti–Si) 3.250	0.008	148		(Ti–Si) 3.345	0.009	156	
	(Ti–Si) 3.250	0.008	148		(Ti–Si) 3.250	0.009	141	
	(Ti–Si) 3.246	0.008	144					
	$N_{\text{ind}} = 11^a$				$N_{\text{ind}} = 11$			
1.2% Ti Untreated	(Ti–O) 1.808	0.008		15.46	(Ti–O) 1.810	0.008		15.65
	(Ti–Si) 3.367	0.009	162		(Ti–Si) 3.386	0.006	167	
	(Ti–Si) 3.367	0.009	162		(Ti–Si) 3.298	0.004	152	
	(Ti–Si) 3.249	0.009	145		(Ti–Si) 3.188	0.004	140	
	(Ti–Si) 3.213	0.009	141					
	$N_{\text{ind}} = 11$				$N_{\text{ind}} = 11$			
1.2% Ti NH ₄ Ac Treated	(Ti–O) 1.812	0.007		24.27	(Ti–O) 1.813	0.007		23.13
	(Ti–Si) 3.374	0.011	159		(Ti–Si) 3.368	0.009	161	
	(Ti–Si) 3.374	0.011	159		(Ti–Si) 3.226	0.009	142	
	(Ti–Si) 3.374	0.011	159		(Ti–Si) 3.226	0.007	142	
	(Ti–Si) 3.232	0.010	142					
	$N_{\text{ind}} = 9$				$N_{\text{ind}} = 9$			
1.81% Ti Untreated	(Ti–O) 1.818	0.010		15.21	(Ti–O) 1.825	0.011		15.87
	(Ti–Si) 3.380	0.011	162		(Ti–Si) 3.386	0.007	164	
	(Ti–Si) 3.380	0.011	162		(Ti–Si) 3.284	0.008	147	
	(Ti–Si) 3.260	0.011	143		(Ti–Si) 3.228	0.008	137	
	(Ti–Si) 3.260	0.011	143					
	$N_{\text{ind}} = 9$				$N_{\text{ind}} = 11$			

^a N_{ind} is the number of independent parameters refined. Typical errors: coordination number (CN) $\pm 10\%$; Debye–Waller factor $\pm 10\%$; Ti–O–Si angle $\pm 5^\circ$; distances ± 0.02 Å.

example, in some cases we see that a distribution of three Ti–O–Si at 140° and one Ti–O–Si at 160° is preferred (0.58% Ti treated) whilst in others we see that two Ti–O–Si bond angles at 140° and two at 160° are preferred (1.2 wt.% Ti

untreated and 1.81% Ti untreated). These two models are shown schematically in Fig. 5A and B, respectively.

It is interesting to note, from Table 2, that the results obtained for the 1.2 wt.% TS-1 catalysts treated with ammonium acetate show different coordination environment compared to the same material without treatment. In particular, 4 oxygen shells and 3 Ti–O–Si shells, *i.e.* a tripodal model (Scheme 1, model 2), are adequate in achieving the best fit for the treated material. Inclusion of 4 Ti–O–Si shells, *i.e.* a tetrapodal model (Scheme 1, model 1), yielded a poorer fit (see Fig. 4 and 6 for comparison) and a higher fit-index (see Table 2) compared to that achieved for the tripodal model. However, FTIR and micro-calorimetric measurements show a decrease in the amount of terminal hydroxyl species upon treatment with ammonium acetate, suggesting that there is a decrease in defects due to the formation of Si–O–Si(Ti) linkages. The comparison of the EXAFS, IR and calorimetric data seems to indicate that Si–OH and Ti–OH show opposing behavior

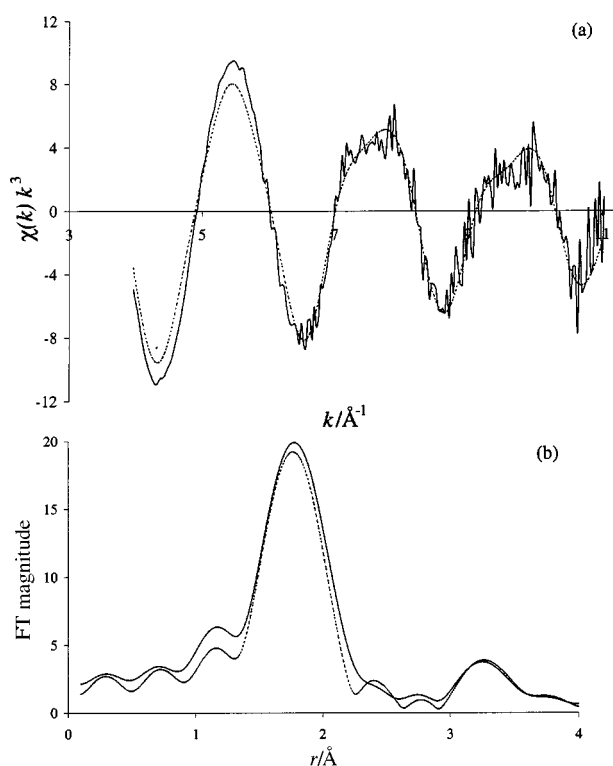


Fig. 4 Best EXAFS fit (a) and the associated FT (b) for dehydrated 1.2% Ti containing TS-1 catalyst *after* treatment with ammonium acetate using tripodal model.

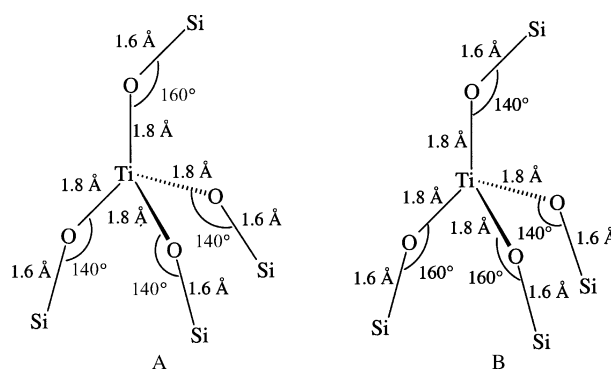


Fig. 5 Schematic showing the two different tetrapodal environments. Model A (left) characterised by 3 Ti–O–Si angles of 140° and 1 at 160° . Model B (right) characterised by 2 Ti–O–Si angles of 140° and 2 at 160° .

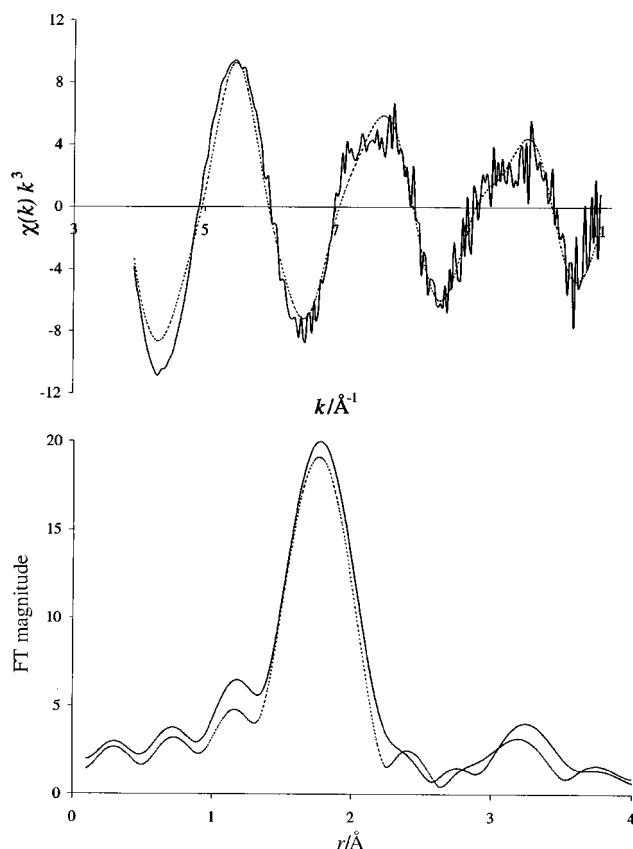


Fig. 6 Typical EXAFS fit (a) and the associated FT (b) for dehydrated 1.2% Ti containing TS-1 catalyst after treatment with ammonium acetate, showing the tetrapodal model is unsatisfactory compared to the tripodal model shown in Fig. 4.

upon treatment with ammonium acetate. In this regard, we wish to note that it is formally impossible to separate the features of Si-OH (which are the major species, typically 98–99%) from those of Ti-OH (the minor species, typically 1–2%) by FTIR and microcalorimetry experiments alone. In view of this, and the fact that EXAFS is atom specific, it is necessary to investigate several loadings of titanium containing TS-1 and related systems to unambiguously determine the local structure of titanium in these catalysts.

The present study confirms, in agreement with all previous studies, that titanium is in a tetrahedral environment in TS-1. It also demonstrates that not only the inclusion of the full multiple-scattering cluster method is essential in obtaining the best description of the local environment, but it also allows us to distinguish between closely similar models. It is also clear from this and other studies^{5,35} that use of MS methodology is the most appropriate way of assessing the local environment of metal ions, in particular present in open-framework structures.

Indeed, we are currently working to perform *in-situ* EXAFS measurements at liquid nitrogen temperature. Future work will further investigate these and related systems using computational techniques.

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