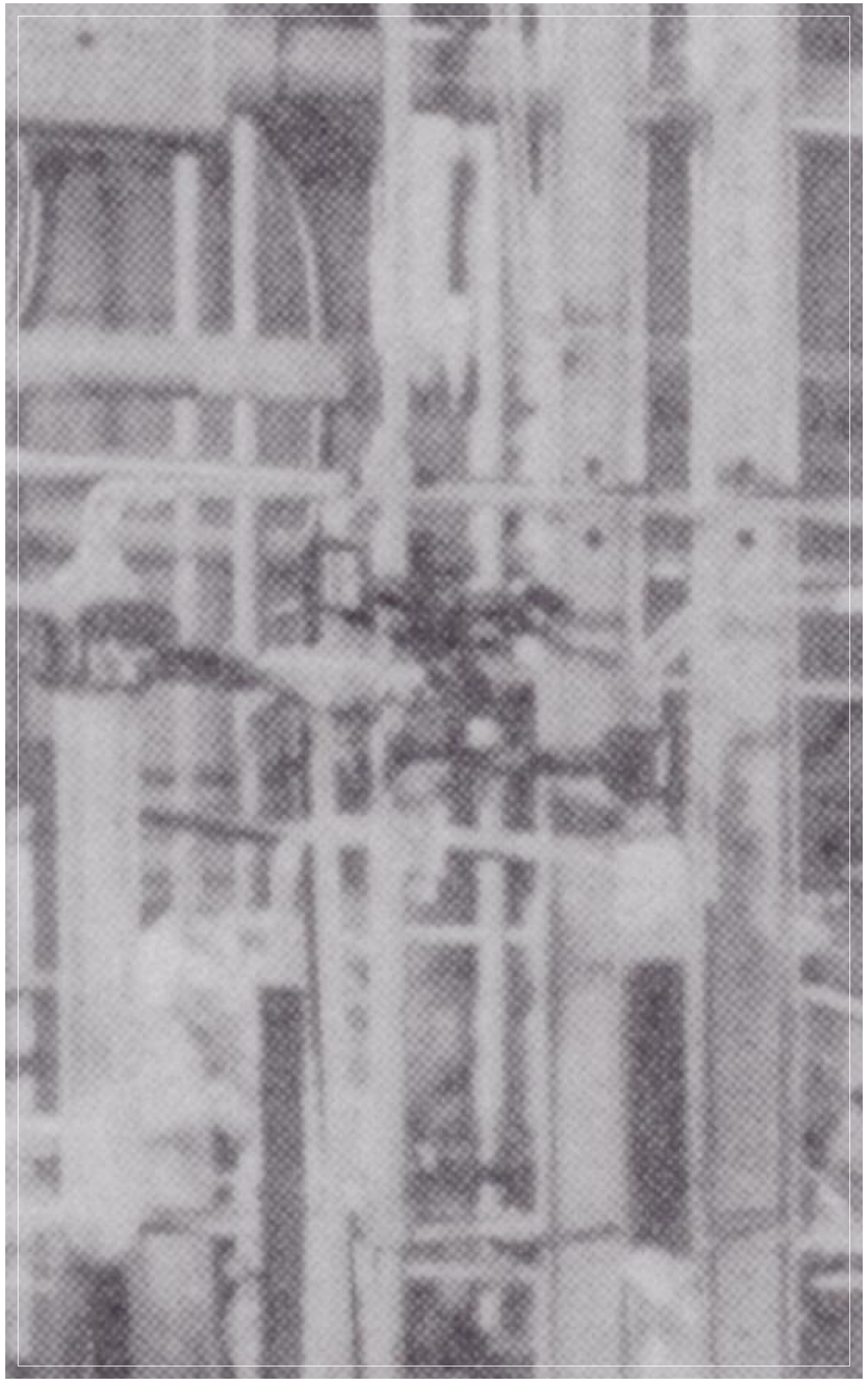


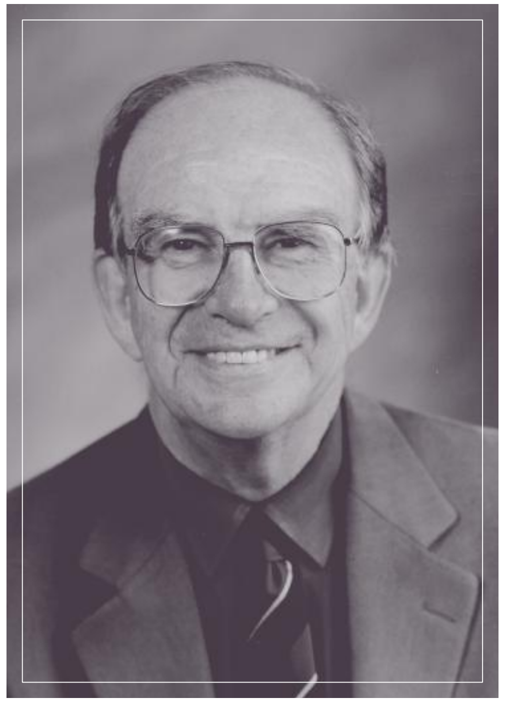
Solid state chemistry and the design of heterogeneous cataysts

"Everything is interesting: not everything is important". **Sir John Meurig Thomas**

Aspects of solid state chemistry have been implicated in catalytic activity for much of the century. The role of lattice defects, and in particular the significance of doping to control whether a solid exhibited n- or p-type conductivity, has been one of the central pillars for rationalising reactions at oxide surfaces with the Mars-van Krevelin mechanism dominating selective oxidation catalysis. Associated with theoretical discussions was the boundary layer theory of chemisorption and whether it was of the cumulative or depletive type (Aigrain and Dugas, Hauffe, Weisz, Stone, Kubukawa and Toyama, Germain). Some of the earliest studies of heats of chemisorption were obtained by Garner, Gray and Stone for oxygen on copper oxide in 1950 and their relevance to catalysis discussed. The Bristol School had considerable influence on this aspect of heterogeneous catalysis particularly in Europe where many groups emerged: Cimino, Zecchina, Garrone, Indovina and Collucia in Italy, Haber in Poland and Gravelle in France with the activation of alkanes being a significant theme over the last two decades.

Thomas at the Royal Institution in London, with his background in high resolution electron microscopy and close association with J.S. Anderson, one of the father figures of solid state chemistry, pioneered techniques to unravel the relationship between catalyst structure and activity and therefore develop methodologies for assembling and designing new catalysts. Stimulated by his earlier work with Purnell on silicates and other layered materials Thomas turned to zeolitic materials and other microporous systems and with Catlow used modelling studies to predict the behaviour of new catalyst systems. Although pioneering work by Barrer in the late fifties and early sixties had laid the foundation for understanding zeolite adsorption behaviour, it was Rabo of the Union Carbide Research Institute at a Faraday Meeting in 1966 who drew attention to the advantages which zeolites had in presenting both uniform adsorption sites and huge surface areas ($1000 m^2 g^{-1}$) and therefore their attractiveness for establishing the nature of the "active site". Ten years later P.B. Weisz and C.D. Chang reported that HZSM-5 could convert methanol to gasoline. This become one of the most extensively studied reactions in catalysis with Derouane in association with Haldor Topsøe developing the TIGAS process. At the 1996 Faraday Meeting in Reading Thomas reviewed the progress made in the study of microporous materials and how through combining infrared and neutron diffraction with x-ray diffraction and absorption spectroscopies detailed atomic-level information became available.

During the first 50 years of this century catalysis was discussed largely through the two central pillars of physical chemistry: thermodynamics and kinetics. However, with the advent of highly sophisticated instrumentation for precise structure determination, key catalytic roles began to be recognised for many of the more subtle aspects of the solid state. These included both point and extended defects, atom coordination, intergrowth structures, and phase boundaries. There developed an impetus for searching for correlations between some structural feature and catalytic activity and since the vast majority of catalysts in the chemical industry are oxide-based, particular attention was given first to the role of oxides in selective oxidation catalysis. Stone who had benefited when at Bristol from the influence of Garner's interest in solid state chemistry,



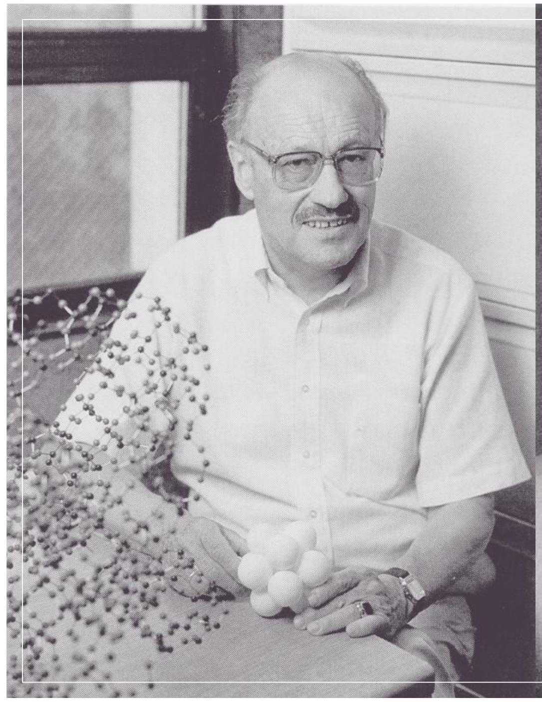
Sir John Meurig Thomas

and Haber, in Krakow, were two of the first to explore structural aspects of solid state chemistry relevant to the understanding of oxidation catalysis. Stone in collaboration with the Turin group - Zecchina, Garrone and Collucia - and Cimino in Rome, favoured reflectance spectroscopy for studying the model catalyst MgO and in particular the influence of transition metal ions as dopants. Reactivity in oxidation reactions was related to the presence of co-ordinatively unsaturated oxygen sites, with electronic changes in both the solid and the chemisorbed species being monitored together. Surface exciton absorption bands were ascribed to surface ions present in magnesium oxide in two different states of co-ordinative unsaturation. The influence of chemisorbing oxygen, nitrous oxide, carbon dioxide and carbon monoxide on the exciton spectrum provided evidence for the electron transfer steps involved and in the case of carbon monoxide for the formation of both dimers $(CO)_2^{2-}$ and more condensed species $(CO)_n^{x-}$. The surface coverage of such species was generally no more than 1% of a monolayer. Infrared spectroscopy was the dominant influence in the area of oxide surface chemistry, Knözinger in Germany and Rochester in the United Kingdom being active proponents of the technique.

Much attention was given during this period, the early 1970s, to the relevance of surface complexes through analogies with inorganic coordination chemistry, a growth area during the late 1960s. The main points for discussion were how the structure of such complexes determined reactivity - with emphasis on the metal oxidation state, the coordination number of the metal atom and the stereochemical arrangement of the donor ligand atoms around the central metal atom.

Haber's interests were largely in the selective oxidation of hydrocarbons, combining structural studies of the oxides with catalytic activity and later, as computational methods became feasible, with theoretical studies. He divided catalytic oxidation into two groups: electrophilic oxidation, proceeding through the activation of the oxygen and nucleophilic oxidation, when the first step is the activation of the hydrocarbon molecule followed by consecutive steps of nucleophilic oxygen insertion and hydrogen abstraction. The ability to activate the hydrocarbon molecule was related to the properties of individual cations and their nearest neighbours, which constituted the active centres. The catalyst surface was considered to be in dynamic interaction with the gas phase so that depending on the reactant mixture different phases could exist at the surface.

By the early 1980s it became clear, as for example in the work of Brazdil, Teller and Grasselli at the Standard Oil Company, that the most effective oxidation catalysts were usually multiphase in nature. This was particularly true of vanadium oxide and various bismuth molybdate catalysts, specific compositions being shown to exhibit maximum selectivity. The search for a rational understanding of synergism that existed in multiphase catalysts began. Simultaneously there was a drive for the preparation of new materials than might offer advantages over those in use. Much of the latter was driven by the rapid development of high resolution electron



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microscopy in being able to determine the *specific* structure (rather than the *average*) of each individual crystallite. In 1983 Jefferson who was a colleague of Thomas, first at Aberystwyth and subsequently at Cambridge, reviewed critically the contribution of high resolution electron microscopy in elucidating the structures of oxides derived from bismuth oxide by the incorporation of tungsten and molybdenum. The results indicated beyond any doubt that simple ternary oxides such as Bi_2MoO_6 have an inherent structural adaptability to oxygen content, that regions of differing stoichiometry are highly likely and furthermore contribute to the observed catalytic activity. There was strong collaboration between Thomas' group in Cambridge and Grasselli at Standard Oil Company during this period.

Industrial interest in zeolites grew rapidly and both Union Carbide and Mobil were involved in creative synthetic methods which led to molecular sieves being synthesised with many of these still being investigated in academic and other industrial laboratories. They exhibit variable acidities, pore sizes and pore structures and have, with and without metal loading, unique properties which find application in selective adsorption, gas separation, catalysts for fine chemicals etc.

Thomas' interest in the relationships between heterogeneous catalysis, surface structure and microscopy has been central to his research over the last 40 years - starting with the role of dopant transition metals in the gasification of carbon, to catalysis by the pillared clays with Purnell and more recently to zeolitic catalysis. However, it was his seminal studies in the 1970s concerned with high resolution electron microscopic studies of the solid state that provided the platform for his interest in zeolites and microporous materials in general.

Although it had long been recognised that emergent dislocations, is related defects, might function as centres of enhanced surface reactivity, with for example a Faraday Discussion, 'Crystal imperfections and the chemical reactivity of solids', held in 1959, Thomas in 1972, using conventional microscopy, addressed directly the question of elucidating the actual structural defects which function as active centres for enhanced chemical reactivity. By coupling this approach with "gold decoration", monoatomic steps could be preferentially decorated and easily revealed in an electron microscope at a magnification of 30,000. This was some 20 years before the first commercial Scanning Tunnelling Microscope became available! The crystallographic sensitivity of the cobalt catalysed oxidation of graphite had, however, been observed optically even earlier, in 1964, by Thomas and Walker. This was clearly an example of what would be described today as 'reactive oxygen spillover' - the origin of the reactive oxygen being activation of the gaseous dioxygen by the dopant cobalt leading to dioxygen or atomic transients which oxidized the graphite resulting in surface pitting with "deep" channels being generated.

In the early 1970s Thomas, at that time still at Aberystwyth, turned his attention to layered silicates and in particular to elucidate the detailed structure of intercalated organic molecules. Systematic studies of some thermally stable intercalates of montmorillonites were carried out using both x-ray diffraction and x-ray photoelectron techniques. It is not surprising that a few years later, when at Cambridge, Thomas initiated extensive studies of aluminosilicate catalysts. The aim was to elucidate the ultramicrostructure of, and the long-range order with the catalysts, using both high resolution electron microscopy and magic-angle-spinning multinuclear NMR (MASNMR). These showed the existence of coherent or recurrent intergrowths; anomalous (defective) structures; novel variants of the parent structure, all of which emerged from HREM with a resolution of 2.4Å point to point. Much attention was given to ZSM-5 with comparison made between computed and observed images of the structurally pure crystal with information on the cavity structures providing fundamental clues as to their operation as catalysts and in particular the distribution of hydrocarbon products they permit in the conversion of methanol to petrol.

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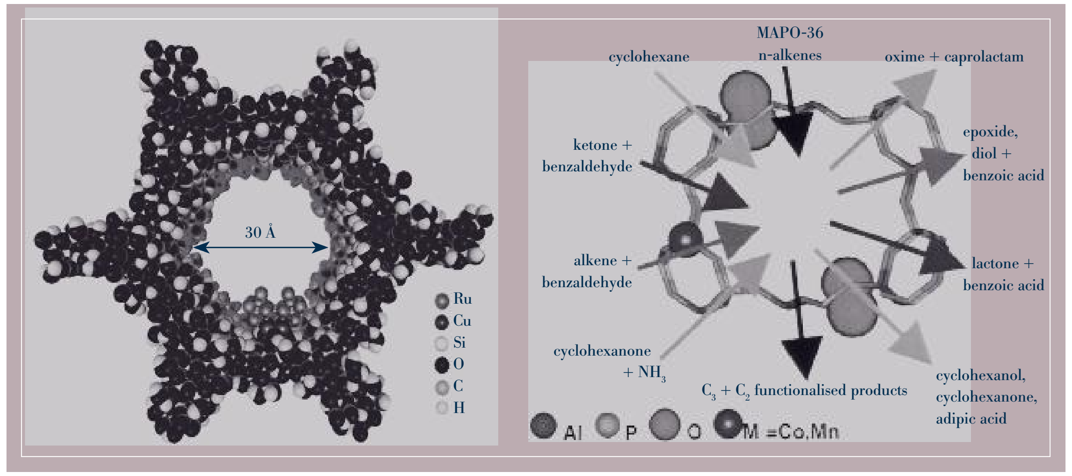
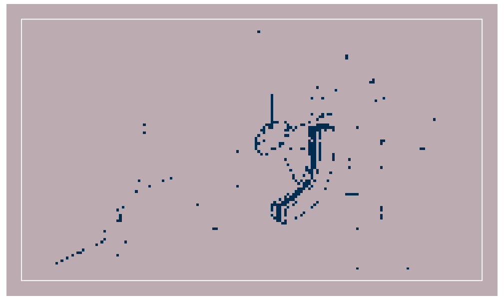
In the case of aluminosilicates ^{29}Si MASNMR was shown to be able to distinguish all five Si(nAl) building units, enabled Si/Al ratios to be determined; distinct peaks were obtained for crystallographically non-equivalent Si(OSi)$_4$ groupings and non-crystalline materials were shown to be amenable to investigation. Other nucleic eg. ^{17}O, ^{71}Ga, ^{27}Al were also shown to be capable of providing important structural information on zeolites.

One of the great advantages of zeolites is that their surfaces are three dimensional exposing an area of up to 1000m^{2}g^{-1}. It was this that Thomas took advantage of, but in addition there was the possibility of introducing well defined single catalytic sites into a particular cage within the zeolite framework. During the last 15 years or so Thomas at the Royal Institution has given serious attention to exploring whether structural changes occurring within the catalyst surface occurs during the reaction, the aim being a rational approach to the design of catalysts. Naturally the structures must be those present during catalysis so that in situ methods must be employed. In the Introductory Lecture to the Faraday Discussion Meeting "Catalysis and Surface Science at High Resolution" in 1996 Thomas discussed the portfolio of in situ methods that he had developed for zeolite studies. He drew attention to Zecchina's FTIR work for exploring the nature of the active site in HZSM-5 and the initial stages in the oligomerization of ethene. The advantages of polarisation modulation RAIRS for high pressure studies and how powder neutron diffraction patterns of crystalline zeolites revealing both the active sites within the zeolites and also the bonding of adsorbates at these sites discussed. It was, however, HREM that provided the unique information on the real-space crystallography of zeolite structures revealing previously unknown phases as well as intergrowths in, or between recognised phases. It provided the key to the understanding of the catalytic aspects of a range of zeolites including theta-1, ZSM-23. ECR-1 and MCM-22.



The AIPO -36 microporous structure with either Mn^{or} CO^{111}ions at frameworksites give rise to excellent catalysts for the various processes (after J.M. Thomas)

Thomas, in 1994, when reviewing the various approaches that had become available for zeolite studies, made the telling point that *"whereas spectroscopic and all other experiments can fail as well as succeed, in the practices of computation and simulation the criteria - even the awareness - of failure are less sharply defined"*. He, however, emphasised the advantages of the Car and Parinello method introduced in 1985 - the ab initio molecular dynamics method - which enabled the existence of vast new ranges of solids not hitherto prepared or imagined to be explored. Monte Carlo and molecular dynamics calculations, together with other computational techniques such as docking and energy minimisation calculations, enabled diffusion of molecules in zeolite channels to be calculated with high precision with Catlow at the Royal Institution very much the leader in the field. There is continuing to be a world-wide interest in zeolite science and technology with for example the summer school on zeolites held in Taejon, Korea, in 1996 providing an overview of the important findings over the preceding 10 years on the synthesis, characterization and application of zeolite materials. These included possible applications of zeolite based membranes (van Bekkum), characterization of zeolites by various methods (Howe, Stöcker and Kaliaguine) computational methods (Newsam) and the contents of zeolite frameworks (Seff). I found the article by Stöcker which reviewed the 'state of the art' NMR characterization of zeolites particularly valuable in that it provided the genesis of the subject arising from Andrew's paper in Nature in 1958 and the developments by



Schematic representations of the set-up used for the in-situ parallel recording of X-ray absorption (XRA) spectra and X-ray (XRD) of solid catalysts in contact with either liquid or gaseous reactants (after J.M. Thomas)

Thomas and Klinowski in Cambridge and by Fyfe in Canada in the early 1980s.

Inclusion chemistry with zeolite has emphasised the possibility of being able to design catalytic materials at the nanoscale, with the "ship in the bottle" approach introduced by Herron in 1988 dominating much of the field over the last decade. The activity has been world wide and involving a plethora of approaches both computational and experimental. Metal complexes have been encapsulated in well defined channels and cavities of zeolites with their inherent advantage over other solid supports in that the metal complex can be physically trapped within the pores and not necessarily bound to the oxide support's surface. In this sense the zeolite-complex can be regarded as bridging a homogeneous and heterogeneous system. A good example of this is the recent report from the Royal Institution - Cambridge group that the titanium active centre in *heterogeneous* titano-silica expoxidation catalysts is the same as the Ti(IV) centre bound to the soluble *homogeneous* silesquioxane catalyst.

Hutchings (1999) has reviewed what he describes as "New approaches to rate enhancement in heterogeneous catalysis" - emphasising the molecular (rather than the empirical) approach and drawing attention to the various methods adopted for adapting zeolites for improving specifically selective reactions. He referred to the work of Iglesia for the hydrogenation of prochiral alkenes using Rh and Ni complexes supported on zeolite Y, Thomas' studies of titanium metallocenes grafted on to MCM-41 as effective oxidation catalysts, the pioneering studies of Jacobs using large complexes encapsulated within zeolites X and Y. Ogunmumi and Bein and Saboter who extended the encapsulation idea to prepare heterogeneous catalysts for epoxidation and most recently his own work on the modification of zeolites by pure enantiomers to provide a chiral environment. Hutchings and his colleagues used dithiane oxide in zeolite Y to create a new high activity acid site - it was this that provided the impetus for the successful preparation of a new enantioselective catalyst which reacted preferentially with one of the enantiomers of racemic butan-2-ol even though both enantiomers were present in equal concentrations. The comparisons between zeolite catalysis and enzyme catalysis has also been emphasised by Jacobs in Belgium, Shilov in Russia and Thomas - with the geometry of the zeolite pores determining specificity in zeolite chemistry analogous to the geometrical restrictions present in the action of an enzyme on a substrate molecule. In both cases chemical transformation occurs in a space of molecular dimensions with Jacobs introducing the term zeoenzyme (NATO Meeting 1991).

A particular facet of selective oxidation which has been elusive is the oxidation of a linear hydrocarbon exclusively at the terminal methyl position. Labinger highlighted the obvious advantages of being able to use alkanes rather than olefins and emphasised the recent advance made by Thomas and colleagues using aluminium phosphate molecular sieves where the aluminium has been partially replaced by either Co(II) or Mn(II). These materials have been shown (Nature 1999) to be active in the oxidation of linear alkanes by oxygen under mild conditions with the catalysts with the smallest pores being most active. Labinger discusses Thomas' free radical mechanism involving a ROO• species, suggesting that it offers optimism for future developments in the area of hydrocarbon oxidation. That oxygen complexes (with ammonia and hydrocarbons) can provide low energy reaction pathways in oxidation reactions has been established in surface science studies by the Cardiff group of both metal or alkali doped metal surfaces, with caesiated silver surfaces being active in dehydrogenation and selective oxidation, complete oxidation being a minor pathway. At Cambridge Lambert has for many years made extensive and very significant contributions to our understanding of the role of alkali metal doping in the selective oxidation of hydrocarbons by surface science techniques but zeolite inclusion chemistry has provided a new impetus.

The present status of this rapidly moving field emphasising how inclusion chemistry can control oxidation and hydrogenation reactions is discussed thoroughly in the book 'Inclusion Chemistry with Zeolites' (1995), with the progress made through computational methods described by Henson and Cheetham. In 1991 Csicery, when summarising a NATO sponsored meeting, drew attention to the over-emphasis that had hitherto been given to structural studies and the need to give more attention to catalysis. There is no doubt that the community has taken heed of his advice!

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