

# Engineering uniform active sites in inorganic solid catalysts

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## Abstract

One of the reasons why such remarkable progress has been achieved in understanding the mechanisms of enzyme action is because crystalline enzymes, replete with their uniform active sites, are amenable to X-ray structural elucidation in a time-resolved fashion. The same is true of the catalytic behaviour of ribozymes, where the precise location and stereochemistry of crucially important cations within the RNA may be identified by synchrotron-based X-ray studies. When certain, carefully chosen, organometallic species are appropriately heterogenised on selected, high-area solid hosts, new, high-performance catalysts may be designed, and their structures may be elucidated—generally under in situ conditions—by synchrotron radiation supplemented by other (*ex situ*) techniques. Armed with precise knowledge of the nature of the active site, improvements may be engineered so as to boost the performance of the original catalyst. In addition, related studies may be carried out on homogeneous analogues of the identified (heterogeneous) catalytically active site, thereby deepening further our understanding of catalysis. Novel designed catalysts (derived from mesoporous silica) that effect such processes as epoxidation (and hydrogenation) of alkenes on the one hand, and allylic amination (in regio- and stereoselective modes) on the other are described, along with the *de novo* design of high-area redox molecular sieve catalysts that preferentially oxyfunctionalise linear alkanes (in air under mild conditions) at terminal carbon atoms. The increasing importance of computational chemistry in the broad landscape of catalysis is also adumbrated. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

To achieve progress in the design and understanding of inorganic catalysts it is profitable to note the remarkable achievements accomplished in the last 30 or so years in the realm of enzymes and, more recently, ribozymes. Phillips' determination [1], by X-ray crystallography, of the structure of lysozyme and in par-

ticular of the precise atomic environment of the catalytic pocket within it, transformed the world of enzymology. Not only did a knowledge of the structure of the active site give rise to a plausible mechanism for the catalytic action, it also gave birth to a wide range of illuminating studies—ranging from molecular dynamics of the flexible catalyst and its reactant substrates or inhibitors to the design, much later (after the discovery [2] of site-directed mutagenesis), of new mutant (improved or deteriorated) forms of so-called wild enzymes. With the realisation

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that RNA can also serve as a catalyst, there arose the new world of ribozymes. Here again, X-ray structural elucidation of the binding of divalent cations such as  $\text{Pb}^{2+}$  to the tRNA backbone—which could be studied both prior to and after scission of the RNA by time-resolved (or pH-resolved) X-ray analysis—addresses directly the mechanism of catalytic action [3].

The key points to note in all this is that crystalline enzymes and ribozymes have within them vast numbers of active sites (catalytic pockets) in well-defined environments, and that X-ray crystallography, used under in situ conditions, yields the precise nature of the active sites. Distributed throughout the crystals of the enzyme, in a translationally repeated form, are the individual macromolecular enzymes. This is why it is possible to arrive at the structure of the active site by X-ray analysis.

Using this methodology, Scott et al. [4] have recently solved the crystal structure of an unmodified hammerhead RNA in the absence of divalent metal ions, and they showed that the ribozyme can undergo cleavage in the crystal when divalent metal ions are added.

In general, it is not possible to utilise such X-ray crystallographic approaches in the study of heterogeneous catalysts, principally because the bulk of the catalyst contributes vastly more to the scattering of the X-rays than the minute numbers of active sites distributed in a random manner at the exterior surfaces of the solid.

When, however, high-area crystalline solids that are microporous or mesoporous are used as catalyst supports, the atomic structures of the active sites may be retrieved by X-ray based methods, but this time more by use of X-ray absorption spectroscopy than by X-ray diffraction. Microporous and mesoporous hosts (see below) may have internal surface areas that are so large—in excess of  $1000 \text{ m}^2 \text{ g}^{-1}$ —that, effectively, these solids are best envisaged as possessing three-dimensional surfaces. By heterogenising well-defined organometallic precursors on such hosts advantage may be taken of special in situ methods, described more fully

elsewhere [5–8], to determine in atomic detail the nature of the catalytically active sites during the course of chemical transformation.

## 2. Solid hosts with large areas enable uniform active sites to be engineered

Zeolitic solids, irrespective of whether they are naturally occurring minerals or synthetic, aluminosilicate analogues, possess three-dimensional surfaces, the areas of which are seldom less than  $800 \text{ m}^2 \text{ g}^{-1}$  and often in excess of  $1000 \text{ m}^2 \text{ g}^{-1}$ . In general, however, their pore apertures are too small to permit ingress of even moderately sized organometallic (homogeneous) catalysts into their cages and channels, so that there is little scope for delicate variation in heterogenising homogeneous catalysts with such hosts. There is, however, the possibility of creating so-called ‘tea bag’ [9] or ‘ship-in-bottle’ [10,11] catalysts in which the zeolitic cage merely serves as a receptacle inside which the bulky ‘homogeneous’ catalyst—assembled there either during or after synthesis of the zeolite—has adequate space to rattle, to receive reactant species, and to liberate reaction products that are small enough to permeate through its pores.

Aluminium phosphates (AIPO) can be induced [12,13] to crystallise in a wide variety of open structures (in the presence of an organic template), some of the structures that they form being the counterparts of aluminosilicate zeolites, others being unique. Just as heteroatoms, notably titanium in its (IV) oxidation state, or zinc ((II) state) may be accommodated in small amounts within zeolitic frameworks, TS-1 (titanosilicalite) being one of the best-known, so also may a variety of transition metal and other ions ( $M = \text{Zn}, \text{Mg}, \text{Mn}, \text{Co}, \text{Fe}, \text{Ni}, \text{etc.}$ ) be accommodated in AIPO structures.

As we shall see below, zeolites and AIPOs with heteroatoms substituted in their framework are often powerful examples of catalysts that function in ways comparable, where not superior, to the homogeneous variants of the struc-

ture surrounding the heteroatoms in the framework.

But AlPOs, like zeolites, are microporous, and therefore not suitable as hosts for grafted organometallic entities. When it became possible in the early 1990s routinely [14,15] to prepare mesoporous hosts, of silica especially, where channel diameters of 25 to 100 Å could be readily and adjustably produced, horizons of heterogeneous catalysis were greatly expanded. This was because by anchoring or substitution at the walls of the pores highly selective and active catalysts could be produced. An early example [16] was the grafting of metallocene complexes to yield powerful, Ti(IV)-based epoxidation catalysts.

Here, we were able to engineer uniform active sites—in this case, proven by in situ X-ray absorption spectroscopy—of tripodally anchored Ti(IV) ions, of precisely determined structure (Fig. 1). Later work showed [8,17–19] that expansion of the coordination shell to six around the Ti(IV) ions occurs during the course of epoxidation.

The expansion in the number of materials (generally metal or non-metal oxides) that may be produced in high-area, mesoporous states,

continues unabated. But unlike the situation that exists with microporous solids, where computational algorithms (like ZEBEDDE [20,21]) have generated candidate structure-directing organic templates for use in the synthesis of AlPO and zeolitic structures, no reliable computational strategy or tactic has yet emerged that leads to the de novo design of mesoporous solids.

### 3. Techniques of characterisation

The importance of combined in situ X-ray absorption (XAS in its XANES and EXAFS modes) and X-ray diffraction as a means of determining the nature of active sites has been alluded to already. In situ FTIR (in its high-temperature diffuse reflectance mode), along with various NMR techniques, is so well known that it requires no elaboration here. Numerous other in situ techniques are also available, as described elsewhere [8,22]. But one ex situ technique that does merit comment, especially in view of its role in identifying the location and nature of bimetallic nanocatalysts is annular dark field electron microscopy, which, because it takes advantage of Rutherford scattering

### Tripodal Titanium Active Sites

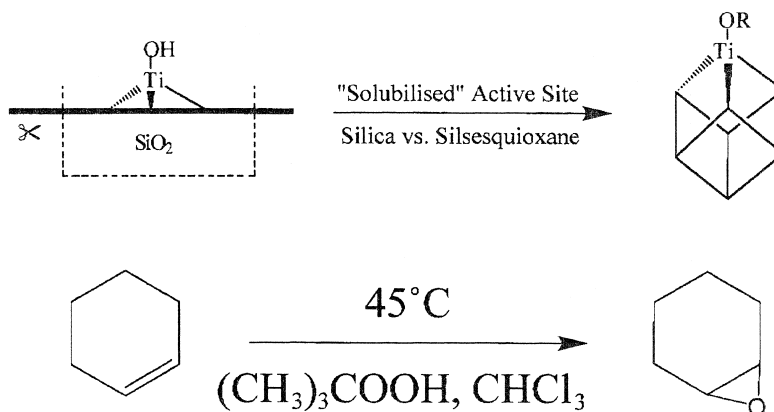


Fig. 1. EXAFS analysis shows that the Ti(IV)-centred active site in the epoxidation catalyst (Ti/SiO<sub>2</sub>) is a tripodally attached titanol group (top left), which is akin to a titanolsilsesquioxane species (top right) that may function as the analogous homogeneous reactions such as that shown on the lower half.

(rather than Bragg scattering), highlights [19,23] the precise location of minute particles (of high atomic number material) dispersed on a material (such as mesoporous silica) of low atomic number.

#### 4. Examples of uniform heterogenised homogeneous catalysts on silicious supports

##### 4.1. Ti(IV) centres for alkene epoxidation

Individual Ti(IV) centres on silica supports are, to date, among the most intensively characterised of uniform heterogeneous catalysts. Recent summaries [8,24] include comparisons between tripodally bound Ti(IV) centres (Fig. 1) on ordinary, non-porous silica (Cabosil), on mesoporous silica (MCM-41) and on two deliberately modified MCM-41 silicas where the Ti(IV) centre was, in the one case, attached bipodally to silicons (via oxygen bridges) and to one germanium (Ti↑Ge↑MCM-41), and in the other, to two silicons and on tin atom (Ti↑Sn↑MCM-41). The Ti↑Ge↑MCM-41 catalyst, with its specially engineered active centres, was significantly more effective in cyclohexene epoxidation than the parent Ti↑MCM-41 one.

##### 4.2. Oxo-centred Co(III) catalysts for the oxidation of cyclohexane [25]

In homogeneous mixtures of Co(III) acetates rich in acetic acid many oligomers of the cobalt salt are present. By isolating and testing the catalytic activity of each separate oligomer it was found that the trimer displayed exceptional selectivity in oxidising the CH groups of adamantane. Specimens of the trimer were accordingly tethered to the inner walls of MCM-41 mesoporous silica, and the resulting uniform heterogeneous catalyst exhibited high activity in

the oxidation of cyclohexane to cyclohexanol and cyclohexanone using the sacrificial oxidant tertiary butyl hydroperoxide (THBP). Moreover, in situ X-ray absorption spectroscopy measurements revealed that significant changes occurred in the structure of the trimer during the initial period of induction prior to the onset of catalysis.

##### 4.3. Metallocene-derived, isolated Mo(VI) active centres on mesoporous silica for the catalytic dehydrogenation of methanol

Isolated Mo(VI) active sites have been grafted [26] on to the inner surfaces of MCM-41 mesoporous silica, via a molybdenocene dichloride precursor, to generate a catalyst which oxidatively dehydrogenates methanol. Mo K-edge X-ray absorption spectroscopy shows that, after calcination, at low Mo loadings (ca. 1 mol% with respect to SiO<sub>2</sub>), isolated MoO<sub>4</sub> species are generated on the surface, whereas at higher loadings (ca. 4 mol%) there is some evidence for the formation of polymeric oxo-molybdenum species. There is higher selectivity for the production of formaldehyde with the lighter loadings of Mo.

##### 4.4. Alumoxane-zirconocene grafted oligomerisation catalysts [27]

The anchoring of alumoxane, synthesised by the in situ hydrolysis of trimethylaluminium on the internal walls of mesoporous silica (MCM-41) generates a highly active and selective host for Cp<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> in the oligomerisation of propene. The regioselective preference of the immobilised metallocene is preserved and a typical Schultz–Florey distribution of the propene oligomers is obtained.

##### 4.5. Vanadyl active centres

Again using the metallocene as precursor, in this case vanadocene, Oldroyd et al. [28] grafted

vanadyl active centres of determined (by XAS), well-defined structures on to the inner surface of MCM-41; and these were shown to be moderately effective in the selective oxidation of hydrocarbons. These workers compared the behaviour of such mesoporous catalysts with those prepared in an analogous fashion using so-called amorphous mixed-metal oxides (AMMO) (of the type described by Maier [29,30]) as essentially microporous hosts (Fig. 2). It was possible to boost the catalytic performance of these catalysts by deliberately enhancing the hydrophobicity of the immediate vicinity of the active site by grafting pendant methyl groups to the wall of the host (Fig. 3).

## 5. New titanosisilsesquioxanes for the epoxidation of olefins

The use of silsesquioxanes as models for a wide variety of heterogeneous silica-supported catalysts has received considerable attention recently [31–33]. In particular, efforts have been made to compare the catalytic performance of the uniform, heterogeneous (tripodally-anchored), and isolated Ti(IV)OH active centres of a metallocene derived [16,18] Ti-MCM-41 catalyst with Ti(IV) substituted silsesquioxanes as homogeneous [32,33] catalysts.

The essence of this work which is currently underway [34] devolved upon the access to the

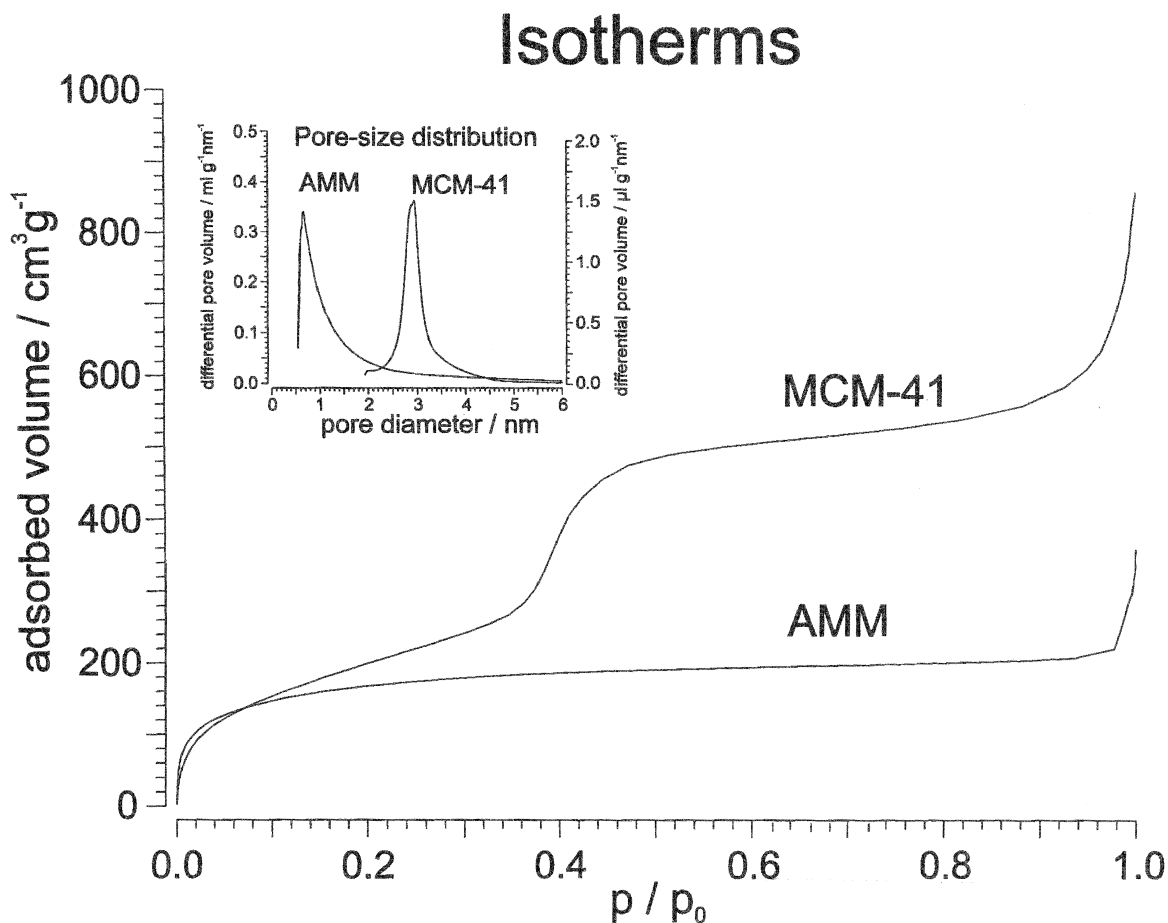


Fig. 2. Adsorption isotherms yield distinctly different pore-size distributions for mesoporous (MCM-41) silica and microporous amorphous mixed-metal oxides (AMMO) of the type described by Maier [29,30].

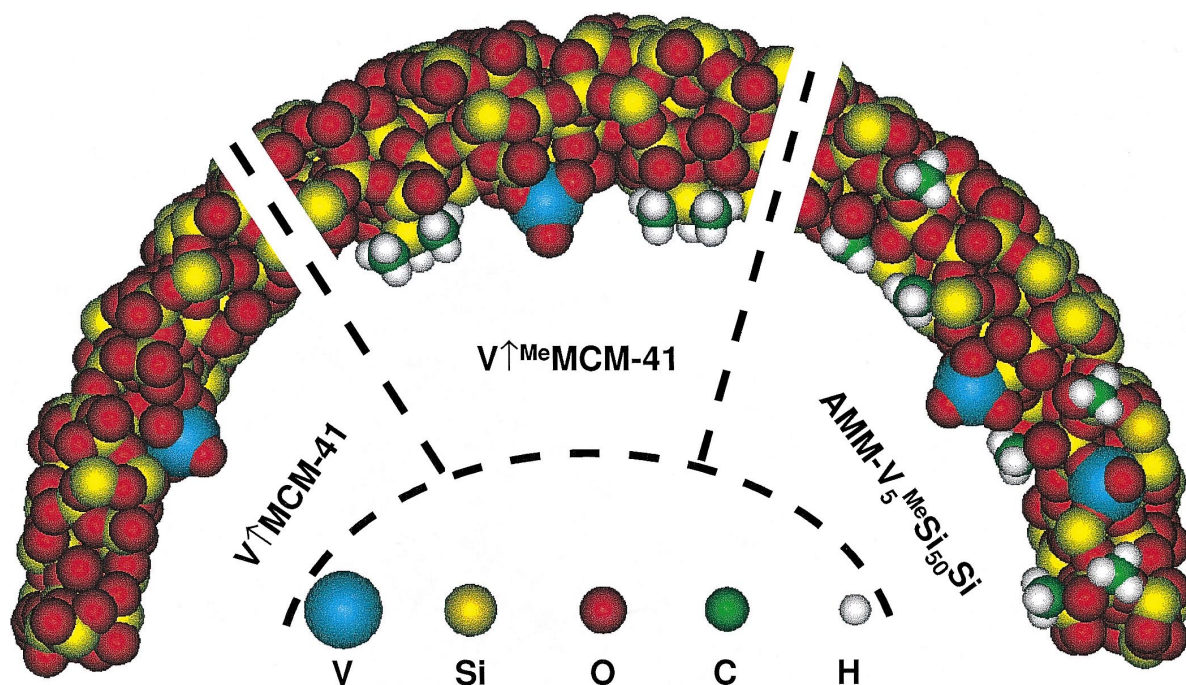


Fig. 3. A vanadyl active site (for selective oxidation of hydrocarbons): (a) grafted on to MCM-41 (left), (b) surrounded by nearby surface methyl groups (centre), and (c) in a vanadium-rich AMMO microporous solid [28].

tetrahedrally coordinated Ti(IV) active site in the silsesquioxane, and therefore upon the facil-

ity with which the four-coordination of the Ti(IV) may be expanded to five or six—an

### Steric Influence on Reactivity

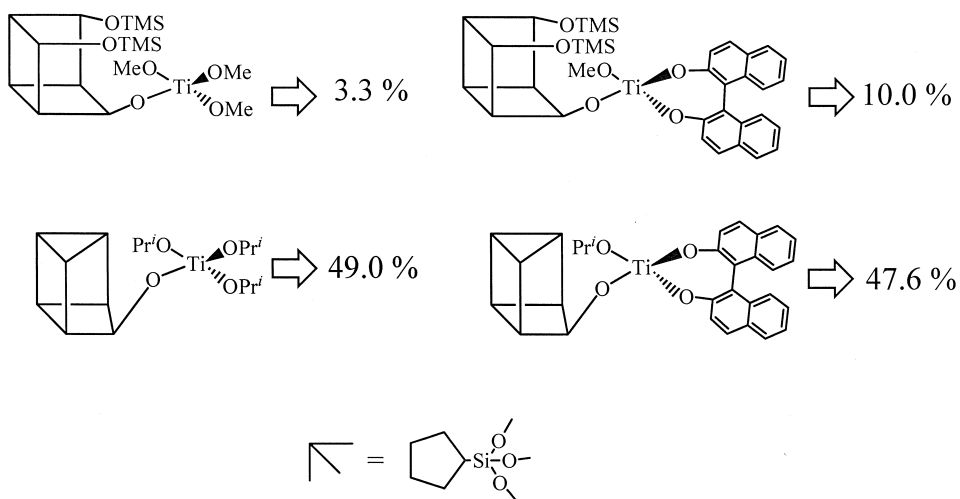


Fig. 4. Experiments [32,34] with titanasilsesquioxane (homogeneous) analogous of the tripodally bound heterogeneous catalyst (Fig. 1) show the influence of steric restrictions in the vicinity of the Ti(IV) centre upon its catalytic activity.

expansion which is essential for catalysis to ensue. The importance of this steric influence is illustrated in Fig. 4.

## 6. Constrained chiral catalysts [35]

The mesoporous (diameter ca. 30 Å) of MCM-41 and related silicas permit the direct grafting of complete chiral metal complexes and organometallic moieties on to the inner walls of these high area solids by a variety of ways, including tethering by functionalising the surface with organic groups such as alkylhalides -amines, -carboxyls and -phosphines. This opens routes to the preparation of novel catalysts consisting of large concentrations of accessible well-spaced and structurally well-defined (i.e., uniform) active sites.

Exploratory experiments, involving microanalysis, XAS and solid-state NMR, indicate that various organometallic chiral catalysts, such as the chiral bis-diphenyl-phosphinoferrrocene derivative (dppf) shown in Fig. 5, can be tethered to the inner walls of the mesopores.

The key concept in this approach is the reactants interaction with both the pore wall and the chiral directing group which is an integral part of the grafted chain. We have tethered various

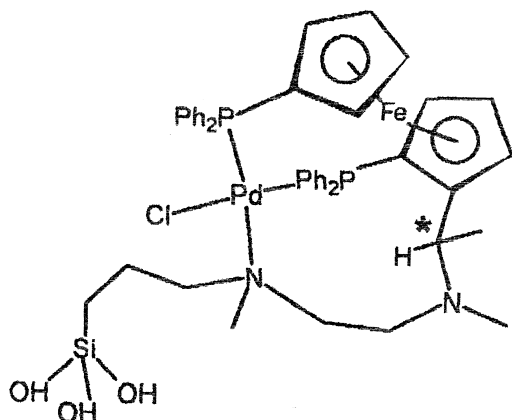


Fig. 5. The chiral diphenyl-phosphinoferrrocene derivative (anchored to the inner walls of MCM-41 silica) used in our stereoselective allylic amination work [36].

dppf-complexes to the *internal* surface only. (The exterior surface was first passivated by reacting the pendant silanols with an appropriate amount of  $\text{Ph}_2\text{SiCl}_2$ , so that all external surface silanols are converted to non-reactive  $\text{Ph}_2\text{Si}$  groups). Preliminary results show that the Pd-centred Trost–Tsuji (so-called allylic amination), when the cationic Pd (allyl) species undergoes nucleophilic attack at one of two possible sites ( $\alpha$  and  $\delta$ ) in non-symmetric allylic substrates, exhibits definite evidence of both regio- and stereoselectivity arising solely from the confinement of the chiral backbone within the silica mesopores.

## 7. Encapsulated bimetallic nanocatalysts

The advantages of producing high-performance, bimetallic nanoparticle catalysts from their precursor metal-cluster carbonylates anchored inside the mesoporous channels of silica have recently been demonstrated [37,38]. In situ XAS and FTIR spectroscopies as well as ex situ high-resolution scanning transmission electron microscopy were used to chart the progressive conversion, by thermolysis, of the parent carbonylates to the denuded, bimetallic nanoparticle catalysts. Separate copper and ruthenium K-edge X-ray absorption spectra yield a detailed structural picture of the active catalyst (ca. 15 Å diameter). It is a rosette-shaped entity in which twelve exposed Ru atoms are connected to a square base composed of relatively concealed Cu atoms. These are, in turn, anchored by four oxygen bridges to four Si atoms of the mesopore lining.

The novelty of this type of catalyst is that the bimetallic nanoparticles exhibit no tendency to sinter, to aggregate or to fragment into their component metals during use. The nanocatalysts perform well in the hydrogenation of hex-1-ene and several other alkenes.

## 8. Molecular sieve catalysts designed for the selective, low-temperature oxidation of linear alkanes in air

Several approaches have been made to devise appropriate selective oxidation catalysts that mimic the behaviour of enzymes (such as  $\omega$ -hydroxylase). A few of these are 'ship-in-bottle' catalysts [11,39]. We have recently reported [39,40] the design of two transition metal-containing molecular sieve (heterogeneous) catalysts that have a framework structure akin to that of the zeolitic mineral chabazite (cage diameter 3–8 Å), and which efficiently oxyfunctionalise linear alkanes (*n*-pentane, *n*-hexane, *n*-octane and *n*-dodecane) in dry air (1.5 MPa at temperatures between 373 and 403 K) preferentially at the terminal methyl group. The active sites are established to be isolated Co(III) or Mn(III) ions substitutionally incorporated in the place of Al(III) ions in an open-structure aluminophosphate known as AIPO-18. These catalysts display a high degree of regio-selectivity: some 66.5% of the products of oxidation of *n*-hexane after 24 h are the result of substitutions at the terminal methyl group for MnAIPO-18 (61.3% for CoAIPO-18) [40].

We believe that such oxidations involve free radicals, but we also have reasons for believing that it is the Co(III) (or Mn(III)) ions in tetrahedral coordination in the AIPO framework (and hence in a coordinatively unsaturated state) that holds the key to the remarkable catalytic performance.

Here, in effect, we have a high-area solid, the inner surfaces of which contain at isolated locations, coordinatively unsaturated active sites. With this type of designed heterogeneous catalyst, it is not necessary to graft an organometallic precursor on to the walls: it is simply necessary to grow the crystals of heterogeneous catalysts with deliberately introduced impurity ions (Co(III) or Mn(III)) at the inner surfaces. These 'latent' sites are converted into catalytically active ones by oxidation in air.

The above is an extended summary of the themes covered in my plenary lecture. A full account of my talk, which can only be satisfactorily conveyed by reproducing the numerous colour illustrations shown in the lecture itself, will be submitted for publication elsewhere [41].

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