The Ineluctable Need for In Situ Methods of Characterising Solid Catalysts as a Prerequisite to Engineering Active Sites

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Abstract: Ultimate success in the design of solid oxide catalysts as well as other covalently bonded or heterogenised organometallic catalysts predicates knowledge of precisely what structure it is that has to be targetted. This, in turn, demands the greatest possible precision in determining, under operating conditions, the structure of the catalyst in general and of the active site in particular. Combined X-ray absorption spectroscopy and X-ray diffraction are ideal tools for such in situ investigations. Examples of such studies and of engineered catalysts, the structure of which have been determined in atomic detail, are given.

Keywords: enzyme catalysis · EXAFS spectroscopy · heterogeneous catalysis · synchrotron radiation · X-ray absorption spectroscopy

Introduction

It is a paradoxical but indisputable fact that the vast majority of fundamental studies of heterogeneous catalysts have been carried out on model systems and generally at pressures far below atmospheric. Whilst it is recognised that there is intrinsic merit in the reductionist approach, which entails detailed separate investigations of the perceived individual steps involved in an overall process—for example, the rates of adsorption of reactants, of their surface migration and rearrangement and of desorption of products—it is also necessary, especially if the ultimate aim is to engineer new catalysts, to focus on the real-life situations that solid catalysts experience. Such catalysts often operate at quite elevated pressures and generally at high temperatures and frequently have surface phases and structures which are thermodynamically and kinetically unstable at low ambient pressure (ca. 10^{-6} Torr), the conditions used for model studies with single crystals. For instance, supported particles of palladium (as in an auto-exhaust catalyst), when exposed to air, form an oxide layer at elevated pressures; but this layer is unstable at the low pressures typical of those used in ultra-high vacuum systems for single-crystal studies. It is therefore highly desirable to seek ways of retrieving information about the nature and structure of the active sites and to do so using tools and techniques that yield atomic details pertaining to the catalyst during the actual course of turnover of reactants.

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Discussion

Lessons from the Enzymologist and Protein Crystallographer: Enzymologists, protein engineers and biologically oriented chemists have long adopted such a strategy, the first step of which consists of determining detailed structural aspects of their particular brand of catalyst. And this they do usually by pursuing X-ray structural investigations of the solid catalyst (enzyme) prior to, during, and after the reactants (substrates) or inhibitors are bound to the active site. Take, for example, the landmark studies (thirty years ago) of Phillips[1, 2] who, through his structural determination of lysozyme and his discovery of the catalytic pocket—lined with a diad of amino acids that constitute the active site—was able to formulate a plausible mechanism for the mode of action of this enzyme. In the intervening years, molecular biologists have been so successful in probing the mechanisms of enzymatic conversions by time-resolved high-resolution X-ray diffraction that standard texts[3, 4] now describe the merits of their conceptual approach in the elucidation of both the mode of action and also in the deliberate modification of the active centres of these catalysts. The recent work of Verschueren et al.[5] on haloalkane dehydrogenase—where the structure of the enzyme and the mechanistic details of its function were elucidated by X-ray studies in the presence of substrate (1,2-dichloroethane) at low pH and low temperature (4 °C) as well as at higher pH and room temperature—is a striking example. So also is the earlier study of Brown et al.[6] on the catalytic breakdown of transfer RNA by lead ions, where the precise siting of the latter and their role in cleavage of the sugar–phosphate backbone of *t*-RNA was deduced from a difference Fourier analysis of the (Pb) RNA above and below a certain temperature at which solid-state reaction becomes appreciable.

Assembling Artificial Enzymes: In due course, armed with refined structural information about the essence of the active

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sites—be they a diad of amino acids in enzymes or of the immediate atomic environment of a metal ion in a ribozyme—it then becomes feasible to assemble modified or miniature variants of natural biological catalysts.

Work on so-called artifical enzymes may be illustrated by reference to the proteolytic enzyme chymotrypsin, the structure of the active site of which was elucidated[7] by in situ X-ray crystallography. The key components of the catalytic reaction cavity of this enzyme are imidazolyl, phenolic and carboxylic groups. Equipped with this knowledge, a way of assembling a miniature artificial chymotrypsin presented itself to Bender et al.[8] They took β-cyclodextrin as the shallow cavity to serve as the molecular recognition pocket and grafted on to its rim—appropriately juxtaposed just as in chymotrypsin itself—the three components (the triad of groups) that constitute the active site. Although there is now some doubt about the validity of the claims made by Bender and co-workers, the conceptual framework that lies behind their overall strategy remains: a synthetic molecular entity of about a hundredth the size and mass of the parent enzyme can be made to function as a catalyst in such a manner as to rival the performance of the natural enzyme. Very recently, Karmalkar et al.[9] have demonstrated that certain hydrogels, when subjected to the techniques of molecular imprinting,[10, 11] exhibit catalytic activity comparable to that of chymotrypsin. The so-called "gelzyme" version of chymoprysin that they assembled by imprinting procedures possess the added virtue of retaining their catalytic performance when subjected to substantial variations in pH and temperature and on repeated cycling.

The Power of Site-Directed Mutagenesis: Of even greater precision, ease of application and significance (so far as the fundamentals of designing catalysts are concerned) is the technique of site-directed mutagenesis.[3, 4, 12, 13] This genetic manipulation procedure enables one or all (sequentially) of the amino acids of the catalytic pocket to be replaced at will by any one of the twenty amino acids used in the processes of life. Moreover, also by site-selective mutagenesis of the amino acids situated at the exterior of the enzyme surface, it is possible to execute subtle structural changes in such a manner as to alter in a profound fashion the electrostatic field in the vicinity of the active site and also the pH dependence of the enzyme. All this enables one to factorise out the various individual influences of the series of deliberate structural modifications upon the overall catalytic performance of the enzyme.

To what degree may the concepts and strategies that have proved so dazzlingly effective in the biological domain be adopted and adapted for fashioned inorganic catalysts? At first sight the prospects look rather bleak. Unlike solid enzymes, made up of myriads of individual molecules each with its characteristic active site and packed into well-behaved molecular crystals readily amenable to X-ray structural analysis, inorganic catalysts, typified by, say, minute crystallites of metal distributed unevenly on amorphous supports (as in Fischer–Tropsch or ethylene oxide catalysts) appear to be singularly ill-suited for well-defined X-ray (or other) crystallographic attacks on the structure of their active sites. Moreover, there is not—and there may never be, in the very nature of things—an inorganic analogue of site-directed mutagenesis.

A Strategy for the Rational Design of Solid Catalysts: But, on closer examination, the real situation is far more encouraging. For reasons that are amplified further below, there are supreme advantages in coming to grips with the fundamentals of heterogeneous catalysis via the agency of molecular sieve, mesoporous or microporous crystalline solids. Briefly, these advantages consist of having—and of creating—solid catalysts which have effectively three-dimensional surfaces of enormous magnitude (up to 1000 $m^2 g^{-1}$) at which there may already exist, or on to which may be quite readily introduced, well-defined single catalytic sites, which are amenable (Figure 1) to a wide range of powerful high-resolution techniques, be they diffraction-based or spectroscopic.

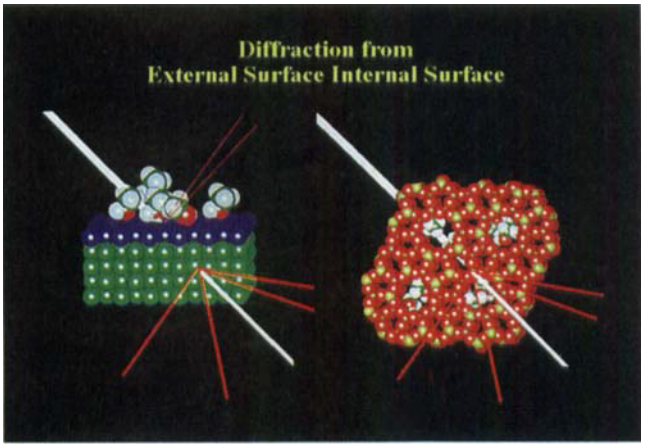

Figure 1. Microporous and mesoporus solids (schematised on the right) have, effectively, three-dimensional sufaces. When their large internal surfaces have active sites it is relatively easy to probe their structure, and that of bound reactant or product species, by means of the appropriate primary beams (of X-rays or IR or UV radiation). With ordinary non-porous solids, active sites or adsorbed species at two-dimensional surfaces (left) yield far smaller signals.

When catalysis proceeds inside (i.e. at the three-dimensional surfaces) of a solid, it is feasible to track,[14] by a panoply of powerful techniques, subtle structural changes at the active sites of the catalyst during the actual catalytic turnover of reactants. This has been the ethos that has governed my own group's work on heterogeneous catalysis for some time.[14–19] My colleagues and I have been motivated by the belief that ultimate success in the rational design of solid oxide catalysts predicates knowledge of precisely what structure it is that we have to target. This, in turn, demands the highest possible precision in determining the structure of the catalyst in general, and of the active site in particular.

It follows ineluctably that such structures must be determined under the conditions of catalysis and that, therefore, in situ techniques should be deployed.[20] And when, in due course, enough becomes known about the nature of the active site the next task is for it to be "recreated" or transplanted in an appropriate (where possible superior) atomic environment.

There are numerous techniques now available for in situ studies of catalysts. Table 1, adapted from a recent monograph,[20] highlights most of them. But potentially new methods constantly continue to appear ranging between such exotic extremes as femtosecond time-resolved FTIR[21] and atomic force microscopy under conditions of hydrodynamic flow.[22] Using

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Table 1. A selection of in situ methods for characterising catalysts (adapted from ref. [20]) [a].

Spectroscopic and optical
Infrared: diffuse reflectance [b], transmission (compressed discs); reflection–absorption
Raman, resonant Raman (laser stimulated) [b]
X-ray absorption (XRA) [b]: pre-edge; near-edge; extended-edge fine structure
Inelastic neutron scattering
Mössbauer [b]
Magnetic resonance [b]: multinuclear, MASNMR, 2D, etc.; ESR (EPR); spin-echo
Fluorescence [b]: lifetime and emission
Sum-frequency generation (SFG)
Elipsometry
Scanning tunnelling
Confocal laser microscopy
Conventional hot-stage microscopy
Diffraction
X-rays [b]: conventional; energy-dispersive; position-sensitive detection
Neutrons
Scanning probe methods
STM
AFM
Tracer and other methods
Positron emission spectroscopy [b]
IR thermography [b]
Nuclear-chemical reactions
Acoustic emission
Kinetic and temporal
Transient response [b] (isotopic labelling)
Temperature-programmed desorption (TPD) [b]
Temporal analysis of products (TAP)
Temperature-programmed reaction spectroscopy (TPRS) [b]: reduction; desulfurisation, etc.
Chromatography [b]: frontal; vacancy; stopped-flow, etc.
Microreactor studies [b]
Combined approaches (examples)
XRD/XRA [b]
SFG/STM
FTIR, XRD, multinuclear NMR
Mössbauer, TPR, XRD
FTIR/microreactor/TPD

[a] None of the methods that require reduced pressure (e.g. controlled-atmosphere electron microscopy or photo-emission electron microscopy) are included here. [b] Readily adaptable for study of commercial catalysis.

synchrotron radiation, a particularly powerful combination of techniques for porous oxide and many other catalysts is that of X-ray absorption spectroscopy (XRA) and X-ray diffraction (XRD). From the former—i.e. the pre-edge, near-edge and extended-edge fine structures (EXAFS)—information pertaining to the immediate atomic environment of the absorbing atom (which is selected to be at, or close to, the active site) is obtained, whereas XRD yields information about the overall structural integrity, and other aspects of long-range order within the phase in question. Figure 2 outlines the deployment of the XRA/XRD combination in in situ studies of either solid–liquid or solid–gas heterogeneous catalytic systems.[23, 24]

Along with major advances in the means of probing solid catalysts under in situ conditions there have been parallel advances in preparative solid-state chemistry, aided by even more recent de novo design of structure-directing[25] organic molecular templates, which have resulted in a burgeoning of the number of distinct mesoporous and microporous solids (which are of catalytic relevance) that now exist. These advances[26–29] have led to an enormous variety of crystalline, porous oxides of nonmetals as well as of metals, encompassing silicas, silica–aluminas, aluminophosphates and aluminoborates, and mesoporous forms (diameter of pores from ca. 20 to 80 Å) of TiO_2, SnO_2, V_2O_5, Nb_2O_5, Ta_2O_5, HfO_2 and so forth. These so-called crystalline sponges,[30] along with the ever-growing families of microporous open-structure phosphates (based on aluminium, gallium, tin and/or transition metals) now mean that about half of the elements of the Periodic Table—with all the catalytic scope and potential that that implies—may be incorporated in the framework of such open crystalline structures which have the three-dimensional surfaces symbolised in Figure 1. With so many new mesoporous hosts to manipulate, great opportunities exist for the grafting or transplanting of accessible, single active sites into such high-area solids. We note that one may:

1) heterogenise an organometallic,[31] or any proven homogeneous catalyst,[32, 33] on a wide variety of oxide or covalently bonded surfaces;
2) control—by adroit change of conditions of synthesis[34, 35] or post-preparative treatment[36]—the hydrophobicity or hydrophilicity of the surface on to which the desired active site is transplanted.

Figure 3 sets out in chart form a selection of some well-known, as well as some very recent additions to the ever-growing number of mesoporous and microporous solids that are important in the context of catalysis. Mesoporous silicas belonging to the so-called MCM-41 family[26] are now so readily preparable that it is often quite straightforward to incorporate during synthesis a heteroatom into their filigree framework. Rey et al.,[37] for example, were readily able to adapt the conditions of synthesis of MCM-41 silicas so as to accommodate one or other of the elements shown in Figure 4.[38]

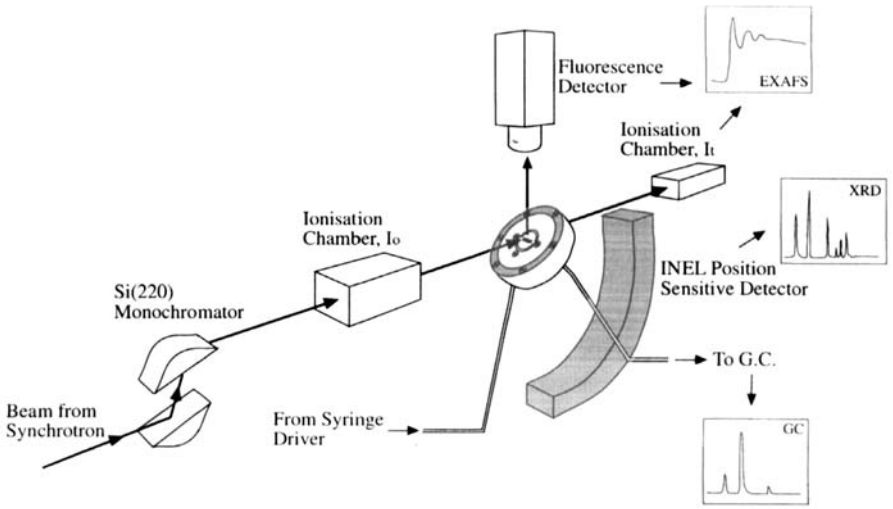

Figure 2. Set-up used (at station 9.3 of the Synchrotron Radiation Source at Daresbury, UK) for the in situ parallel recording of X-ray absorption (XRA) spectra and X-ray diffractorgrams of solid catalysts operating at elevated temperatures and pressures [23].

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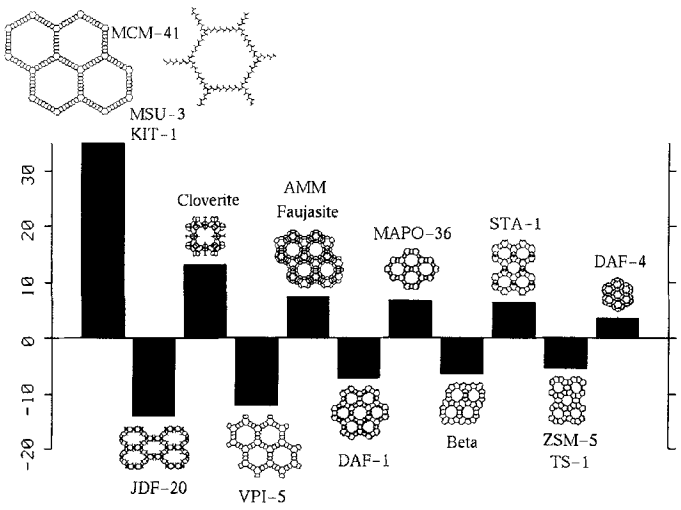

Figure 3. The number of new microporous and mesoporous solids of catalytic significance (see text) has increased dramatically in recent years. The height and depth of the rectangles in this chart are proportional to the pore diameter (in Å) shown at the ordinate (symbols: MCM: Mobil Catalytic Material; MSU: Michigan State University; KIT: Korea Institute of Technology; JDF: Jilin-Davy-Faraday; VPI: Virginia Polytechnic Institute; DAF: Davy Faraday Laboratory; STA: St. Andrews University; etc.—see ref. [24]).

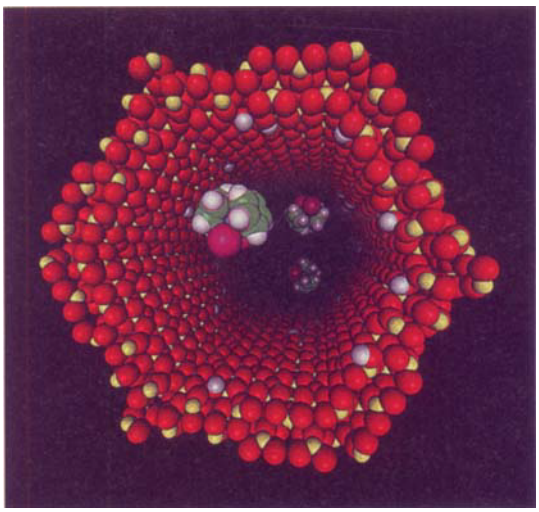

Figure 5. For clarity, a single channel (dia. 30 Å) of a mesoporous MCM-41 silica with its various kinds of pendant silanol (Si–OH) groups, as determined by Chen et al. [40], is shown in the state just prior to reaction with titanocene dichloride.

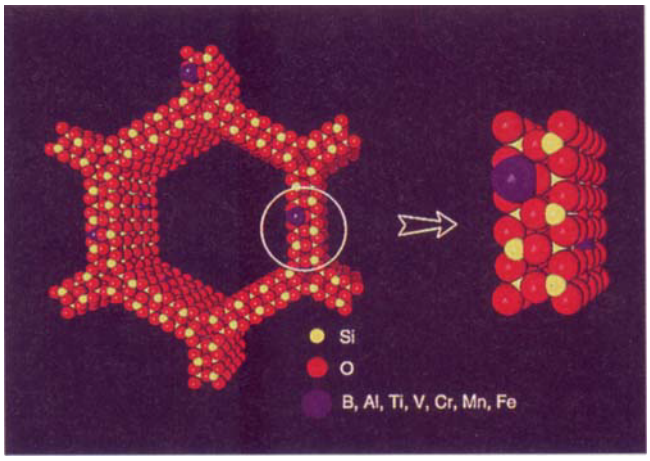

Figure 4. By altering the usual conditions [26] of formation of mesoporous silica of the MCM-41 type, e.g. by deliberate addition of other ingredients (see refs. [37] and [39]) heteroatoms of various kinds (B, Al, Ti, etc.) may be incorporated during synthesis into the thin walls of the filigree silica structure. When Ti^{IV} ions are incorporated in place of Si^{IV} in this way, the resulting material is designated Ti → MCM-41 (see Figure 8).

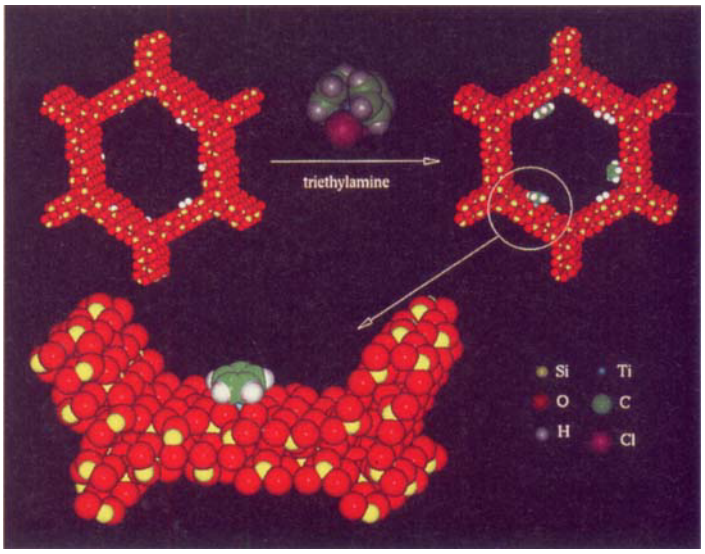

Figure 6. By elimination of HCl (in the presence of Et_3N) between the titanocene dichloride and the pendant silanols, a half-sandwich intermediate is formed (see also Figure 7).

Specific Examples of Atomically Well-Defined Active Sites: We now proceed to illustrate the concept of uniting in situ characterisation on the one hand with engineering active sites on the other.

Fresh insights were obtained by my colleagues and me when we used combined in situ XRA/XRD to investigate catalysts (prepared as described below) differing from one another in the most minor fashion. The Ti^{IV} ions are incorporated into the framework of the mesoporous silica during synthesis in the one (designated Ti → MCM-41),[39] and onto the walls of the large pores of the silica after synthesis by use of titanocene dichloride in the other (designated Ti↑MCM-41).[31] We have shown[31] that the direct grafting of titanocene onto the pendant Si(OH) groups[40] of the inner walls of MCM-41 (see Figures 5 and 6) generates a high-performance catalyst with a large concentration of accessible well-spaced and structurally well-defined Ti^{IV} active sites that are tripodally anchored to the underlying mesoporous silica, as schematised in Figure 7. In situ investigations by XRA of this catalyst yields the results shown in Figure 8a, from which we see the feasibility of quantitatively tracking the Ti^{IV} site from its calcined to its active state. In the case of the synthesis-incorporated Ti^{IV} active sites (Figure 8b), XRA shows a closely similar expansion of the coordination shell from 4 to 6 during catalysis. Note that in both Figures 8a and 8b the pre-edge peaks, prominent when Ti^{IV} is tetracoordinated, decrease in intensity (as expected) during the course of catalysis when the coordination number expands to six. Moreover, when two different *tert*-alkyl hydroperoxide sacrificial oxidants are used—*tert*-butyl hydroperoxide and methylphenylpropyl hydroperoxide (TBHP and MPPH, respectively)—it is found[41] that the turnover frequency of the Ti↑MCM catalyst surpasses that of Ti → MCM by more than an order of magnitude. This is

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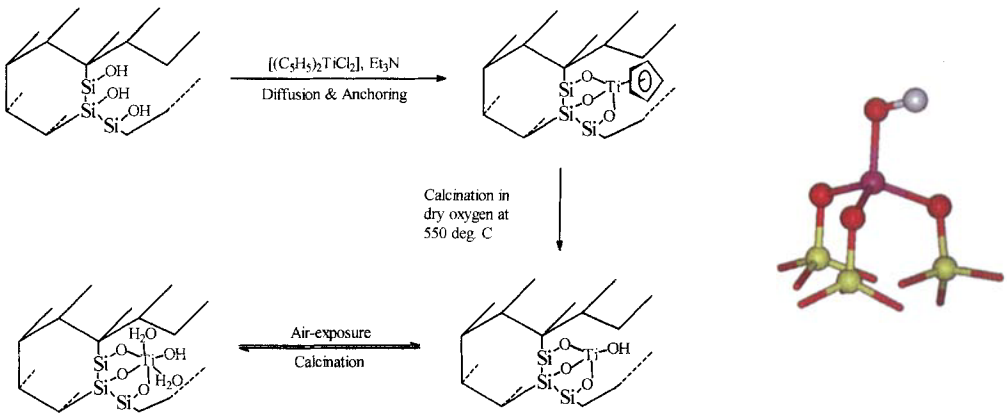

Figure 7. In situ XRA measurements reveal that both the half-sandwich (Figure 6) and calcined materials are tripodally attached to the silica.

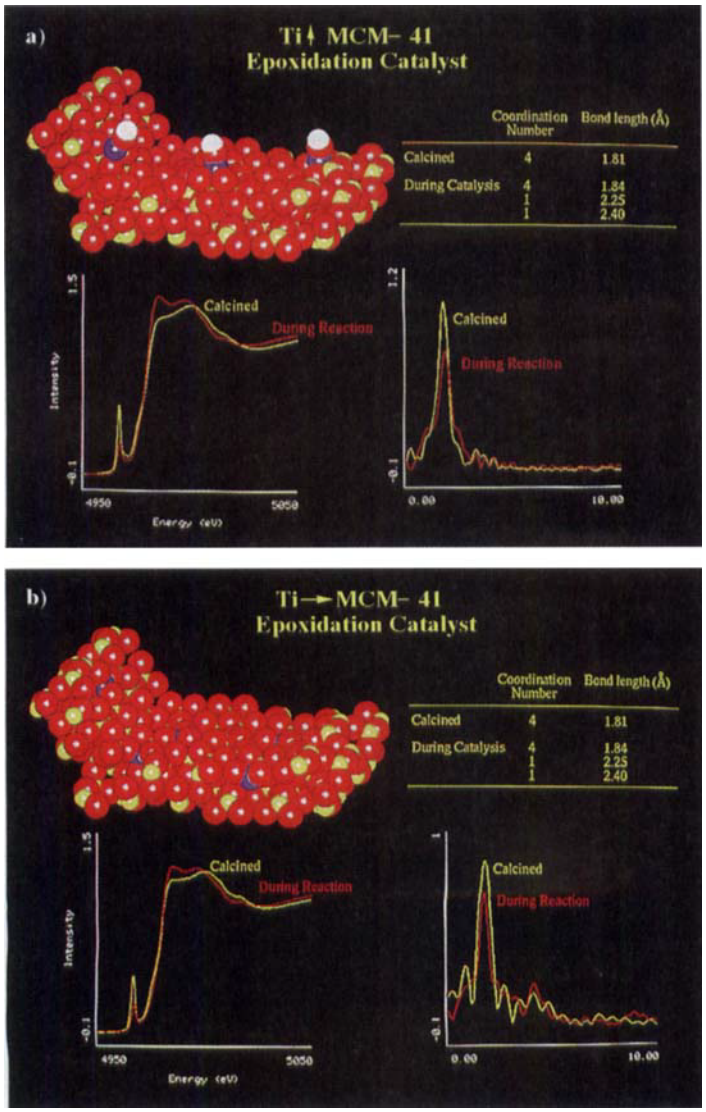

Figure 8. In situ XRA spectra of the reacting epoxidation catalysts Ti↑MCM-41 (a) and Ti → MCM-41 (b) reveal an expansion of the co-ordination shell of the Ti^{IV} ion from four to six. EXAFS analysis, corroborated by the observed changes in pre-edge absorption intensities, yields quantitative data pertaining to the reaction sphere of the active site.

readily understood in view of the contrasting accessibility of the Ti^{IV} sites in the respective catalysts (contrast Figures 8a and 8b). (For both the Ti^{IV}↑ and Ti^{IV} → variants of the engineered active sites, density functional quantum mechanical calculations on appropriate model clusters reveal[42] that there is considerable thermodynamic driving force in proceeding from fourfold coordination, as in the calcined states, to 6-fold coordination, as in the catalytically active states).

By synthesizing a soluble titanosilsesquioxane (Figure 9),[43] which also has Ti^{IV} tripodally attached to silicons via oxygen atoms, one may further test the correctness of the characterisation (by in situ EXAFS) of the Ti^{IV}-centred active site in the heterogeneous catalyst. Solution NMR studies of this molecular analogue (homogeneous) catalyst, as well as an X-ray structure determination of the crystalline form completely vindicate[44] both the catalytic performance and the nature of the active site of the Ti↑MCM-41 heterogeneous catalyst.

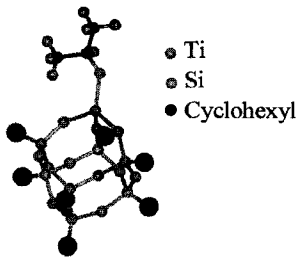

Figure 9. The soluble homogeneous titanosilsesquioxane catalyst, the anologue of that shown in Figure 7 [44].

The second example of an engineered active site is that which we have designated[45] Ti↑Ge↑MCM-41. Here one of the three linkages of the tetrahedrally bonded Ti^{IV} active site is attached, via oxygen, to germanium and two, via oxygens, to silicons, the fourth bond being the exposed hydroxyl. Figure 10 summarises the steps involved in assembling this active site. Briefly, tetrabutylgermanium is used to introduce a veneer of ≡GeOH groups at the mesoporous silica surface. X-ray absorption spectroscopy permits us to track each step in the synthesis of this new catalyst and to retrieve quantitative data pertaining to the precise atomic environment of the active site. The resulting catalyst, which had been modified from the ones described earlier by a single change in the tetrahedral environment of the Ti^{IV} ion, is superior in its activity to its parent (which may be symbolised $Ti(OSi)_3OH$) by a factor of a 140 per cent in the epoxidation of cyclohexene at 30 °C using *tert*-butyl hydroperoxide (THBP) as oxidant.

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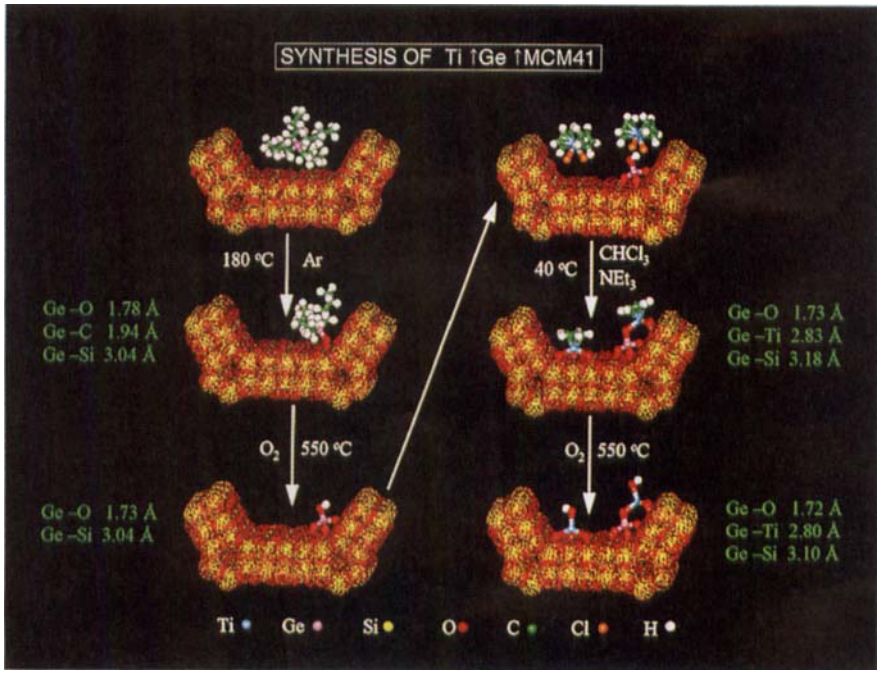

Figure 10. Schematic illustration of the steps involved in converting a MCM-41 silica into a surface that consists of TiOH attached tripodally through three Si-O-Ti bonds and also TiOH attached tripodally to two Si-O-Ti and one Ge-O-Ti bonds. Quantitative data, derived from in situ XRA measurements, are also given [45] for all stages of the conversion from the introduction of tetrabutylgermanium to the silica, to the first calcined state (after introducting some GeOH groups) and to the final calcined state.

The methodologies described above are readily adaptable to many other oxidic and related systems, including designed catalysts[46] for selective low-temperature oxidation of cyclohexane with anchored oxo-centred trimeric cobalt acetate. For the many variants of catalysts based on mesoporous silica or other mesoporous solids of different compositions (such as TiO_2, V_sO_5 etc.) numerous subtle changes in the immediate environment of an active site grafted on to such well-defined high-area surfaces may be wrought by procedures that, conceptually, are akin to the combinatorial chemical approaches adopted for the synthesis of therapeutically important organic compounds (such as the 1,4-benzodiazepine library[47]) or superconducting metal oxides.[48] Whilst preparations of combinatorial libraries of candidate catalysts may ultimately prove to be quite feasible, the evolution of reliable in situ methods of characterisation, involving highly spatially resolved X-ray absorption spectroscopy, may prove more difficult.

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