

The Three-Dimensional Structure of the Titanium-Centered Active Site during Steady-State Catalytic Epoxidation of Alkenes

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Combined in situ X-ray absorption fine structure (XAFS) measurements and density functional theory (DFT) computations yield a quantitative three-dimensional picture of the six-coordinated Ti^{IV}-centered active site (in Ti/SiO₂ catalysts) during production of epoxides from alkenes in the presence of hydroperoxide as oxidants.

Silica-supported, titanium-based heterogeneous catalysts are employed^{1,2} industrially in the production of epoxides using alkyl hydroperoxides (typically, *tert*-butylhydroperoxide, TBHP) as the oxidant. It has been shown^{3–6} by XAS measurements, and further corroborated,^{6,7} that laboratory variants of such catalysts, prepared from titanocene dichloride and the mesoporous silica, known as MCM-41,⁸ possess active centers that are “single-site” in the sense that they are spatially well-separated at the inner surfaces of the mesopores and consist of Ti^{IV}–OH groups tripodally anchored to the silica via covalent bonds to oxygen.

Under reaction conditions,^{3,9} when the alkene (typically cyclohexene) and TBHP interact with the active site, XAS reveals that the coordination around the Ti^{IV} centers increases from four to six, with two sets of Ti–O distances at steady state. A variety of models has been proposed for the steady-state structures of the Ti(IV) active sites on the basis of both experimental^{12–15} and computational¹⁶ techniques. Our aim in this letter is to interpret this experimental observation and thereby to shed light on the mechanism of epoxidation using the Ti^{IV}MCM-41¹⁰ and other related titanosilicate selective oxidation catalysts, such as TS-1^{12,13} and Ti-zeolite β .¹⁴ To do so, we have employed the in situ X-ray absorption spectroscopic method, which is well-known^{5,17} to yield local structure around (specific metal ions) catalytic sites, but only in a spatially averaged (one-dimensional) sense. By combining the information deduced from the XANES and EXAFS on one hand with that computed using density functional theory on the other, a stereo picture of the structure around the Ti^{IV} center may be obtained at the steady state during epoxidation, showing that there is an expansion in coordination from four to six.

The decrease in the pre-edge intensity of the XANES upon reacting with alkyl peroxide, in comparison with the calcined and dehydrated catalysts (see inset in Figure 1), strongly suggests an increase in coordination number around titanium centers. To determine unambiguously the titanium coordination of the reacted catalyst, we have employed the procedure discussed by

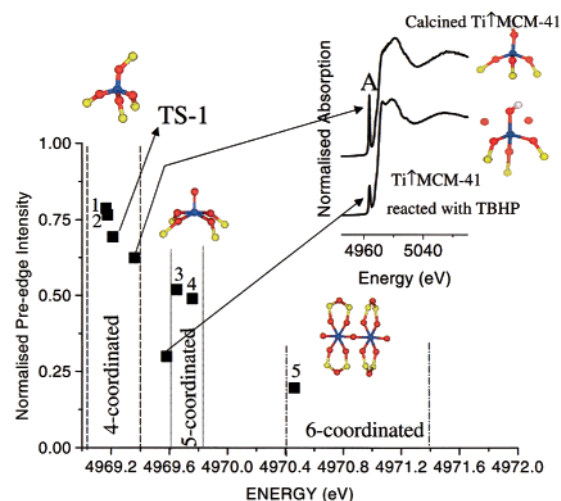


Figure 1. Variation of the pre-edge peak (marked A in the inset) intensity and its position for several titanium containing model compounds and catalysts. The model compounds used in this study are (1) Ti–(OSiPh₃)₄, (2) Ti–(OGePh₃)₄,⁶ (3) Fresnoite (Ba₂TiSi₂O₈), (4) JDF-L1 (Jilin–Davy Faraday–Layered 1, Na₄Ti₂Si₈O₂₂·4H₂O),²² and (5) ETS-10.²³ The dashed lines in the figure show the spread in pre-edge peak position determined on the basis of a number of crystallographically well characterized systems, reported in ref 18. Note that the energy positions were calibrated with respect to a 5 μ m titanium foil, taking E_0 at 4966 eV. In the inset, we show the Ti K-edge XANES of the calcined Ti^{IV}MCM-41 catalyst (top) and the one recorded during the reaction with TBHP (bottom).

Farges and co-workers.¹⁸ With the aid of several model compounds, it has been shown that the coordination geometry around titanium centers influences not only the pre-edge intensity but also the position of the pre-edge peak.¹⁸ In this work, we have used our own titanosilicate specimens throughout, since it is necessary to use identical experimental conditions such as slit size, step size for data collection, etc., to make direct comparisons with the catalytic material. A plot of pre-edge intensity and its position for several model compounds and with the calcined and reacted (with TBHP) Ti^{IV}MCM-41 catalyst is shown in Figure 1. It is seen that both the position of the pre-edge peak and its height for all the dehydrated catalysts, including TS-1 and Ti^{IV}MCM-41, are not completely the same.

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SCHEME 1

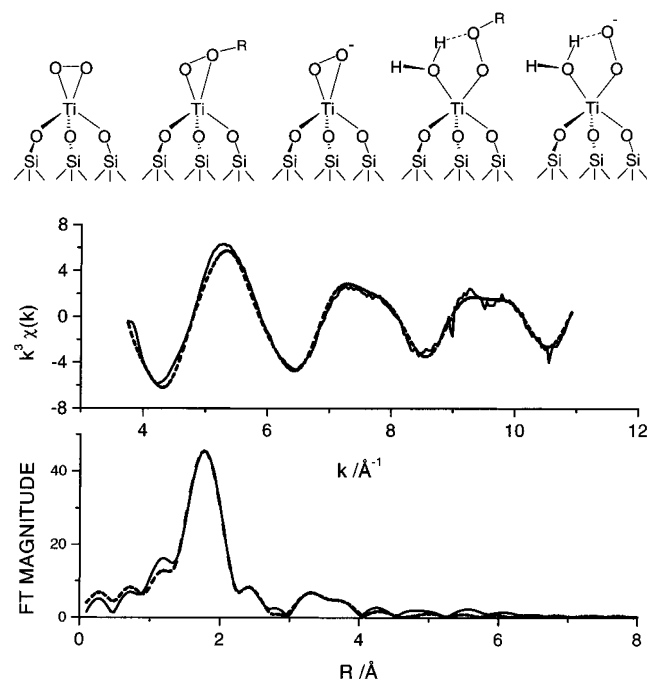


Figure 2. Best fit between Ti K-edge EXAFS data recorded during the reaction of 4% titanium-containing (prepared by grafting method) MCM-41 catalyst with TBHP and calculated EXAFS taking DFT derived local geometry as the starting model. For the EXAFS calculations, we used full multiple scattering procedure to include all the silicon shells and C1 symmetry was used for this purpose. The solid line shows the experimental data and the dashed curve represents calculated EXAFS for the model of six coordinated titanium center shown in Figure 3. The distances obtained are shown in Figure 3. The R -factors (goodness of fit) obtained for all the six coordinated centers were found to be around 16, while those for other coordination geometries the values were above 19.

Nevertheless, considering the similarity in the spread in both position and intensity of the pre-edge peak, reported for the titanium containing minerals¹⁸ (well within the uncertainty in the position shown as dashed line in Figure 1), we conclude that titanium is present in the tetrahedral coordination in the calcined catalyst prior to the reaction with hydroperoxides. This is also supported by the EXAFS derived Ti–O distance of 1.81 Å.⁵

The pre-edge intensity of the reacted catalyst is considerably less than that for a four coordinated system (see Figure 1), and more importantly, its energy position is slightly higher. Considering both the intensity and position of the pre-edge peak, we rule out the presence of a five-coordinated titanium species.

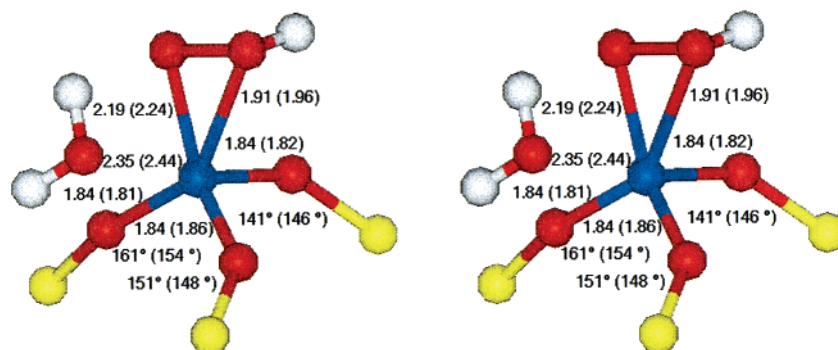


Figure 3. Stereographic projection of the DFT computed and minimized based on experimental EXAFS data. The distances shown in this figure were the final values derived from Ti K-edge EXAFS data. The DFT computed distances are given in parentheses, and the computed energy is -65.1 kJ/mol.

Our EXAFS analysis of the reacted system suggested that we have at least three Ti–O distances close to 1.83 Å (a slight elongation compared to the activated catalyst) and two of the other three oxygen distances are at distances between 2.2 and 2.4 Å.¹⁹ It may be that this type of short and very long distances present in our reacted catalyst system may give rise to a different value for both the position and intensity of the pre-edge peak compared to a typical solid-state system in which titanium is present in octahedral coordination. (The majority of the octahedrally coordinated titanium systems contain bond distances between 1.93 and 2.02 Å; even the distorted ones have most Ti–O distances close to 1.95 Å.)

On the basis of theoretical studies¹⁶ together with IR, UV, and other measurements,^{14,15} a variety of models has been proposed²⁰ for the steady-state structure of the Ti^{IV}-centered active site (Scheme 1). Proceeding on the plausible basis that the peroxide is bound to the Ti^{IV} center in preference of the alkene, we computed, using nonlocal DFT techniques (details of which will be published elsewhere²⁰) as embodied in the DGauss code,²¹ the initial and final geometries and energies of all the relevant possible steady-state structures.

Among the various models, the Ti– η^2 –OOH and Ti– η^1 –OOH structures showed the lowest energy, and it transpires that the best fits between the experimental EXAFS data and computed EXAFS taking the DFT optimized geometry as the starting point for the refinement agree well with the energy-minimized structures²⁰ (see Figure 2). This enabled us to arrive at a three-dimensional, time-averaged structure (Figure 3) of the active site under the conditions of catalytic reaction. In particular, we see (Figure 3) from the combined approach described here that the precise nature of the oxygen donating species at the titanium site in a catalyst that lacks crystallographic order may be determined. Only by combining XAFS and DFT studies can such unique information be retrieved giving details of the 3D structure of a catalytic center.

Experimental and Computational Methods

Ti K-edge X-ray absorption spectra were collected at station 8.1 of the Daresbury Synchrotron radiation source, which operates at 2 GeV with a typical current of 200 mA. This station is equipped with Si(111) double-crystal monochromator, ion chambers for the incident (I_0) and transmitted (I_t) beam intensities, and a 13-element Canberra fluorescence detector. A 4 wt % Ti/MCM-41 catalyst was prepared by the well-established grafting procedure of reacting dehydrated (200 °C in a vacuum) mesoporous silica (MCM-41) and titanocene dichloride in the presence of triethylamine.^{3a} This as-prepared catalyst was

calcined in oxygen at 500 °C, in an in situ cell, prior to the XAS measurement of the activated catalysts. Further measurements were made after admission of TBHP. All the XAS data were processed using suite of programs, namely, EXCALIB, EXBROOK, and EXCURV98, available at the Daresbury laboratory. Ti K-edge XAS data of several model systems (named below) possessing different coordination environments were also collected under conditions as close as possible to those of the epoxidation reaction. The model compounds used in the present study are Ti-(O-SiPh₃)₄ and Ti-(OGePh₃)₄ (both of which represent titanium in tetrahedral coordination, see ref 6), JDF-L1 and Fresnoite (both of which possess five-coordinated titanium centers with one of the Ti-O bond is titanyl), and ETS-10 (contains six coordinated titanium).

All calculations used gradient-corrected DFT, as embodied in the code DGAUSS²¹ which is part of the Uni-Chem 4.1 Package.²¹ The gradient corrections due to Becke²¹ and Perdew²¹ were employed (BP86) with a polarized double- ζ basis set (DZVP). The active site was represented by a tetrahedral (H₃-SiO)₃TiOH cluster which extends two coordination spheres from the central titanium ion. Initial geometry was taken from our previous work,¹⁶ and only partial geometry optimization was performed with the Si atoms being held fixed to represent the rigidity of the silica framework. Proceeding on the plausible basis that the peroxide is bound to the Ti^{IV} center in preference to the alkene, we computed several final geometries (and energies) of all the relevant possible steady-state structures.

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- (9) TBHP was reacted with a freshly calcined catalyst at 25 °C for 1 h. The white catalyst turned yellow in color during this reaction. This reacted material was used for the Ti K-edge XAS measurements.
- (10) The notation Ti^{IV}MCM-41, described more fully elsewhere,¹¹ refers to a mesoporous silica (MCM-41) in which the Ti(IV) active sites have been grafted onto the inner surface such that the Ti atoms stand proud of the surface (see Figure 1 of ref 11 for a color representation of Ti^{IV}MCM41 and Ti^{IV} → MCM41, where the Ti atoms are in the walls of the silica).
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