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Determining the structure of active sites, transition states and intermediates in heterogeneously catalysed reactions

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With open-structure (nanoporous) oxidic solids, numerous distinct kinds of single-site catalysts may be precisely designed. Apart from serving as a means of generating a range of powerful new catalysts (especially for selective oxidations), in which well-defined active sites are carefully engineered, the detailed local atomic environment of these sites may be determined by *in situ* X-ray absorption fine-structure (XAFS) spectroscopy. Moreover, by combining steady-state XAFS studies with density functional (DF) computations the structure of intermediate and transition states along the pathway of heterogeneously catalysed reactions may also be determined.

When **John Meurig Thomas** moved from the Headship of Physical Chemistry in the University of Cambridge to be Director of the Royal Institution of G.B. in 1986, he focussed his research work, hitherto broadly based in solid-state and materials chemistry, on the design, synthesis and *in situ* characterisation of new solid catalysts. **Richard Catlow**, with whom Thomas had been collaborating since 1982, was Professor of Chemistry at the University of Keele and became Professor of Natural Philosophy at the Davy Faraday Laboratories of the Royal Institution in 1989. **Gopinathan Sankar**, formerly of the Indian Institute of Science, Bangalore, joined Thomas' group in 1990. Together with their colleagues, and especially with their collaborators in Cambridge (Brian Johnson and Robert Raja) and Daresbury, these three authors have produced many new catalysts and elucidated their mode of action. One of Thomas' contributions in solid-acid catalysis—the invention of a single-step solvent free synthesis of ethyl acetate—is now the basis of an industrial plant for the production of this substance on a 220,000 tonne per annum scale.Thomas is Professor of Chemistry at the Davy Faraday Research Laboratory (DFRL) and Honorary Professor of Solid State Chemistry at the Department of Materials Science, Cambridge; Catlow is Director of the DFRL and Head of the Department of Chemistry at University College London, where Sankar also holds a joint post as Reader in Geology. The photograph (left to right, Sankar, Thomas and Catlow) was taken alongside the portrait of Michael Faraday who, like his predecessor as Director, Humphry Davy, made pioneering studies in catalysis at the Royal Institution in the early decades of the nineteenth century.

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A brief recapitulation

At the fiftieth Discussion Meeting of the Faraday Society in 1928, T. M. Lowry, seeking to unify the essential features of heterogeneous, homogeneous, biological and photo-catalysis, concluded that their dissimilarities outweighed their similarities. In particular, he highlighted biological (enzymatic) catalysis as by far the most complicated and least understood of these four categories. Paradoxically, this is now the best understood, principally because enzymologists have, in the intervening years, carried out structural studies that have yielded the atomic details of the active sites of enzymes prior to, during, and after the catalytic turnover of the substrates (reactants). (Two 'textbook' illustrations[1] of the veracity of this statement are, first, the Pb ion-catalysed cleavage of the sugar-phosphate backbone of *t*RNA and, second, the dehalogenation of 1,2-dichloroethane by a dehalogenase enzyme—see colour plate 3 and p. 241, respectively, of ref. 1 for experimental details of these *in situ* X-ray structural studies.)

Enzyme catalysts lend themselves rather readily to *in situ* X-ray diffraction studies: a crystal of the enzyme with the reactant bound to its active site at a low temperature (typically *ca.* 5 °C) yields the structure of both the active site and the nature of the bonding of the reactant to it. A repeat structural determination at a temperature sufficiently high (*ca.* 20 °C) to effect conversion reveals details of which bonds have been broken and formed.

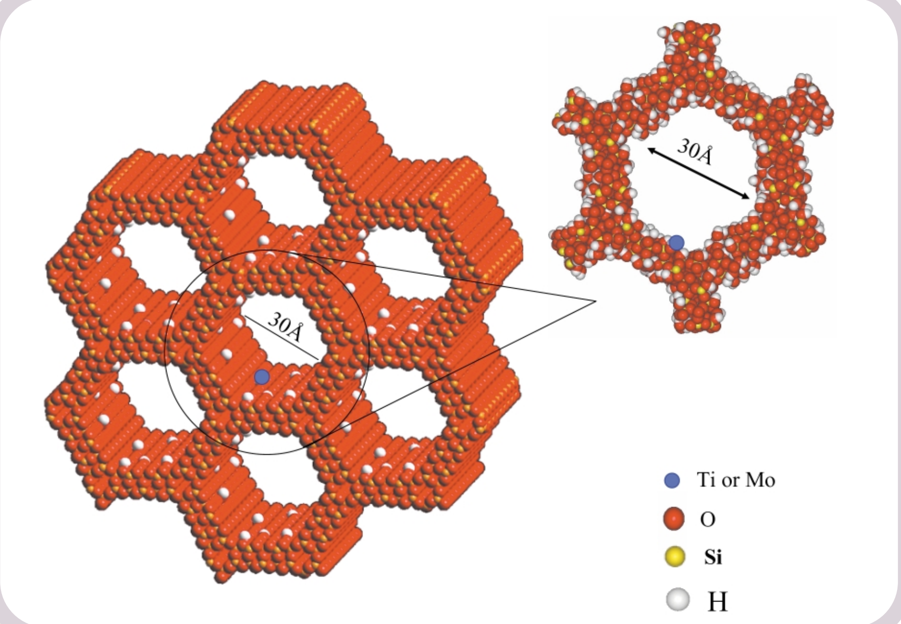

Fig. 2 A large family of nanoporous oxides (SiO_2, TiO_2, Ta_2O_5, Nb_2O_5, *etc.*) may be readily prepared in which the pore diameter may be 'selected' to fall in the range 1.5 to 25 nm. By appropriate methods (see text), catalytically active sites (*e.g.* Ti or Mo) may be 'placed' in a spatially uniform fashion on the interior (three-dimensional) surfaces of nanoporous oxides such as silica. The walls of the mesopores are atomically disordered, as seen in the structure shown as an inset.

In situ experiments of this kind are very difficult, if not impossible, to perform with inorganic heterogeneous catalysts involving supported nanoparticles of metals on oxide or carbonaceous supports or with several other kinds of heterogeneous catalysts that operate at high pressures and high temperatures. In the first place, the residence time of a reactant gas phase molecule (which impinges at a rate of *ca.* 500 m^2 s^{-1}) is extremely short, being of the order of a nanosecond, and, secondly, the movement of reactants in such systems is not restricted to the cavity active sites—generally there are no such cavities in supported metal catalysts.

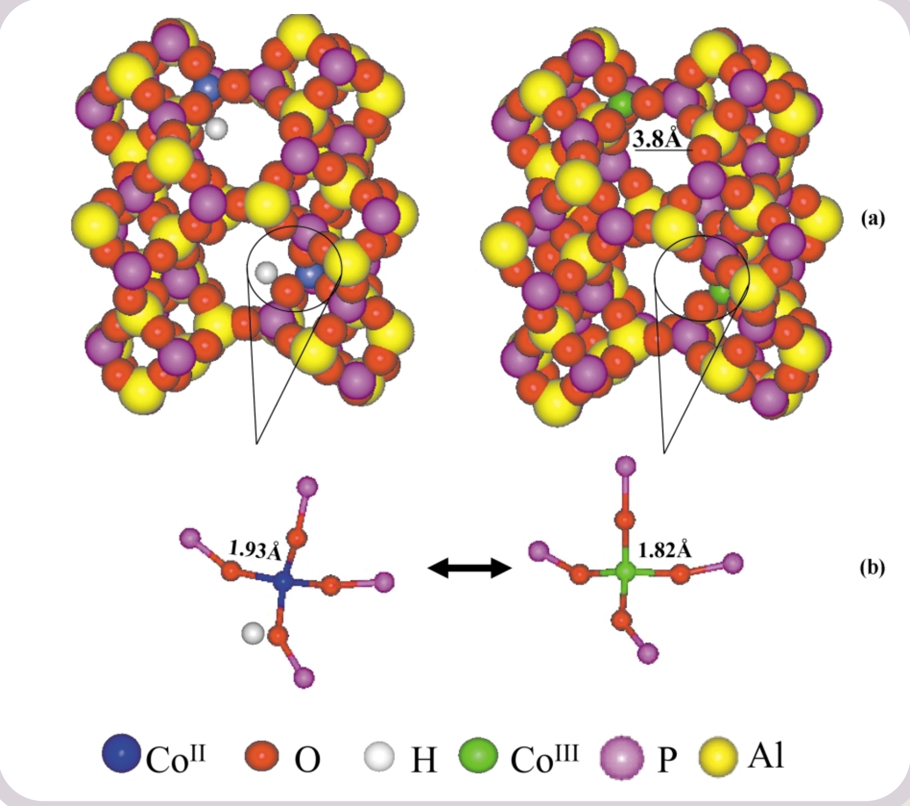

Fig. 1 (a) In the open-structure aluminophosphates (AlPO) (No. 18) some of the Al^{III} framework ions have been replaced by cobalt ions in a spatially uniform fashion. In the Co^{II}AlPO state, the uniform catalyst has Brønsted acidity and in the Co^{III}AlPO state redox properties. The atomic structure of the active sites (b) is determined by *in situ* X-ray absorption fine-structure spectroscopy XAFS.[5]

Uniform heterogeneous catalysts

There is, however, a large and rapidly growing family[1–4] of so-called *uniform* heterogeneous (inorganic) catalysts where well-defined active sites are distributed in a spatially uniform fashion and accessible (to reactants) throughout the bulk of the solid. A specific example is the Co-ion-framework-substituted alumino-phosphate (No. 18) (Fig. 1), abbreviated CoAlPO-18,[5] which in its Co^{II} state is a powerful shape-selective, Brønsted acid catalyst for the dehydration of methanol to yield light olefins,[3]and in its Co^{III} state a regio-selective catalyst for the air-oxidation of linear alkanes at their terminal methyl groups.[6] Open-structure, uniform catalysts of this kind—another example is shown in Fig. 2—have exceptionally large surface areas (often in excess of 600 m^{2}g^{-1}), 95%

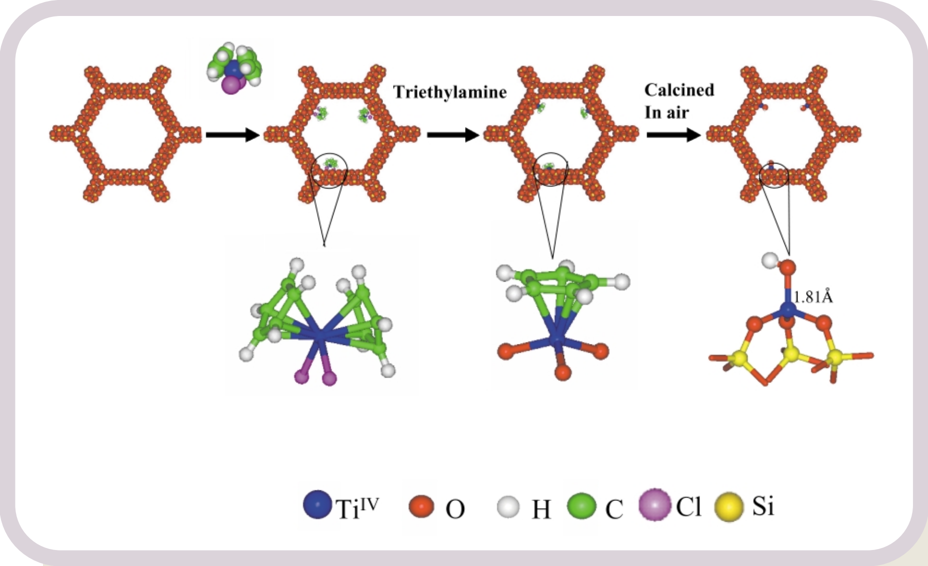

Fig. 3 The interaction of titanocene dichloride ($Ti(Cp)_2Cl_2$) with a porous silica surface leading to the formation of isolated single-site Ti active centres, as well as their precise structure, may be followed and determined by XAFS.[14,15]

(or more, depending on crystal size) of which are inside the solid. In effect, they are inorganic oxides with single-site active centres distributed uniformly over three-dimensional surfaces that permeate the entire materials and are accessible to all molecules small enough to enter (or diffuse out of) the apertures at their exterior surfaces. Because the active sites are distributed throughout their bulk, these uniform heterogeneous catalysts are amenable to the entire panoply of spectroscopic, diffraction, scattering and computational techniques traditionally used in solid state studies.[7] (In the case of CoAlPO-18, the structure of the active site, centred at the Co^{II} ion for the solid acid (Fig. 1(b)), was determined by *in situ* X-ray absorption fine-structure spectroscopy (XAFS).)

Such uniform heterogeneous catalysts present new opportunities to explore, by various *in situ* methods,[8,9] the relationships between structure and catalytic performance by means that are often similar to the way modern enzymologists pursue their investigations. But because the residence times of reactants at active sites even in uniform heterogeneous catalysts are far shorter than those of substrates within an enzyme, it is not possible to use time-resolved, X-ray Laue diffraction, which has been so effective for *in situ* studies of enzymes and other macromolecular catalysts.

It is important to recognise also that, even in the most favourable investigative circumstances of enzymatic catalysis (when the fastest available pulsed synchrotron radiation sources and CCD detectors are deployed under ideal Laue X-ray diffraction modes), it is not yet experimentally possible directly[10,11] to determine the structure of genuine transition states—in the sense that Zewail has determined (by femtosecond methods) the structure of the transition state in, say, the elimination of I_2 from tetrafluorodiiodoethane via the haloethyl radical to C_2F_4.[12] The most that can be, as yet, achieved in structural studies of enzyme catalysis is a determination of the initial state (with or without the substrate bound to the active site), the final state (when the substrate has been converted to product(s) within the active site) and any intermediate structural states taken up within the time-scale (hours to nanoseconds) of the diffractometric measurements.

To determine the structures of the active site prior to reaction, and the transition state during it, in uniform heterogeneous catalysts such as those shown in Fig. 2, we have adopted a joint approach using XAFS[13] and a computational procedure. To be specific, we focus on a Ti-silica heterogeneous catalyst that is the centrepiece of a much-used commercial process for the epoxidation of alkenes by alkylhydroperoxides.[14,15] But the procedures and principles we outline below are generally applicable for all uniform oxidic heterogeneous catalysts.

Because the Ti atoms are distributed uniformly throughout the bulk (on a three-dimensional surface) the reliable bulk technique of *in situ* XAFS may be used to track the entire synthesis of the active catalyst from its precursor, titanocene dichloride (Fig. 3), to the bare active site and through to its catalytically active (steady-state) condition on the interior surface of the silica. By utilising both near-edge (XANES) and extended-edge (EXAFS) structures, we can pin down the precise structure and electronic state of the 'Ti' active site prior to the introduction of the reactants. *In situ* FTIR also shows that an OH group is attached to the titanium, which the XAFS data identified[14,15]

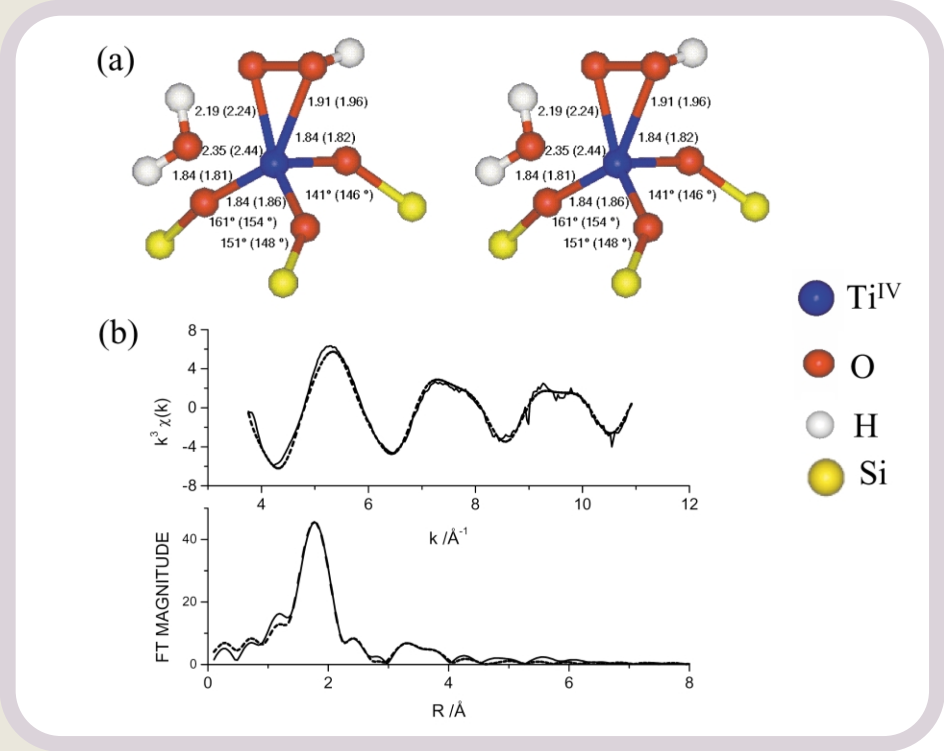

Fig. 4 (a) XAFS analysis shows that, at steady-state during the course of catalytic turnover, the coordination number of the Ti^{IV}-centred active site increases to six (all oxygens), with two of the oxygens at distances greater than 2.2 Å. (The distances and angles shown were derived from Ti K-edge EXAFS data, those in parentheses from DFT computation[16]). (b) Correspondence between experimentally determined EXAFS (full line) and computed data (dashed line) based on measurements made with the Ti^{IV}-centred catalyst during epoxidation.[16]

unambiguously as being in the Ti^{IV} state and tripodally anchored, *via* oxygen bridges, to the silica support. During the actual epoxidation, the XAFS study yields the steady-state structure at the Ti^{IV} centre from which it is seen (Fig. 4(a)) that six oxygens now surround the Ti, two of them at distances greater than 2.2 Å. XAFS measurements show that, at steady-state, no alkene is bound to the Ti^{IV}-centred active sites. To explore further the structural details of the intermediate, we computed,[16,17] using non-local DFT techniques as embodied in the D Gauss code, the initial and final geometries and energies of all the relevant possible routes to it. The calculations were based on the finite molecular cluster approximation using the $(H_3SiO_3)_3$-Ti-OH shown in Fig. 5. As discussed[17] elsewhere, geometry optimisation was undertaken with the silicon atoms fixed to represent the steric constraints of the silica framework.[18]

Our computations examined in detail the reaction between the molecular cluster representing the tripodally anchored Ti–OH active site and the peroxide that lead to the formation of both the η^1 and η^2 intermediates illustrated in Fig. 5, which shows both the calculated geometries of the two resulting intermediates and the transition states for their formation. The computed activation energies are in each case *ca* 40 kJ/mole. Both structures have similar formation energies and the energy barrier for their interconversions is low; both are therefore expected to be present during catalytic turnover. Fig. 4(b) shows a comparison between the calculated and experimental XAFS spectra for the η^2 structure: the agreement is excellent, although the XAFS data are unable to discriminate between the η^1 and η^2 intermediates. However, the key structural feature of the transition state has been identified by this combination of *in situ* XAFS and computation. Our calculations[17] also show how the electrophilic oxygen bonded to the Ti on the Ti–OOH intermediate may readily be attacked by alkenes to form epoxides with the resulting regeneration of the tripodal Ti-OH species as schematised in Fig. 6. In effect, the alkene plucks an oxygen from the peroxy intermediate to form the epoxide.

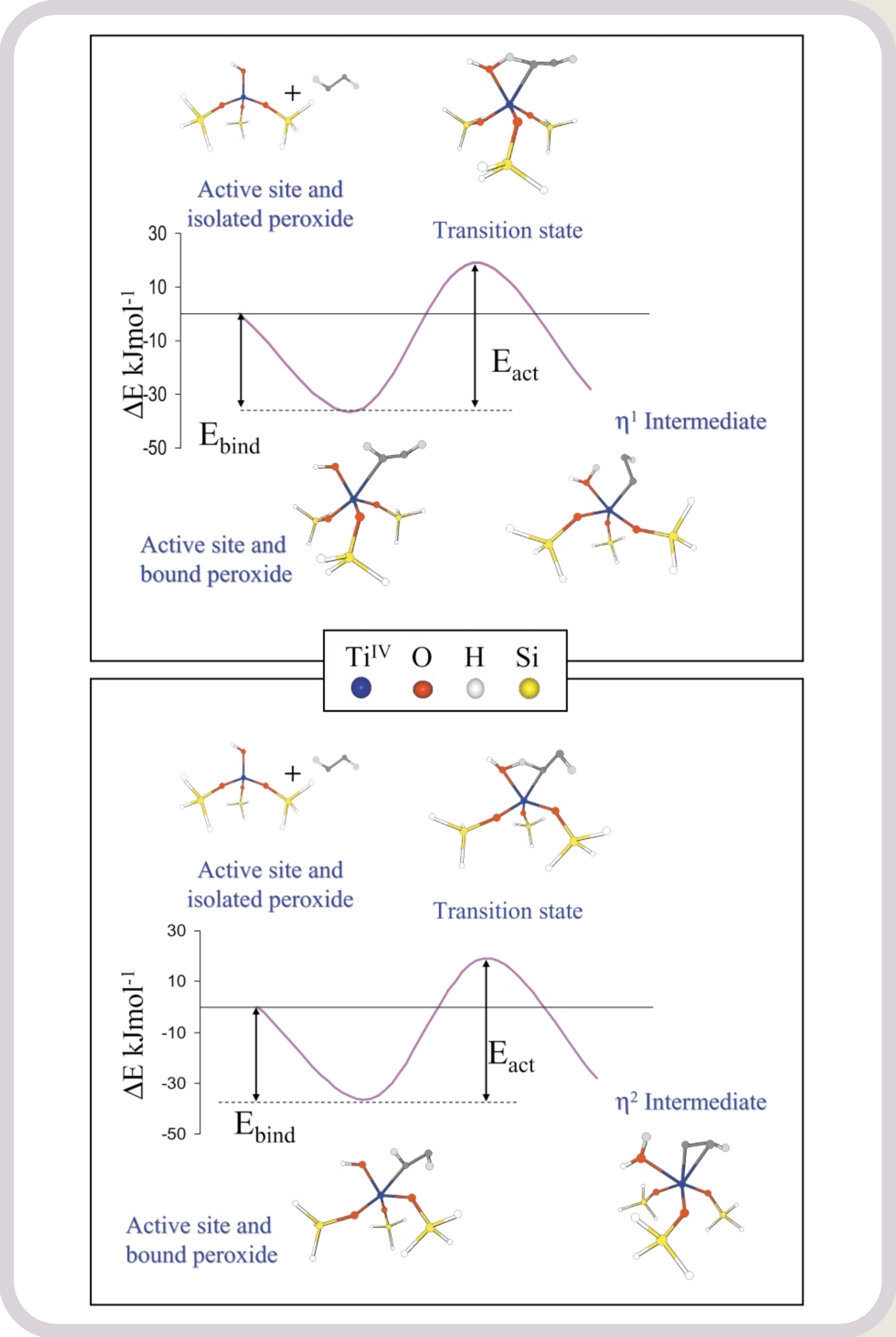

Fig. 5 Computed energetic pathways starting from the bare active site and isolated peroxide, through the occupied active site to the transition state (TS) to the η^1-intermediate (top) or the η^2-intermediate (bottom) and thence, after interaction with the alkene, to the regenerated bare active site. To distinguish between the framework oxygen (shown in red) and the oxygen that belongs to the peroxide, the latter is shown in dark grey.

Envoi

The principal conclusions of this article are as follows:

- the local atomic structure of active sites in oxidic heterogeneous catalysts, both when bare and when occupied under steady-state catalytic conditions, may be determined by *in situ* X-ray absorption fine-structure spectroscopy (XAFS); and
- when the XAFS data are supplemented by density-functional theory (DFT) computations, the local structure of transition state and intermediates (as well as estimates of activation energy) may also be determined.

The above generalisations have been illustrated here by reference to one specific heterogeneous catalytic reaction, the epoxidation of alkenes over Ti-silica, but the results and approach that we have adumbrated have general validity. This approach will benefit from the impending availability of more powerful synchrotron sources[19] as well as from further improvements in computational power. In addition to XAFS, local atomic structures of bare and occupied active sites may also

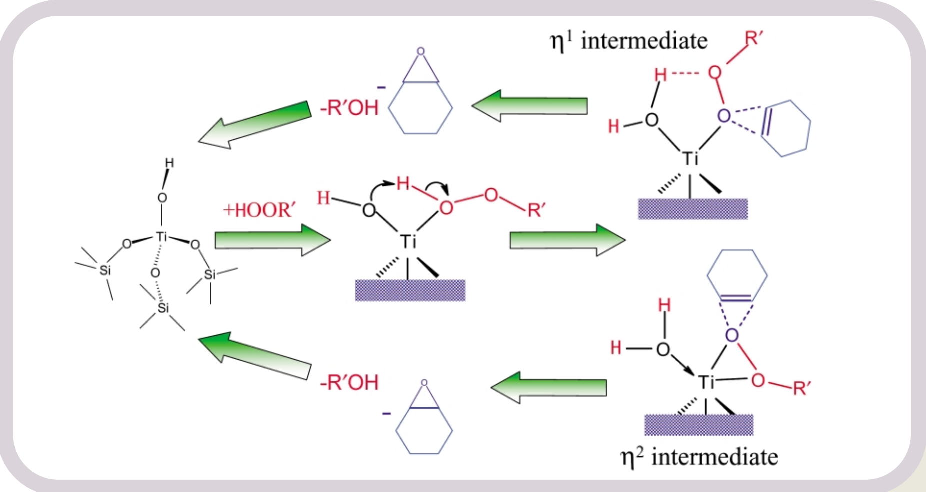

Fig. 6 This schematic picture shows how, by elimination of the epoxide and the alcohol (R′OH) from the η^1 or η^2 intermediate, the Ti active centre is generated. (This is in line with the recent observations of Fujiwara *et al.*[23]).

be explored using time-resolved variants of the multiple anomalous dispersion technique.

As to Lowry's verdict in 1928, the similarities are now seen to outweigh the dissimilarities among the four main categories of catalysis. Certainly the kinship between enzymatic catalysis, on the one hand, and shape- or regio-selective (uniform) heterogeneous catalysis with open-structure solids on the other, is quite marked, as discussed more fully elsewhere.[2,20,21] Recently, it has been demonstrated[22] that, for the Ti^{IV}-centred epoxidation, the structure and environment of the 4-coordinated Ti^{IV}-centre are essentially identical and exhibit the same activity for both the heterogeneous $Ti–SiO_2$ catalyst and its soluble homogeneous (titanium-containing silsesquioxane) analogue. In addition, homogeneous enantioselective organometallic catalysts display comparable and sometimes superior selectivities and activities when they are heterogenised on high-area silica surfaces. Enzymes, too, often display unimpaired performance when they are anchored on the inner walls of nanoporous silicas.

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