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The Role of Synchrotron-Based Studies in the Elucidation and Design of Active Sites in Titanium−Silica Epoxidation Catalysts

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ABSTRACT

X-ray absorption fine structure (XAFS) measurements unambiguously establish the structure of the active centers in high-performance Ti−SiO$_2$ epoxidation catalysts. Subtleties in structural changes in proceeding from the dispersed titanocene dichloride precursor to the anchored Ti^{IV} centers are charted, *in situ, by* both near-edge (XANES) and extended-edge (EXAFS) measurements. The active centers are tripodally attached titanol groups: (Si−O)$_3$−TiOH. These permit facile expansion of the coordination shell (also monitored by *in situ* XAFS studies) during catalysis, and thereby lead to the formulation of a plausible mechanism of epoxidation of alkenes that is consonant with recent DFT computations. Previously proposed mechanisms, based on a three-coordinated titanyl group (as well as possible five- or six-coordinated active sites), are discounted. Comparable XAFS studies of soluble catalytically active four-coordinated Ti^{IV}-containing molecular entities establish that the heterogeneous Ti−SiO$_2$ catalyst has "single-site" active centers. Equipped with such information, minute changes in hydrophobicity and local composition (e.g., replacement of one Si by a Ge) can be wrought so as to boost the performance of the catalyst. The merits of using combined *in situ* X-ray absorption spectroscopic and X-ray diffractometric measurements are also highlighted.

1. Introduction

If it is our ambition as experimentalists to design new or superior solid catalysts, it follows inexorably that we must first acquire detailed structural information about the nature of the active sites present in existing, highly efficient ones. For heuristic purposes, consider the situation in regard to enzymes. Less than 40 years ago, essentially nothing was known in quantitative terms about the structure of a single enzyme. Consequently, in the absence of an awareness of the atomic architecture of the active sites of enzymes, there were only rather vague mechanistic pictures of how particular enzymes functioned. Still less was there any possibility of assembling a modified enzyme, either chemically or by genetic manipulation.

In 1965, thanks to detailed *in situ* X-ray crystallographic studies[1] carried out on an enzyme (lysozyme) during the course of its catalytic action, the situation changed dramatically. Ever since that time, protein engineers have become increasingly expert at designing new biological catalysts, principally because they know (i) what the precise, atomically resolved structure of the active sites in many natural (wild) enzymes is, and (ii) the atomic changes that should be made in the vicinity of the active sites so as to boost either the enzyme's activity or its selectivity or both.

Being interested, as we have been for some time,[2] in designing powerful solid inorganic catalysts, X-ray absorption fine structure (XAFS)[3] has presented us with the means of acquiring the information we require—under *in situ* conditions. (Under ideal circumstances, X-ray diffraction is the preferred structural tool, but this technique fails for many catalytic materials, since the concentration of active sites is low and they do not possess any long-range order.) There are other means,[4] besides XAFS, of probing active sites *in situ*. One method entails a so-called "isotopic jump" procedure,[5] whereby ^{18}O-, ^{13}C-, or ^{2}H-rich reactants are suddenly introduced into the sphere of reaction in place of their ^{16}O-, ^{12}C-, or ^{1}H-containing analogues, and their fate is followed as a function of time. This affords useful mechanistic insights as to which bonds are ruptured or formed and in which sequence. But it cannot address the fundamental question of the structure or architecture of the active site, without which we are incapable either of deducing the detailed mechanism of the reaction or of knowing which structural changes to effect in order to alter the performance of the catalyst.

Likewise, FTIR or Raman spectroscopy or ellipsometry can probe[4a,6] catalysts, noninvasively, under *in situ* conditions, but they can seldom, if ever, yield reliable and

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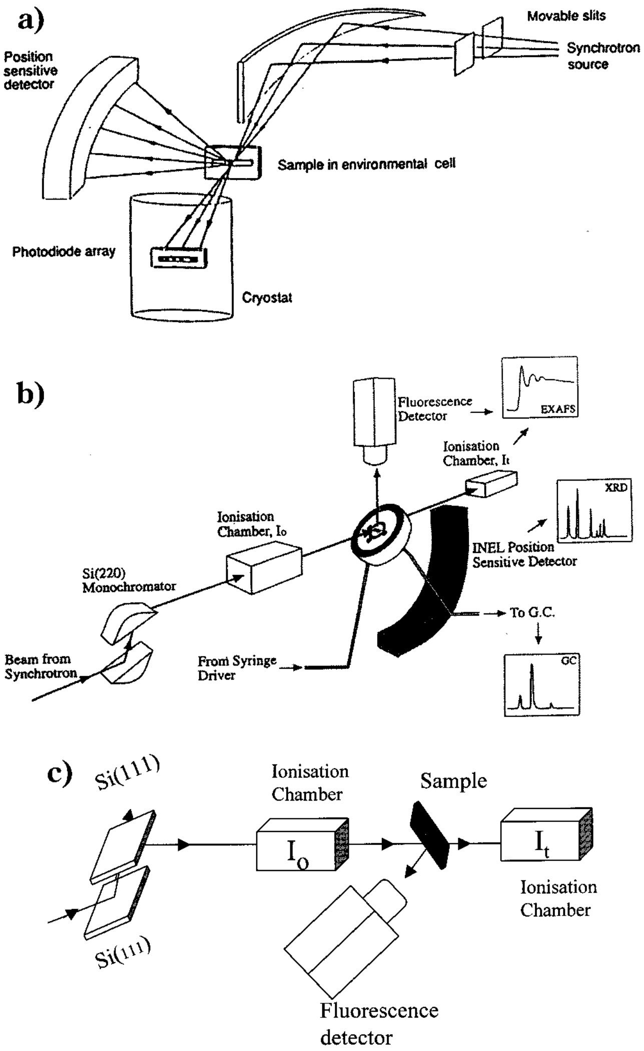
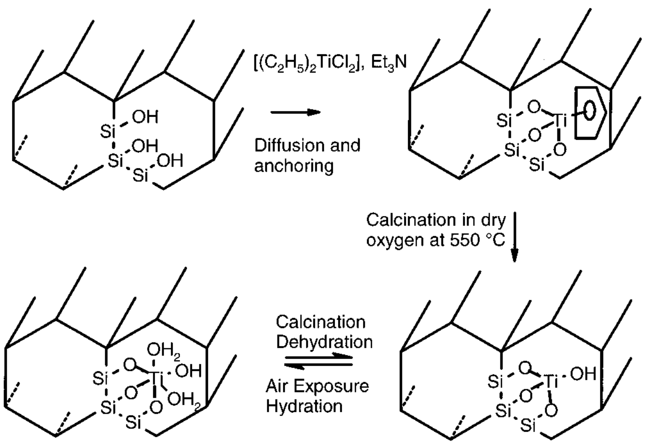


FIGURE 1. (a) Setup for *in situ* combined X-ray absorption spectroscopic and X-ray diffractometric measurements. The photodiode array enables the spectra to be recorded by energy dispersion. (b) Setup for combined XRD/QuEXAFS (quick EXAFS, see text). (c) Typical setup for recording EXAFS by the step-scanning mode.

Scheme 1



comprehensive structural data about the active sites. X-ray photoelectron spectroscopy or photoelectron microscopy as well as a number of electron- or ion-scattering procedures yield useful information, but these techniques, too, like many others such as low-energy electron diffraction or Auger-electron spectroscopy, operate in high vacua and are, therefore, unsuited for *in situ* studies of real catalysts.[4]

It is well known that the structure of a solid surface, as well as its electronic properties, is profoundly influenced by the reactant gases to which it is exposed, and the properties are very different from those of the surface in vacuo. Indeed, some surface phases thought to be implicated in catalysis under ambient conditions (such as palladium oxide, PdO, in auto exhaust catalysts) are unstable and cannot even exist in high vacua, so that there is limited benefit in persisting excessively with the study of certain “model” surfaces in vacuo, when it is known that “real life” catalysts are structurally, compositionally, and otherwise different from their idealized analogues in vacuo.

Of all the techniques now available—and there are many[4–6]—for the targets adumbrated above, few can compare with those based on synchrotron radiation,[4,7–11] and of these XAFS is pre-eminent. With high fluxes of penetrating and continuously tunable X-rays, XAFS yields atom-specific structural and electronic information concerning bond lengths, coordination numbers, and mean-

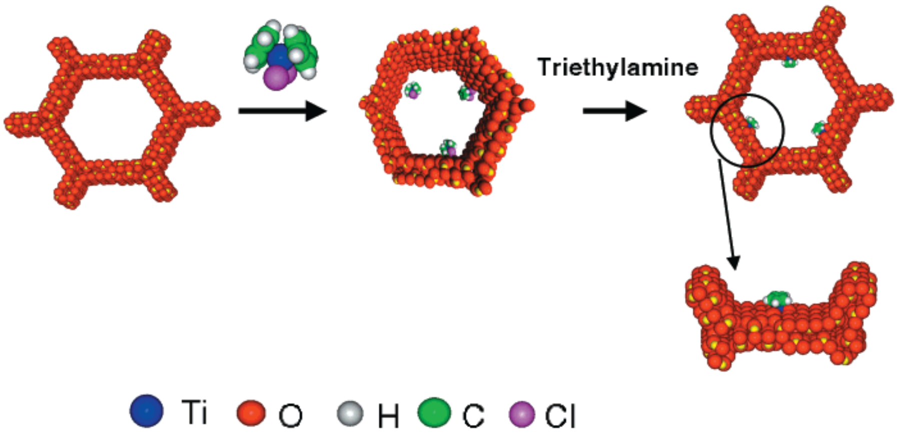


FIGURE 2. Color graphic illustration of the various initial steps in the preparation of the Ti^{IV}-centered active site. The titanocene dichloride in the presence of the triethylamine becomes anchored via the silanol groups on the inner wall of the mesoporous silica (MCM-41) to form a half-sandwich compound. This, on calcination, forms the tripodally anchored Ti^{IV} active center, designated Ti↑MCM-41.[24]

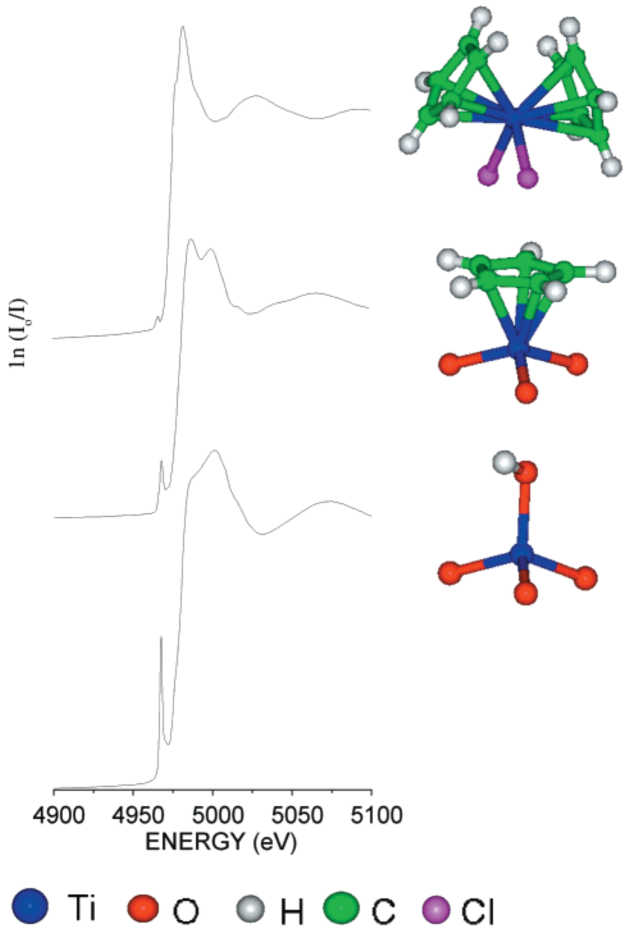


FIGURE 3. Ti K-edge XANES of the Ti↑MCM-41 catalyst before (middle) and after (bottom) calcinations. For comparison, the XANES spectrum of the starting titanocene dichloride is also shown, on the top. The structural models derived from both the XANES and EXAFS spectra—latter not shown—are also given adjacent to the XANES spectra.

square deviation in bond distances as well as the oxidation state. And, if an appropriate *in situ* cell is used, this information may be obtained as a function of temperature and in a variety of ambient conditions involving reactant or product species. Such information may be obtained even when there is no long-range (crystallographic) order: XAFS yields strictly local, short-range structural information. When, however, the technique is used under *in situ* conditions in combination with X-ray diffraction (XRD),[3e,4,10] both short- and long-range structural information becomes available, and this yields far greater insights than the deployment of either technique alone. In a microporous or mesoporous catalyst, it is vital to know not only the atomic structure of an active site, but also whether the long-range structural integrity of the porous catalysts remains intact during use. The activity and selectivity of micro- or mesoporous catalysts may be completely destroyed if their open structure collapses during use, even if the local structure of the active site is preserved.

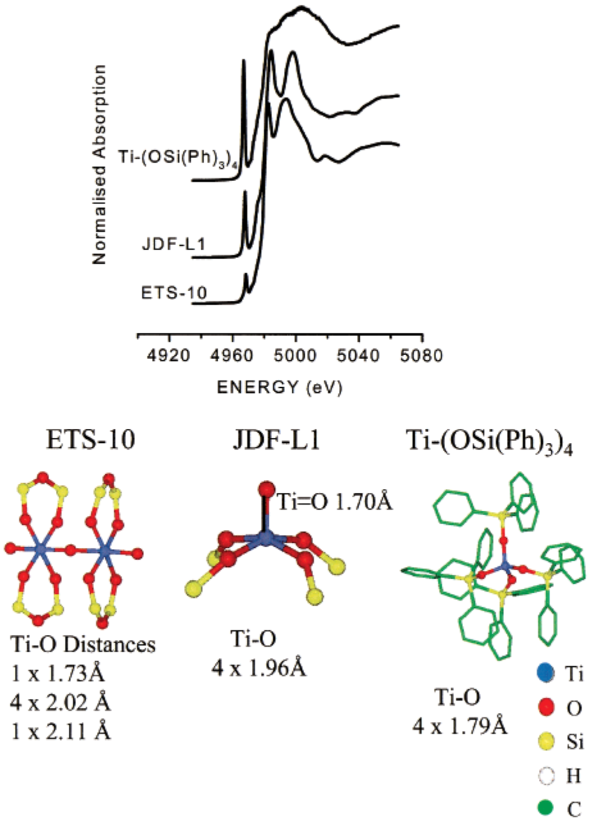


FIGURE 4. (Top) Ti K-edge XANES of three X-ray crystallographically well-defined (see text) titanosilicates in which there is four-fold (Ti-(OSi(Ph)$_3$)$_4$), five-fold (JDF-L1), and six-fold (ETS-10) coordination of oxygens around the central Ti^{IV}. The pre-edge feature, which is primarily due to 1s→3d transition, can be used qualitatively to determine the local coordination geometry of the titanium centers. (Bottom) Salient features, including Ti−O distances, of the three respective model compounds.

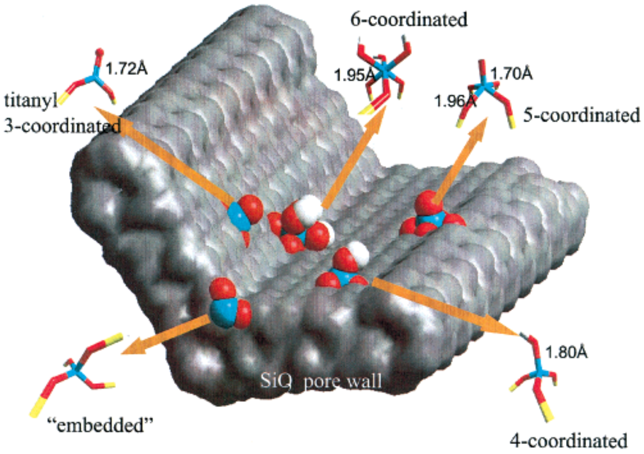


FIGURE 5. In principle, Ti^{IV} ions laid down onto or embedded into mesoporous silica may take up three-, four-, five-, or six-fold coordination, possessing the various (known) bond distances given here. It is the four-coordinated structure (see bottom right) that dominates, as proved by our XAFS measurements (graphics by Dr. D. W. Lewis).

2. Outline of Technique

We and our colleagues have used[10−15] two variants of the combined XAFS−XRD experiment. Greater energy resolu-

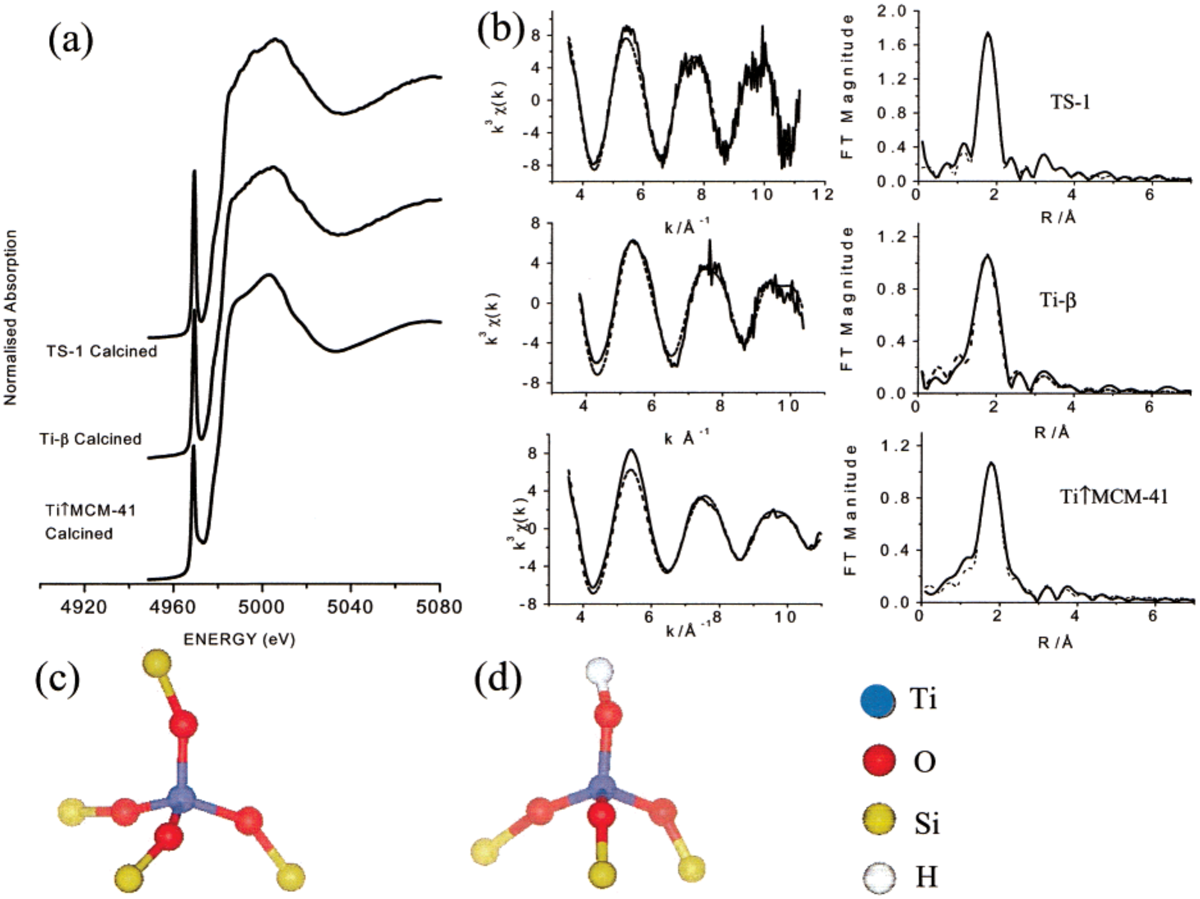


FIGURE 6. Comparison of (a) XANES and (b) EXAFS (with the associated FT's on the right) data for three titanosilicate catalysts: TS-1, Ti-zeolite beta, and Ti↑MCM-41.[4b] The two common local structural models are shown in (c) and (d). It is the tripodally bound (bottom right) Ti^{IV} center that predominates in Ti↑MCM-41. No more than 5% of the sites are bipodally attached to the silica.

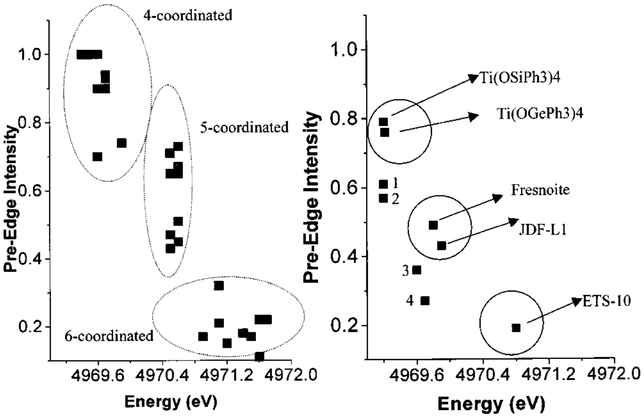


FIGURE 7. Plots of pre-edge intensity versus energy of the pre-edge peak. (Left) Data for a range of Ti-containing minerals.[22] (Right) Data obtained in our studies of a range of titanosilicates. In fresnoite and JDF-L1, there is five-fold (square-pyramidal) coordination of the Ti^{IV}; in ETS-10, six-fold (octahedral). All the others (filled squares) have four-fold (tetrahedral) coordination. Compounds 1−4 refer, respectively, to cyclohexylsilsesquioxane−Ti−$OSiPh_3$, cyclohexylsilsesquioxane−Ti−$OSnPh_3$, cyclohexylsilsesquioxane−Ti−$OGePh_3$, and Ti↑MCM-41 during catalysis.

tion (which is typically ±1.0 eV in the position of absorption edges) is achieved in the scanning mode (Figure 1b), but faster speed in acquiring data is a feature of the dispersion model (Figure 1a), which uses an array of photodiodes as a detector for the absorption spectra. In each case, a position-sensitive detector records the diffractograms over a range of 2θ which typically extends from 10 to 60°. The scanning mode enables so-called QEXAFS (Q for quick) data to be recorded[13] (Figure 1c). (Recently, Frahm has achieved millisecond time resolutions in recording XAFS by using a piezoelectric drive mechanism.) Often, because of the small concentrations of active sites present in inorganic catalysts—in the Ti−SiO_2 catalysts discussed below, for example, Ti/Si ratios seldom exceed 1:50—it is not possible to acquire reliable XAFS data in the transmission mode. Under these circumstances, it is essential to use a sensitive, multielement fluorescence detector, such as the 13-element germanium one that we and our collaborators at Daresbury have routinely used.[13,14]

Reaction cells for our studies were fashioned according to the needs of the reaction conditions under which the catalysts operate. Gas−solid studies have been carried out with cells that permit temperatures up to 900 °C to be explored,[14] and also liquid−solid ones[2c,15] for use at lower temperatures. In each case, the products of catalytic action may be quantitatively monitored using on-line mass spectrometry and/or gas chromatography.

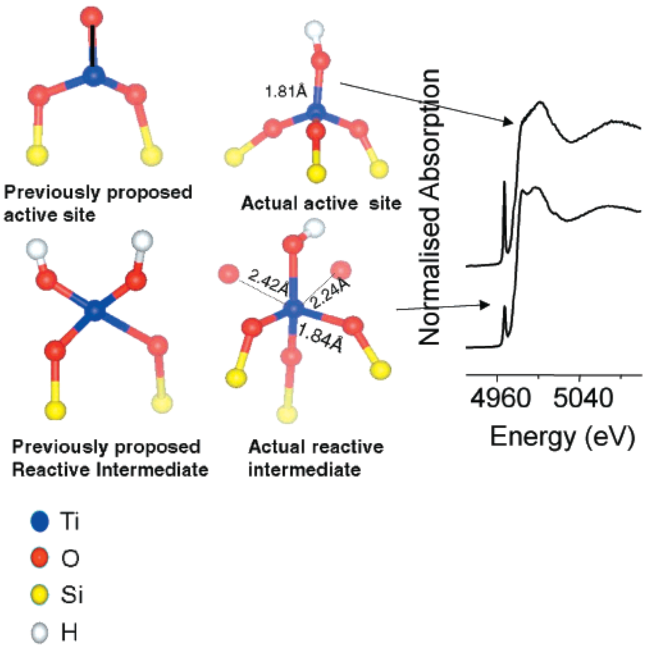


FIGURE 8. XANES spectra of a range of Ti^{IV}-containing species, showing strong pre-edge (1s→3d) peak (on the right). The active site's XANES signature is significantly changed (indicating expansion of the coordination shell) during catalysis. On the left are hitherto proposed[21a] models for the active site and the alleged reactive intermediate. XAFS gives no indication that either of these is implicated in the epoxidation. The average local structural models derived from our EXAFS data for the actual active site and the actual reactive intermediate are shown in the middle.

3. Ti^{IV}-Centered Epoxidation Catalysts

Catalytic oxidation processes play[16–18] an important role in the industrial production of fine chemicals and several other commodities, and, in particular, liquid-phase epoxidations of olefins proceed in the presence of hydroperoxides as oxidants over catalytic systems that contain titanium. For example, the catalytic conversion of propylene to propylene oxide over Ti/SiO$_2$ in the presence of *tert*-butyl hydroperoxides (TBHP) is an industrially important epoxidation that accounts for an annual production of more than a million tons of propylene oxide worldwide. From the outset, there has been much speculation as to both the nature of the active site and the mechanism of this reaction and of other selective oxidations effected by titanium-centered catalysts.[18,19] Five years ago, we set out[20] to prepare single-site Ti^{IV}-centered, silica-based catalysts by reacting titanocene dichloride in the presence of triethylamine with the silanol groups that line the inner walls of mesoporous silica (Scheme 1, Figure 2). Detailed analysis of the XAFS data of the resulting catalyst showed that its structure is as shown in Figure 3. This we designated[25] Ti↑MCM-41.

Both the XANES (X-ray absorption near-edge structure) and the EXAFS (extended X-ray absorption fine structure) results for this catalyst revealed that isolated Ti^{IV}-centered active sites, composed of a tripodally linked titanol groups (Figure 3, bottom), abound on the catalyst surface. There were no signs of Ti–O–Ti linkages, nor of any titanyl (Ti=O) groups of the kind proposed by Sheldon and others,[21] nor of a three-coordinated nor of a five-coordinated kind. Detailed comparisons with several other, independently determined structures (Figure 4) of analogous Ti^{IV}-centered silicates (again encompassing XANES and EXAFS) left no scintilla of doubt that the active sites in our highly active Ti↑MCM-41 catalyst are four-coordinated. In particular, the pre-edge intensity arising from the transition between core level (in this case 1s) to an unoccupied or a partially occupied level (3d, which is unoccupied since Ti^{IV} is a d^0 system) is known to be sensitive to the symmetry of the coordination environment. For example, lack of inversion symmetry for a tetrahedral coordination geometry yields an intense peak, whereas systems with octahedral coordination have small pre-edge intensities. In particular, five-coordinated systems, where there is a double bond (as in JDF-L1, Figure 4), have intensities that are intermediate between those of the octahedral and tetrahedral cases. It has recently been shown[22] that not only the intensity but also the position of the pre-edge is sensitive to coordination environment (see later, Figure 7).

No evidence exists for three-, five-, or six-coordinated Ti^{IV} centers in the activated catalysts (Figures 5–7). Other results involving UV–visible, luminescent spectroscopic, and lifetime measurements[23] suggest that, in addition to the tripodal single-site titanol centers, there are up to 5% or so diol (i.e., bipodal) Ti^{IV} centers also present in the as-prepared Ti↑MCM-41 catalysts.

We also recorded[10b,11,24] XAFS data during the course of operation of the Ti↑MCM-41 catalyst in the epoxidation of cyclohexene to its epoxide with THBP, a convenient test reaction. Significantly, the coordination shell of the original four-coordinated Ti^{IV} centers active site expands to six during catalysis (Figure 8). And, whereas four of the surrounding oxygens are at distances strictly comparable to those in the pristine active site, in the reactive state there are two additional oxygens situated farther away. This observation conflicts with the mechanism proposed in ref 21a (see Figure 8, left). A more realistic picture is one in which, just prior to the act of epoxidation, the Ti^{IV}-centered active site is in 6-fold coordination; a plausible mechanism for steady-state conversion (epoxidation) at the Ti^{IV} center, which takes account of our recent DFT studies with Catlow et al.,[25d] is shown in Figure 9.

4. Creating Catalysts with Enhanced Performance

Just as it is often possible, either by chemical means or by site-directed mutagenesis, to enhance the activity or specificity of a wild enzyme by replacing one of the amino acids in the cleft that constitutes the enzyme's active site by another, it should, in principle, be possible to change significantly the performance of our single-site Ti^{IV}-centered epoxidation catalysts by implementing a subtle

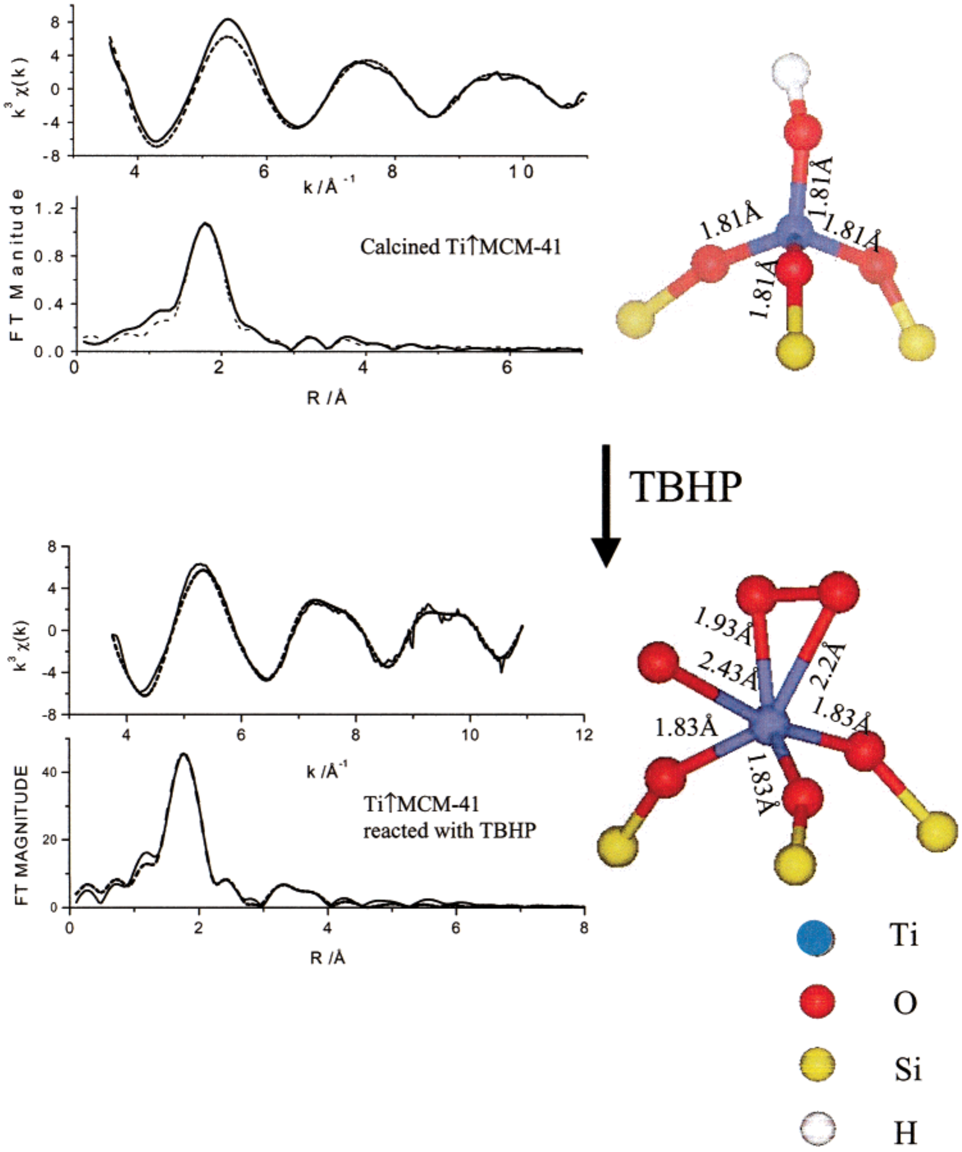


FIGURE 9. Best fit between experimental data and computed EXAFS employing the full multiple scattering method. For this analysis, we considered several plausible starting models proposed on the basis of DFT-optimized structures[25d] for a five-coordinated or six-coordinated species (the numbers refer to the number of near-neighbor oxygen atoms). Of the various types of coordination, one of them yields an excellent fit (bottom left) between the computed and observed (recorded during reaction) EXAFS data. The computed data refer to the model which has the minimum energy derived from the DFT calculation. This model is depicted in the bottom right figure.

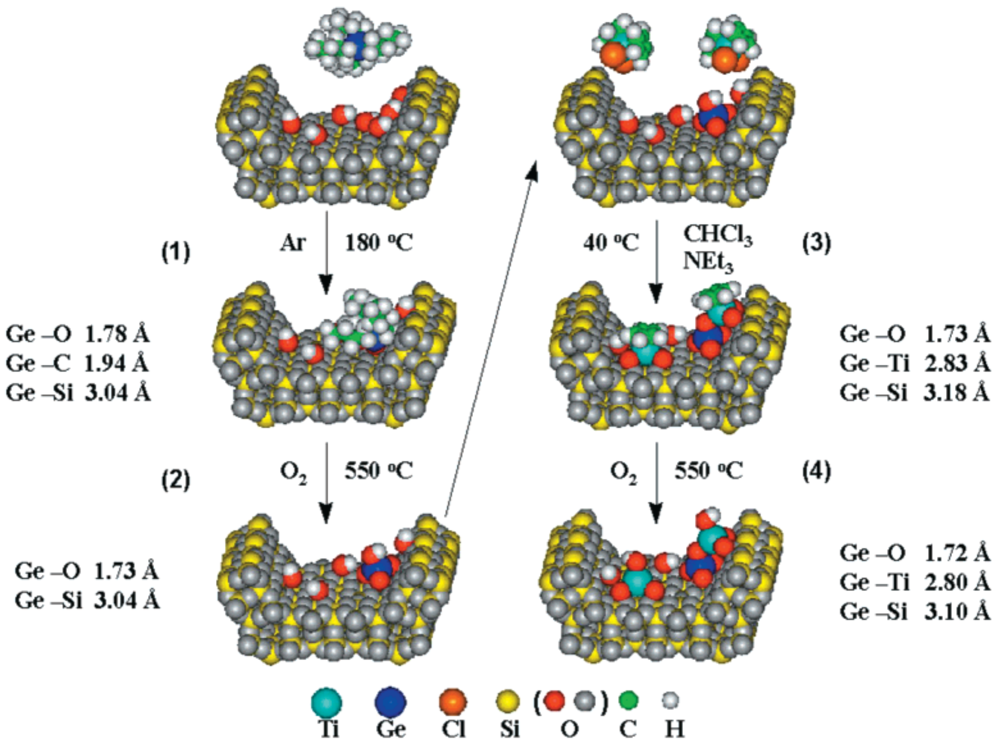
structural-*cum*-chemical change at the active center. This can be done, for example, by replacing one of the silicons in the tripodally attached Ti^{IV} center by germanium using the procedure shown in Scheme 2. The resulting catalyst, with a modified active site, exhibits (Figure 10) an activity for the epoxidation of cyclohexane that surpasses that of the original catalyst, which, in turn, is superior[20b] in activity to the catalyst prepared according to the procedure employed for the preparation of the industrial catalyst. Obviously, there is a favorable electronic influence in proceeding from $(\equiv SiO)_3Ti{-}OH$ to $(\equiv SiO)_2(GeO){-}Ti{-}OH$, its (inorganic) mutant.

There is, however, another quite different method available for improving the activity of the Ti^{IV}-centered epoxidation catalysts that relies on modifying the hydrophobocity of the immediate environment of the active site. By preparing the single-site Ti^{IV}-centered catalyst differently[26] (see Figure 10c), an environment is created around the active site that facilitates the accumulation of organic (olefinic) and alkyl hydroperoxide reactants. This should and does (Figure 10b) indeed lead to a more active epoxidation catalyst, higher in specific activity than any previously reported one.

5. Heterogeneous versus Homogeneous Epoxidation Catalysts

There is merit in examining the catalytic performance of homogeneous analogues of the Ti^{IV}-centered heterogeneous epoxidation catalysts since, inter alia, this will test further the reality of the influence of juxtaposed germanium. Fortunately, soluble, homogeneous analogues of the

Scheme 2



above insoluble heterogeneous Ti^{IV}-centered catalysts may be readily prepared.[27] Titanosilsesquioxanes, in which the Ti occupies one of the eight vertexes of the "cube" formed by alkyl-substituted Si_7O_{12} moieties (Figure 11), are soluble in organic solvents, and they also function as good homogeneous epoxidation catalysts.[28] The compounds Ti($OSiPh_3$)$_4$ and Ti($OGePh_3$)$_4$ are also soluble and function as ideal comparator homogeneous catalysts with an active center akin to that which we have established for the heterogeneous Ti–SiO$_2$ epoxidation catalyst. Moreover, the immediate environment of the Ti-centered active sites in these soluble catalysts may also readily be probed using the XAFS technique.[28]

Significantly, the performances of the heterogeneous and homogeneous Ti^{IV}-centered epoxidation catalysts are comparable,[29] in both the unenhanced and the promoted states, caused by juxtaposing germanium in place of silicon (Table 1). Moreover, the fact that the turnover frequency in absolute terms—number of molecules of the olefin epoxidized per active site per unit time—is essentially the same for the heterogeneous titanosilsesquioxane one lends independent proof, over and beyond that provided by the structural data retrieved by XAFS, that our designed titanosilicate catalyts (see Scheme 1) are indeed single-site ones.

Table 1. Comparison of the Performance of Insoluble Heterogeneous, Single-Site Ti$^{(IV)}$/SiO$_2$ Epoxidation Catalysts with Their Homogeneous Soluble Molecular Analogues

homogeneous catalyst	turnover frequency (h^{-1})	turnover frequency (h^{-1})	heterogeneous catalyst
[c-$C_5H_9)_7Si_7O_{12}Ti(OSiPh_3)$]	18	26 34	Ti↑SiO$_2$ Ti↑MCM-41
[c-$C_5H_9)_7Si_7O_{12}Ti(OGePh_3)$]	52	40	Ti↑Ge↑MCM-41

6. Probing and Improving Active Sites in Other Types of Catalyst by Using Combined XAFS and XRD Studies

The combined XAFS–XRD approach[10,14,30,31] offers unique advantages for the *in situ* investigation of heterogeneous catalysts in that it yields quantitative information which, in turn, (i) establishes the atomic structure of the active site, (ii) offers guidance in the preparation of more powerful catalysts, and (iii) affords reliable insights into the mechanism of the catalytic reaction.

Although we have concentrated in this Account on Ti^{IV}-centered epoxidation catalysts, we have elsewhere employed the combined XAFS–XRD approach for the elucidation of the structure and mode of action of several other heterogeneous catalysts. To emphasize the power of this technique, we conclude by outlining the essence of these studies.

(a) The Active Site in a Solid Acid Catalyst for the Conversion of Methanol to Light Olefins. A family of molecular sieve catalysts in which minute amounts of divalent metal ions (Zn, Mg, Mn, Co, etc.) are framework-substituted in place of aluminum ions in the open structure of a synthetic aluminum phosphate known as AlPO-18 was hitherto described[33] by one of us. Members of this family of Brønsted acid catalysts selectively convert methanol to ethylene, propylene, and butene at modest temperatures. In their calcined (as-prepared) state, Co–

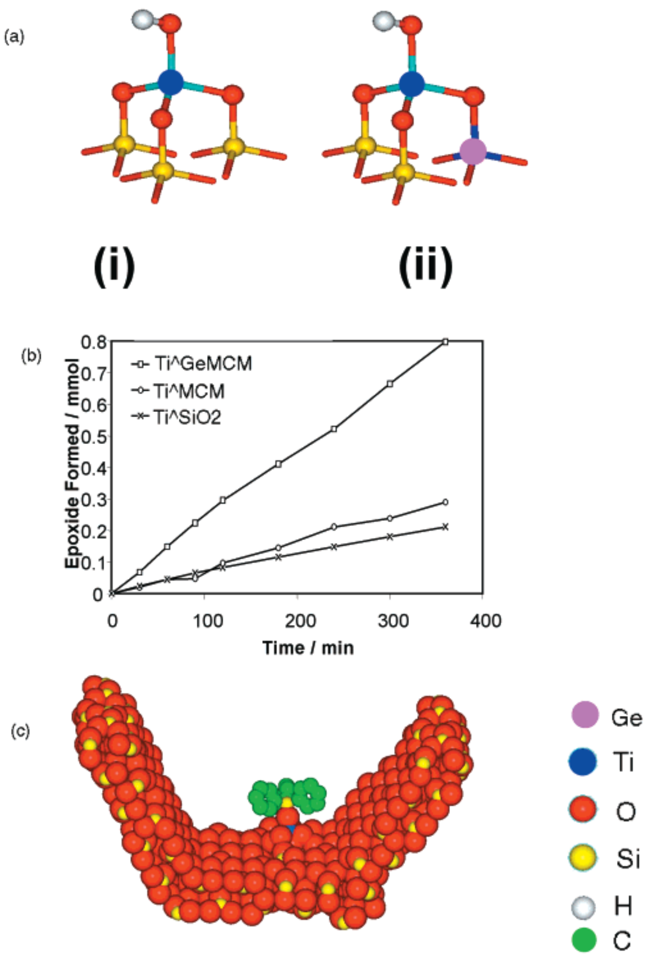


FIGURE 10. (a) Replacement of one of the silicons by germanium in the tripodal active site boosts[20b] the catalytic activity (b), as does the introduction (c) of a hydrophobic[25] group.

AlPO-18 or Mn–AlPO-18 catalysts exhibit no Brønsted acidity (because the transition-metal ions are in their III oxidation states). Upon reduction in hydrogen, however, both the Co^{II} and Mn^{II} forms of the catalysts are very active acid catalysts. Combined XAFS and XRD studies yielded[34] the local structure shown in Figure 12. Similar studies on another Co^{II}-substituted open-structure molecular sieve, known as DAF-4, which has an empirical formula $H_x(Co_xAl_{1-x}PO_4)$, $x = 0.04$, and which also efficiently catalyses the conversion of methanol to light olefins, again yielded precise atomic details of the Co^{II}-centered active site.[35]

(b) Molecular Sieve Catalysts for the Regioselective and Shape-Selective Oxidation of Hydrocarbons by Molecular Oxygen. Combined XAFS–XRD studies on framework-substituted, open-structure aluminophosphates, in which transition metal ions in high oxidation states (such as Co^{III}, Mn^{III}, and Fe^{III}) replace tetrahedrally coordinated Al^{III} ions, leave no doubt[36] as to the electronic nature and precise atomic environment of the catalytically active center. Thus, in the FeAlPO-31 catalyst, which was designed so as to convert preferentially cyclohexane into adipic acid in air,[36c] the Fe^{III} active site could be determined in precise detail. It transpires that the Fe–O coordination number, bond distance, and Debye–Waller factor are 3.85 ± 0.4, 1.85 ± 0.02 Å, and 0.0045 Å, respectively, essentially identical with the corresponding values in framework-substituted Fe–ZSM-5 and $FePO_4$. In all three, the iron ions are present in the Fe^{III} state and are coordinatively unsaturated, with a tetrahedral geometry.

Designed vanadium-centered active sites situated at the inner surface of well-defined microporous (both crystalline and amorphous) and mesoporous siliceous hosts are catalysts,[37] under mild conditions, for both the epoxidation of a typical alkene (such as cyclohexene) and the selective oxidation of a typical alkane (such as cyclohexane). X-ray absorption studies[37] again proved invaluable in determining the nature of these active sties, the performance of which could be boosted (cf. the Ti^{IV}-centered epoxidation catalyst shown in Figure 10) by juxtaposing methyl groups (to enhance the hydrophobicity) in the vicinity of the vanadyl active site (see Figure 13).

(c) Mo-Centered Catalysts for the Dehydrogenation of Methanol. Just as $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ serves as an excellent means of introducing isolated Ti^{IV}-centered, catalytically active sites on a silica support (for epoxidation reactions), so also does[38] $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$ function as a similar precursor for the creation of Mo^{VI}-centered sites (also on mesoporous silica) for the oxidative dehydrogenation of methanol to produce formaldehyde. Mo K-edge XAFS shows that, at low loadings (ca. 1 mol % on mesoporous silica), isolated MoO_4 species are generated on the surface, whereas at higher loadings (ca. 4 mol %) there is evidence for the formation of dimeric and some polymeric oxomolybdenum species.

The isolated oxomolybdenum species in this selective oxidation catalyst are attached less strongly than the oxotitanium species (described earlier) in the Ti–SiO_2 epoxidation catalysts. The tripodally attached Ti^{IV} centers are known[39] to be a good deal less vulnerable to leaching than bipodally attached ones. The same appears to be true of Mo^{VI} centers.

(d) Baeyer–Villiger Oxidations. We have shown[40] that redox molecular sieve catalysts MAlPO-36 (M = Mn or Co) convert cyclopentanone, cyclohexanone, 2-methylcyclohexanone, and adamant-2-one to their corresponding lactones with high efficiency (selectivities in excess of 90%, conversions in the range 50–85%) in the presence of O_2 and PhCHO as a sacrificial oxidant. Again, core-shell XAFS measurements established beyond doubt that the catalytically active sites are framework-substituted Mn^{III} and Co^{III} ions, held tightly within the microporous solid, the structural integrity of which is affirmed by XRD studies. The key point here is that the aldehyde is first converted by O_2, at the Mn^{III} or Co^{III} active sites, *in situ*, into the corresponding peroxy acid inside the micropores, and this, in turn, leads[2c] to the production of the lactone.

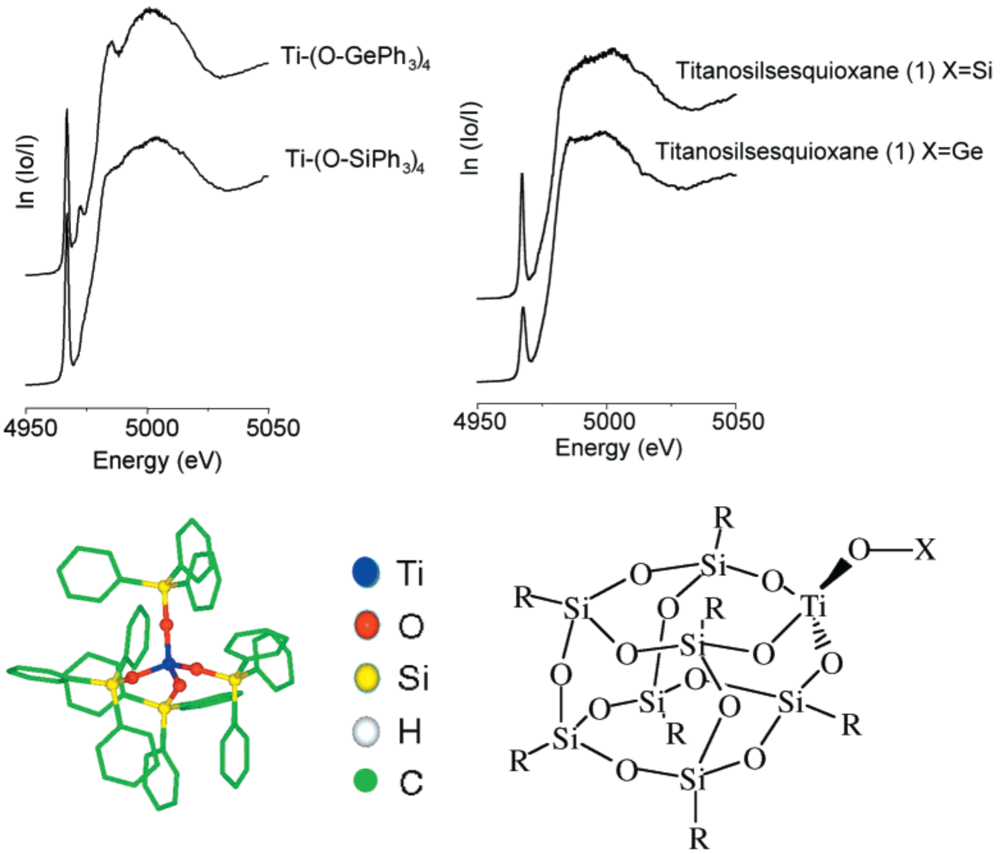


FIGURE 11. (Right) Ti K-edge XANES of $C_6H_{11}Si_7O_{11}Ti{-}O{-}X$ (cyclohexyltitanosilsesquioxanes, with X being either $SiPh_3$ or $GePh_3$) are soluble catalysts with active centers closely akin to that in Ti↑MCM-41 (see Figure 3, bottom left). (Left) $Ti(OSiPh_3)_4$ and $Ti(OGePh_3)_4$, with their respective XANES spectra (see text).

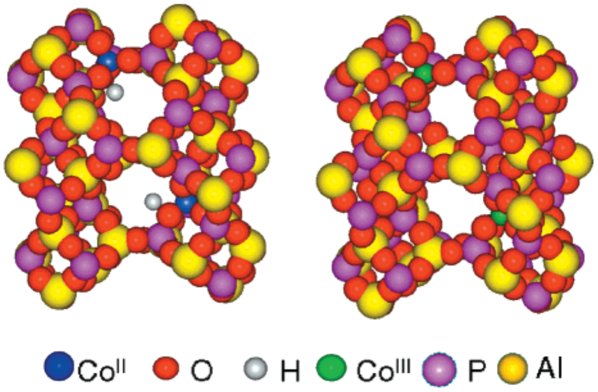


FIGURE 12. Atomically resolved structure of the catalytically active (Brönsted acid) center in Co^{II}−AlPO-18, determined[34] by a combined EXAFS−XRD study using setup shown in Figure 1b.

(e) Catalysts for Environmental Protection. Hydrotalcite structures containing copper, magnesium, and aluminum in the metal hydroxide layers have been investigated[41] by combined XAFS−XRD to ascertain their efficacy as catalysts for the decomposition and reduction of nitrogen oxides. Using *in situ* studies, these combined tools revealed that the copper-centered active species for the decomposition of NO were found to be Cu^{I} ions, and for its reduction Cu^{0} species.

The XAFS−XRD approach is an invaluable one in the design and construction of new solid inorganic catalysts.

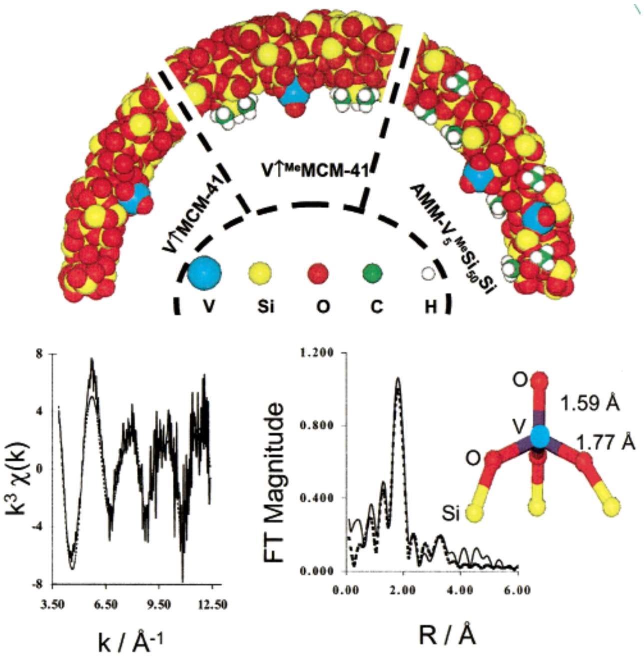


FIGURE 13. (Top) Vanadyl active site (for selective oxidation of hydrocarbons): (left) grafted on to a mesoporous silica; (center) surrounded by nearby surface methyl groups; and (right) in a vanadium-rich amorphous mixed-metal oxide microporous solid.[37] In the bottom, a typical V K-edge EXAFS and associated FT's of the active vanadium sites are shown.

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