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Determination of the Structure of Distorted TiO_6 Units in the Titanosilicate ETS-10 by a Combination of X-ray Absorption Spectroscopy and Computer Modeling

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A detailed picture of the local atomic environment of titanium in the novel titanosilicate ETS-10 has been derived from X-ray absorption spectroscopy aided by lattice energy minimization calculations. It is revealed that, in contrast to previous structural models for this disordered material, titanium exists in a distorted octahedral environment with long and short Ti–O bonds distributed within the chains of TiO_6 octahedra. Plausible models for the extraframework cation distribution have also been proposed.

Introduction

Several titanium-containing microporous and mesoporous silicate molecular sieves have recently been synthesized,^{1–4} there being growing interest in their catalytic performance for the oxidation of organic compounds under mild conditions as well as in their ion-exchange properties.^{1,3,5–7} The majority of these materials contain Ti^{4+} in tetrahedral framework sites^{8–11} as opposed to the recently synthesized family^{12–14} of titanosilicates, among them ETS-10, where, ostensibly, there are TiO_6 octahedra. The basic topology of ETS-10 has come to light^{15–17} by combining electron microscopy, ^{29}Si MAS NMR, lattice refinement through distance least-squares analysis of bond distances and angles, and finally simulation of both X-ray and electron diffraction patterns using models of the disordered solid. The material has the formula $(\text{Na}_{1.5}\text{K}_{0.5})\text{TiSi}_5\text{O}_{13}$ with a framework consisting of “ TiO_2 ” rods, which run in two orthogonal directions, surrounded by tetrahedral silicate units. The pore structure consists of 12-rings, 7-rings, 5-ring, and 3-rings and has a three-dimensional wide-pore channel system whose minimum diameter is defined by the 12-ring apertures. The disorder arises from structural faulting along planes parallel to the 12-ring channel directions, and it is possible to describe the structure in terms of an intergrowth of two ordered polymorphs with tetragonal and monoclinic symmetry, respectively. The alkali-metal cations necessary to balance the excess negative charge of the framework were presumed to be located in the internal channel volume, although it was not possible to determine their exact positions. Although this model framework satisfies the observations seen by the above suite of techniques, the “predicted” structure does not entirely account for the diffraction intensities. This will in part be due to the omission of cations in the calculations and in part due to the inability to refine atomic coordinates via diffraction measurements.

As previously demonstrated^{9–11,18–20} X-ray absorption spectroscopy (XAS) using both extended K-edge absorption fine structure (EXAFS) and near-edge structure (XANES) is well suited to determine the local structure of many titanium-containing porous materials and surface phases of supported catalysts. Although the concentration of titanium in ETS-10 is much higher than in other titanium-containing porous solids (ca. 2 wt % in titanosilicate TS-1), XRD studies^{15,17} of the kind undertaken already are incapable of yielding the necessary structural details. Here we report how an XAS study using a multiple scattering approach, in tandem with computer simulations, yields reliable information pertaining to Ti–O–Ti and Ti–O–Si linkages.

Experimental Section

Preparation of titanosilicate ETS-10 is described elsewhere.¹⁵ Room-temperature XAS measurements were carried out at station 7.1 of the Daresbury Synchrotron Radiation Source. This station is equipped with a Si(111) double-crystal monochromator with ion chambers for measurement of incident (I_0) and transmitted (I_t) beam intensities. Self-supporting wafers of sample were loaded into an in situ cell, and measurements were carried out in a helium atmosphere to avoid loss of intensity due to air absorption. XAS measurements of both as-prepared and dehydrated (300 °C in helium) ETS-10 samples were carried out at room temperature. Ti foil (5 μm) was used to calibrate the Ti K-edge, and TiO_2 (anatase) was used as a model compound.

EXAFS data analysis was performed using the suite of programs EXCALIB (to convert data collected into energy vs absorption coefficient), EXBROOK (for pre- and postedge background subtraction), and EXCURV92 (for detailed curve-fitting analysis of the EXAFS data).

Lattice energy minimization calculations were carried out using the program GULP,²¹ which enables the simulation of a

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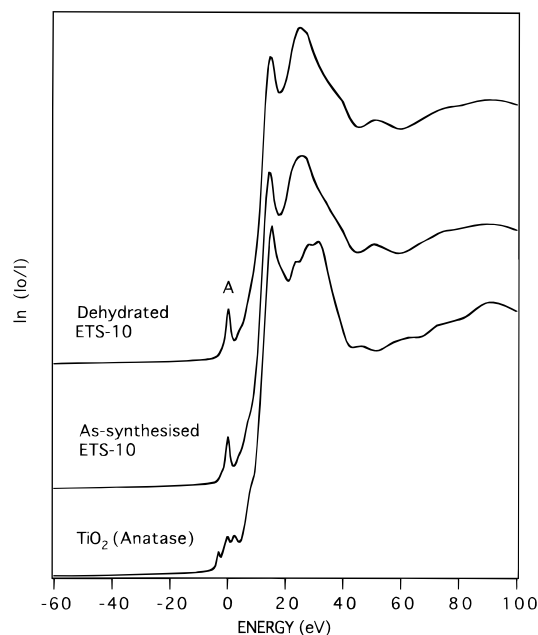


Figure 1. Ti K-edge XANES spectra of ETS-10 and of the model compound TiO_2 . (See text of description of peak labeled A.)

periodic lattice using an ionic, potential-based model. The interatomic potential functions employed by Jentys and Catlow⁸ were used to describe the titanasilicate framework, while interactions between the framework and extraframework alkali-metal cations were represented by the potentials of Jackson and Catlow.²²

Results and Discussion

Framework Structure. The titanium K-edge XANES spectrum of as-synthesized ETS-10 and that recorded after dehydration in helium at 300 °C are shown in Figure 1, along

with that for TiO_2 (anatase, referred to hereafter as TiO_2). The preedge feature (marked A in Figure 1) of TiO_2 is composed of three characteristic peaks (the origin of these have been extensively discussed in the literature, see ref 23) generally due to $1s \rightarrow 3d$ transitions. This preedge peak structure has been used as a fingerprint to distinguish between tetrahedral and octahedral coordination of Ti^{4+} ions. Tetra- and pentacoordination gives rise to an intense preedge peak due to strong overlap between metal 3d and O 2p orbitals coupled with a nonspherical local symmetry.¹⁸ Although the preedge feature in the XANES spectra of ETS-10 (both as-synthesized and dehydrated; see Figure 1) did not show the splitting observed in TiO_2 , the low intensity reflects the presence of octahedral coordination. A similar sharp, low-intensity single preedge peak has been observed in other titanium-containing minerals,²³ inorganic solids,²⁴ hydrated titanium-containing isomorphously substituted zeolitic materials,^{9,10} and mesoporous MCM-41 systems.¹¹ However, in the majority of Ti-containing zeolitic materials the intensity of this preedge peak increases upon dehydration as a result of the removal of H_2O coordinated to the framework transition-metal ion, clearly establishing the four-coordination of titanium in those cases.^{9–11} In contrast, the presence of identical spectral features for ETS-10 in both its as-synthesized and dehydrated states shows that water does not have any influence on titanium coordination in this material. Thus the characteristic fine structure seen in the XANES spectra of ETS-10 indicates the presence of octahedrally coordinated Ti^{4+} , albeit structurally different from the same ion in anatase.

In the initial attempt at analysis of the EXAFS data titanium was assumed to have a single first shell coordination sphere of six oxygens, in view of the crystal structure derived by Anderson et al.,^{15,17} which had three pairs of oxygens with Ti–O distances varying by no more than 0.02 Å (average Ti–O distance of 1.90 Å). This model, which was originally established from a distance-least-squares analysis of bond distances and angles, could not be supported by the EXAFS data. Analysis of EXAFS

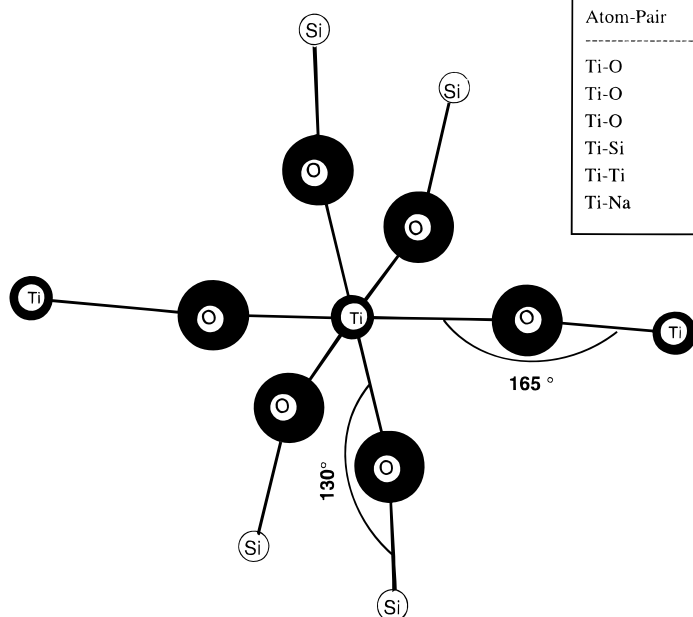


Table 1. Structural parameters obtained for ETS-10 from our EXAFS data analysis

Atom-Pair	N	R (Å)	σ^2 (Å ²)
Ti-O	1	1.71	0.006
Ti-O	4	2.02	0.007
Ti-O	1	2.11	0.006
Ti-Si	4	3.31	0.009
Ti-Ti	2	3.76	0.010
Ti-Na	1	3.07	0.009

Figure 2. Schematic representation of the Ti connectivity used in the multiple scattering EXAFS analysis. The angles shown are the average values obtained from the best fit shown in Figure 3. The table inset summarizes the structural parameters obtained from the best fit (*N*, coordination number; *R*, interatomic distances; σ^2 , Debye–Waller factor). Extraframework cations are not shown in the scheme as they are not part of the connectivity responsible for the multiple scattering.

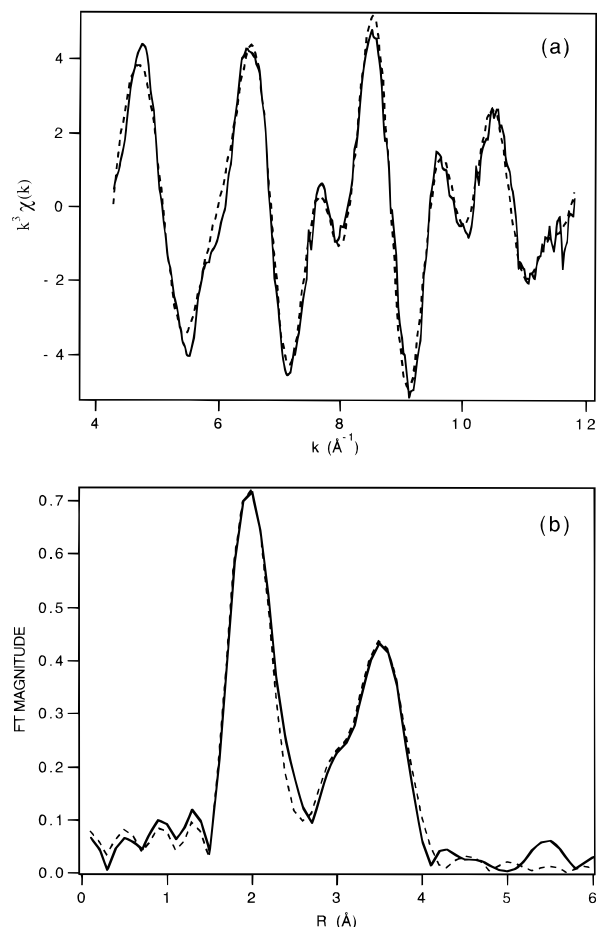


Figure 3. (a) EXAFS data and (b) their Fourier transform, for ETS-10. Solid lines represent the experimental data, while the dashed curves are calculated from the model structure described in Figure 2.

data yielded a Ti—O coordination number close to four (at an average distance of 2.02 Å). Such a coordination, however, would result in a neutral framework with no cation-exchange capacity, which is completely inconsistent with the chemical properties of ETS-10. It also contradicts the conclusions we draw regarding coordination from our XANES measurements. The average Ti—O distance obtained from the EXAFS analysis

is longer than that proposed from distance least-squares refinement (2.02 Å compared to 1.90 Å).¹⁵

To unravel the discrepancies in Ti—O distance and coordination number between EXAFS and distance least-squares refinement (as well as our XANES observation), we carried out energy minimization calculations by taking the proposed¹⁵ framework structure as a starting point. As a first step, several random distributions of Na and K ions (separately) were introduced into the structural voids. For each cation configuration, the crystal structure was then optimized by energy minimization but constrained by the symmetry of the original model (*C2/c*). The structures with the lowest energy cation distributions were then subjected to unconstrained minimization, in which all atomic positions were allowed to relax without regard to any internal symmetry. The minimizations invariably resulted in distortion of the TiO₆ octahedra, with a wider distribution of Ti—O bond distances than in the original model. Results (for either Na- or K-containing ETS-10) indicated that the four oxygens bridging Ti and Si bear an average Ti—O distance of ca. 2.03 Å and the two oxygens forming Ti—O—Ti chains have shorter distances, below ca. 1.90 Å, thus resulting in a more linear Ti—O—Ti chain.

On the basis of these observations, further analysis of the EXAFS data was pursued using a multiple scattering formalism since a multiple scattering path may exist due to a Ti—O—Ti linkage with a Ti—O—Ti bond angle close to 180°. To perform such an EXAFS analysis, we utilized the local structural arrangement shown schematically in Figure 2. It is well-known that the enhancement of scattering amplitude due to multiple scattering in the titania chains will be strongly dependent on the Ti—O—Ti bond angle. Any structural model which takes this effect into account will therefore implicitly include information on the chain Ti—O distances of the backscattering Ti atom, which should be consistent with those of the central Ti atom. Using two short Ti—O distances (below 1.90 Å, as obtained from energy minimization) in the Ti—O—Ti linkages, it was not possible to obtain a good fit in which the first coordination sphere of the backscattering Ti atom was comparable to that of the central Ti. Good agreement between experimental data and the calculated EXAFS could however be obtained by considering one short and one long Ti—O oxygen at average distances of ca. 1.73 and 2.11 Å, respectively, in addition to four Ti—O

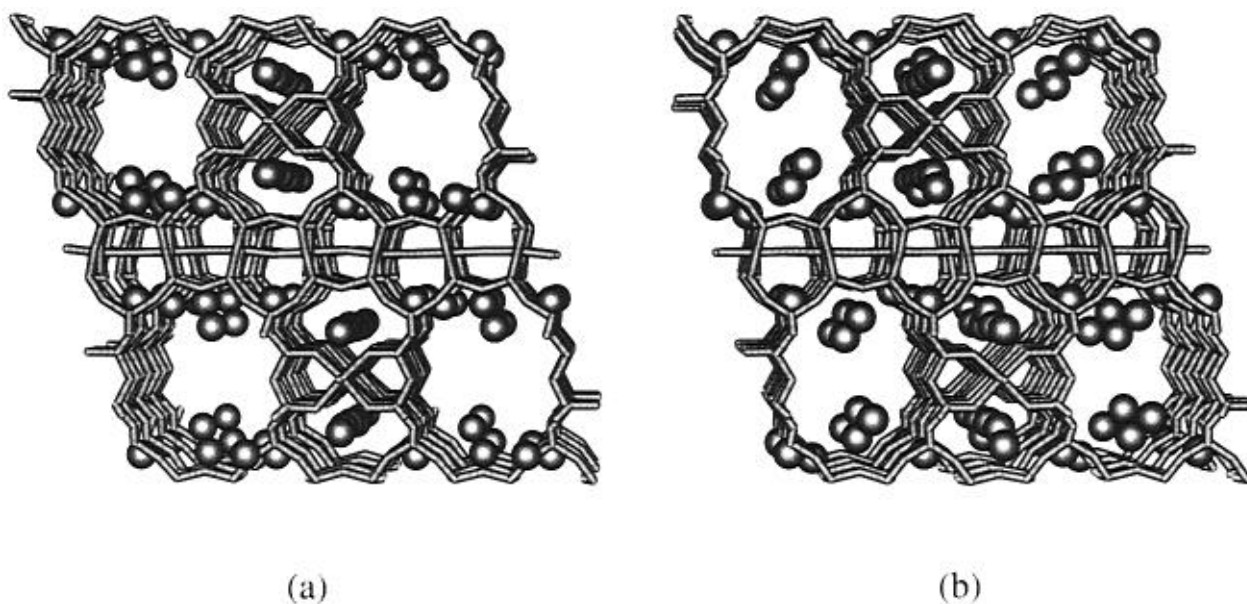


Figure 4. Molecular graphic representation of the minimum energy distributions of (a) Na⁺ and (b) K⁺ in ETS-10 (polymorph B). The cations are represented as spheres. In each case both the framework and extraframework cation positions were optimized by lattice energy minimization.

distances of 2.02 Å. This yielded average Ti–O–Ti and Ti–O–Si bond angles close to 165° and 130°, respectively, both values being in good agreement with those obtained by energy minimization, as well as consistent Ti–O bond distances for the backscattering Ti atom. The best fit between experimental data and calculated EXAFS (using parameters summarized in the table in Figure 2) and their Fourier transforms are shown in Figure 3.

Siting of Extraframework Ions. Figure 4 shows the thermodynamically preferred sites for Na⁺ and K⁺ ions in ETS-10, obtained from the lattice energy minimization calculations. It should be noted that for each cation there were several distributions which gave quite similar lattice energies, and therefore, given the hydrothermal nature of the synthesis (and the overall disorder of the structure) one would expect a more complex distribution of cations in reality. In addition, only extraframework positions which corresponded to general sites in the space group of polymorph B (*C2/c*) were considered, thus excluding the possibility of cations being located on special sites in that space group. Nevertheless a consistent feature of the simulations was the presence of two sets of preferred sites: within the 7-ring cages and in the 12-ring channels, but along the projection of the 7-rings. For sodium this is consistent with ²³Na solid-state NMR measurements¹⁷ which established two chemical environments for sodium cations which differed in the strength of quadrupolar interaction. It might be expected that the 12-ring site would have a higher electric field gradient and therefore stronger quadrupole interaction than the 7-ring cage site. Simulations were also carried out, taking into account a 3:1 Na:K ratio (see ref 17), starting with the lowest energy Na⁺-containing structure and substituting K⁺ at each of the four crystallographically distinct positions in turn. A strong preference for K⁺ ions toward 7- or 12-ring sites, in the presence of Na⁺, could not be inferred from these calculations.

Inclusion of Ti–Na distances, obtained from the energy minimization calculations, in the EXAFS analysis improved the fit between experimental and calculated EXAFS data (see Figure 3), but without any further changes to the Ti environment discussed in the previous section.

The distorted octahedral Ti–O environment found here is not unprecedented in other inorganic solids. Single-crystal structural analysis of the nonlinear optical material KTiO(PO₄) (KTP) and other related titanyl phosphates show that such chain compounds possess a similar Ti–O environment.^{25,26} Ti–O distances in such materials are similar to those we obtain by EXAFS analysis of ETS-10. Computer simulation has also provided models for extraframework cation sites in ETS-10, which have not been determined previously.

We note that, since the submission of this paper, an article by Davis et al.²⁷ has been published detailing XAS studies of ETS-10 and other titanium-containing zeolitic materials.

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