

Designing new inorganic catalysts ¹

John Meurig Thomas *

Davy Faraday Research Laboratory, The Royal Institution of Great Britain and Peterhouse, University of Cambridge, London W1X 4BS, UK

1. Introduction

We are here concerned with the premeditated construction (conceptually) and the laboratory synthesis of new solid inorganic catalysts. We are also centrally concerned with in situ characterisation of such catalysts, and, in particular, with the quantitative determination of the nature of the active site under operating conditions.

The inorganic solid catalysts upon which we focus belong to that ever-growing family which, in effect, possess three-dimensional surfaces. It seems, at first, an incongruity that we may say that solids can have three-dimensional surfaces. Are not all solids made up of an interior bulk and an exterior two-dimensional surface? Not so. Dehydrated zeolites, which are microporous aluminosilicates, have enormous internal surfaces. Indeed, essentially all the bulk atoms of the zeolites are also surface atoms and are accessible to molecules that have cross-sections small enough (ca. 4 to 7 Å) to gain access into the interior via the myriad apertures and channels that exist at the exterior surface. But naturally occurring or synthetic zeolites are not the only solids that have three-dimensional sur-

faces: microporous aluminium phosphates (ALPOs), along with metal-substituted (in the framework), i.e., MeALPOs and Si(IV)-substituted (in place of P(V) in the framework), i.e. so-called SAPOs are others. And so too are crystalline mesoporous silicas on which we shall focus later. Pillared clays and some other solids also fall into this category (see papers in Ref. [1] and Refs. [2–5]).

Such materials, apart from being of key importance as commercially viable catalysts, are eminently amenable to in situ characterisation because:

(i) techniques in standard and extensive use for the characterisation of solid materials in bulk (i.e. the whole range of spectroscopic as well as diffraction or imaging based tools) may be straightforwardly applied for their structural elucidation; and

(ii) the active sites are dispersed throughout the bulk of the solid in a manner that is generally spatially uniform. A high-resolution electron micrograph (taken by my co-worker Dr. Prati-bha Gai-Boyes) of ZSM-5, which is archetypal of the kind of uniform heterogeneous catalyst under discussion here, is shown in Fig. 1. And Fig. 2 (prepared by Dr. Lewis) is a computer-graphic representation of a single 10-membered ring aperture inside which an active site (consisting of Si–O(H)–Al) is ‘visible’. (By a 10-membered ring we mean 10 oxygen atoms each

* Tel.: +44-171-4092992; fax: +44-171-6293569.

¹ Communication presented at the First Francqui Colloquium, Brussels, 19–20 February 1996.

connected to two tetrahedrally bonded atoms such as Si, Al, P.)

Active sites of a comparable kind in a SAPO catalyst (consisting of Si–O(H)–R) have been quantitatively studied by FTIR and neutron diffraction of a deuterated H⁺SAPO-34 catalyst. Full details will appear in a forthcoming paper [7].

The readily detachable proton (Fig. 2), which makes H⁺ZSM-5 such a powerful Brønsted acid catalyst for isomerizations, alkylations, acylations generally and particularly for the dehydration of methanol (to produce benzene, toluene and xylene) arises because Al(III) replaces Si(IV) in the framework. But other ions may be readily incorporated into the ZSM-5 framework with important catalytic consequences, as may be judged from Fig. 3. It is also known that inserting titanium into the framework of a siliceous microporous, pentasil catalyst like that possessed by ZSM-5, generates a powerful catalyst that may be used adroitly for selective oxidation of alkenes and aromatics [10].

By playing preparative times, both in the laboratory [11–13] and on computer [14,15] — not to mention model building [16] — one may

generate ALPOs, SAPOs and MeAPOs (Me ≡ Mg, Co, Ni or a range of other divalent ions) that also have both three-dimensional surfaces and strong intrinsic catalytic activity. In the novel solid-acid catalyst known as DAF-1, for instance, we have a Mg–ALPO with apertures and pores large enough to accommodate molecular species such as isooctane, cyclohexane, cyclooctane and even bulkier ones (Fig. 4(a) and (b)). It is now possible to insert, in a more or less thermally stable fashion, between a quarter and a third of the elements of the Periodic Table into microporous structures possessing three-dimensional surfaces in the sense described earlier.

CoALPO-18 (Fig. 5) is a good catalyst for converting methanol to light alkenes [18]. It so happens that the dimensions of the cages — the walls of which are lined with Brønsted catalytic sites — are just too small to allow the (shape-selective) dehydration of methanol to continue so as to form aromatics. Size restriction in the vicinity of the active sites permits the formation of only light alkenes. (This kind of topic is one to which our awardee, Dr. Derouane, has made major contributions [8] with his constructive

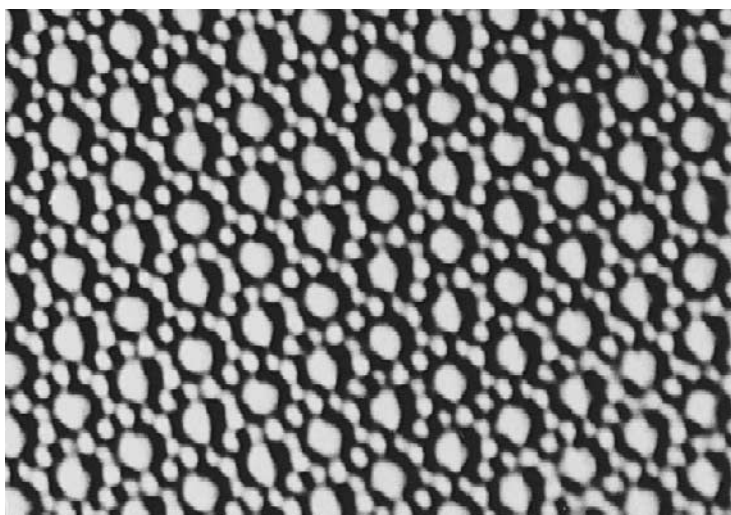


Fig. 1. High resolution electron micrograph of a zeolite catalyst (ZSM-5) showing the projected structure in which all the pores (diameter ca. 5.5 Å) are lined with active sites. (After Thomas and Gai-Boyes [6].)

introduction of such concepts as the nest effect and confinement effect.) The concentration of Co(II) ions in the framework of the parent ALPO seldom exceeds a few percent, too low to be directly addressable by X-ray diffraction. We may, however, use X-ray absorption, thanks to the availability of synchrotron radiation. Furthermore, we have evolved methods of probing

catalysts of this type under operating conditions using combined X-ray diffraction and X-ray absorption spectroscopy (XRD and XAS) recorded with the sample under realistic conditions of catalytic use (see Refs. [8,19,17]). Such combined studies, in parallel with infrared absorption spectroscopy, yield results typified by those shown in Fig. 5, where the changed bond

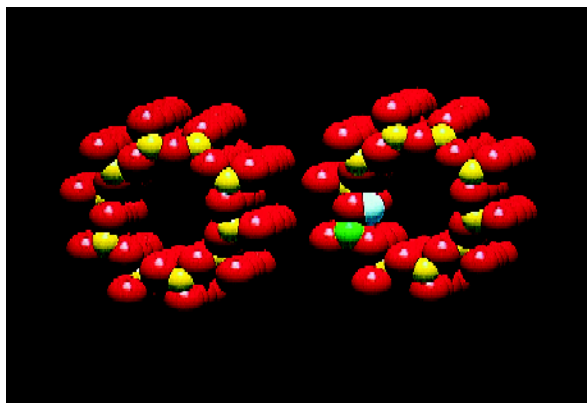


Fig. 2

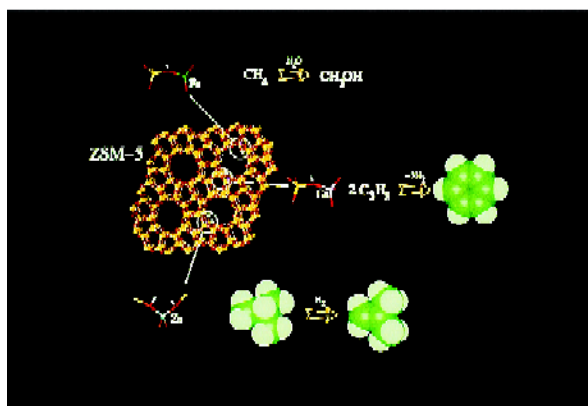
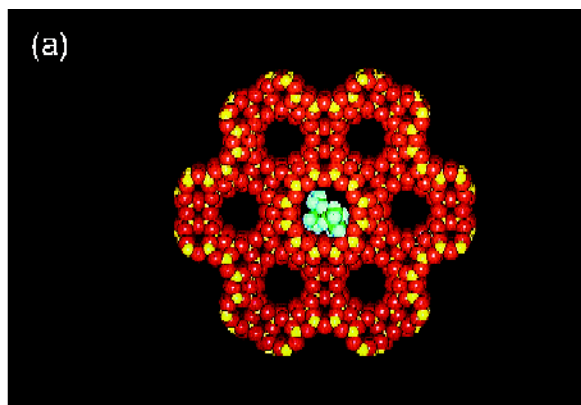


Fig. 3

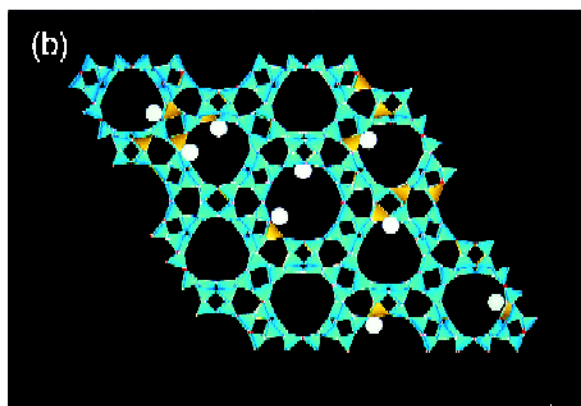


Fig. 4

Fig. 2. A computer-graphic view looking into a 5.5 Å diameter pore of ZSM-5 (i.e. into the large white spots of Fig. 1). In a purely siliceous microporous solid (i.e. SiO_2) the situation is as shown on the left. When Al(III) replace Si(IV) ions in the framework the situation is as illustrated on the right.

Fig. 3. ZSM-5 and its use as a modified catalyst for methane oxidation to methanol [8,9]; propane to benzene; and isobutane to 2-methylpropene (i.e. isobutene or isobutylene).

Fig. 4. (a) Projected view of the magnesium aluminophosphate known as DAF-1 [13] in the pores of which isooctane is lodged. (After R.G. Bell.) (b) Polyhedral representation of the DAF-1 structure where the buff-coloured tetrahedra are those that are Mg(II)-centred. All other tetrahedra are, alternately, Al(III)- or P(V)-centred. (After R.G. Bell.)

lengths associated with conversion of the Co(II) to Co(III) valence states, while still retained in the framework, may be quantitatively specified.

2. The situation up to 1992

In a review article published by Davis [2] in 1993 the natural progression in size of cavity — from a low of ca. 4 Å for zeolite A up to a high

of ca. 14 Å in JDF-20 [20] — was outlined. How far could one expect changes in the conditions of preparation of such solids to yield continually increasing aperture diameters?

Although this question was doubtless worth asking, with hindsight one now sees that a turning point came in 1992 with the arrival [21–23] of the so-called MCM-41 series of mesoporous silicas, in which the diameters of the apertures fell in the range 25 to 100 Å (Fig.

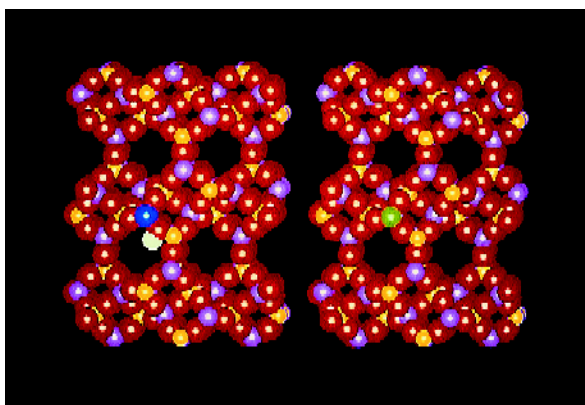


Fig. 5

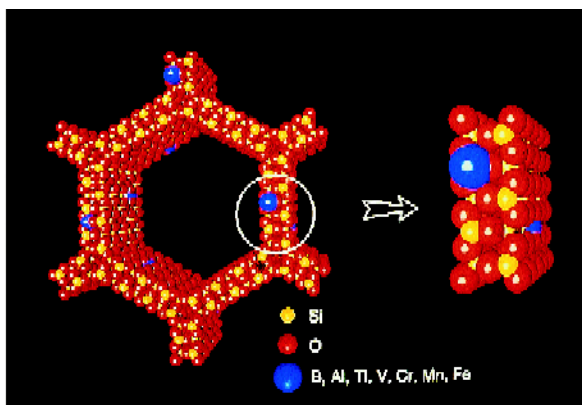


Fig. 7

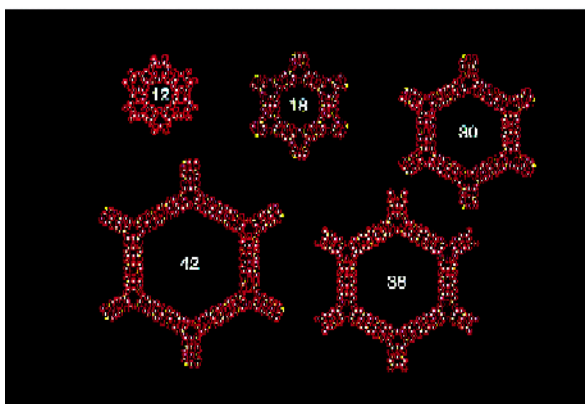


Fig. 6

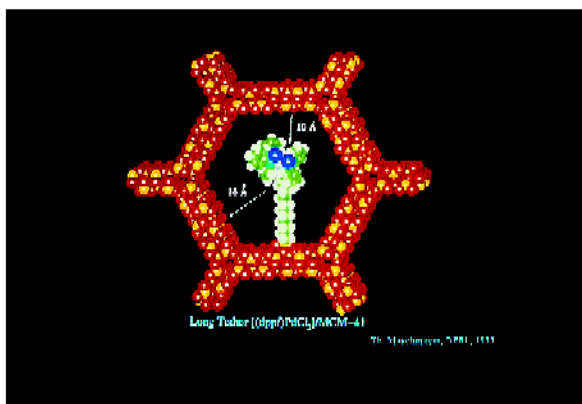


Fig. 9

Fig. 5. Quantitative description (of bond lengths and coordination) at the Co(II) active site in the CoALPO-18 solid acid catalyst for the selective dehydration of methanol. (From Thomas and Greaves [17].)

Fig. 6. Representations of typical (known) as well as feasible (as yet unknown) structures of hexagonal MCM-41 type silicas. The numbers given in the centre of each cage refer to the progressive increase in peripheral, linked SiO_4 tetrahedra. (After R.G. Bell.)

Fig. 7. Idealised, metal-containing MCM-41 structure generated by computer modelling methods. (From Rey et al. [25].)

Fig. 9. An example of tethered metallic catalyst, prepared by T. Maschmeyer (unpublished), at the Davy Faraday Research Laboratory (see also Ref. [26]).

6). What, in effect, took place with the announcement of the formation of mesoporous silica via the Mobil (and other [22]) approach to synthesis of solids with three-dimensional surfaces using liquid-crystal templates, was a minor revolution in the surface chemistry of solids and catalysts. Now, at last, there appeared a route to the rational synthesis of a quite vast range of mesoporous silicas — or many other oxides including those with a formula close to $ZrO_2V_2O_5$ or $Al_2O_3P_5O_5-SiO_2$, and WO_3 [24]. Moreover, it has not proved insurmountably difficult to form MCM-41 materials in which one (or more) of some seven or so different elements may be strategically placed within the cavities of the mesoporous solid as shown in Fig. 7.

So, with MCM-41, came the era in which a

mesoporous solid of great potential (and value to the petrochemist) could be routinely prepared. With the wide apertures of these novel solids — enabling facile ingress and egress of bulky molecules — a vast array of new types of catalytic applications may be envisaged. Some of these have already been realised as we outline below.

3. Grafted and tethered active centres in mesoporous catalysts

The large diameters (ca. 30 Å) channels of the MCM-41 mesoporous silicas that many research groups have synthesised may be modified and adapted for specific catalytic purposes by the direct grafting of complete metal com-

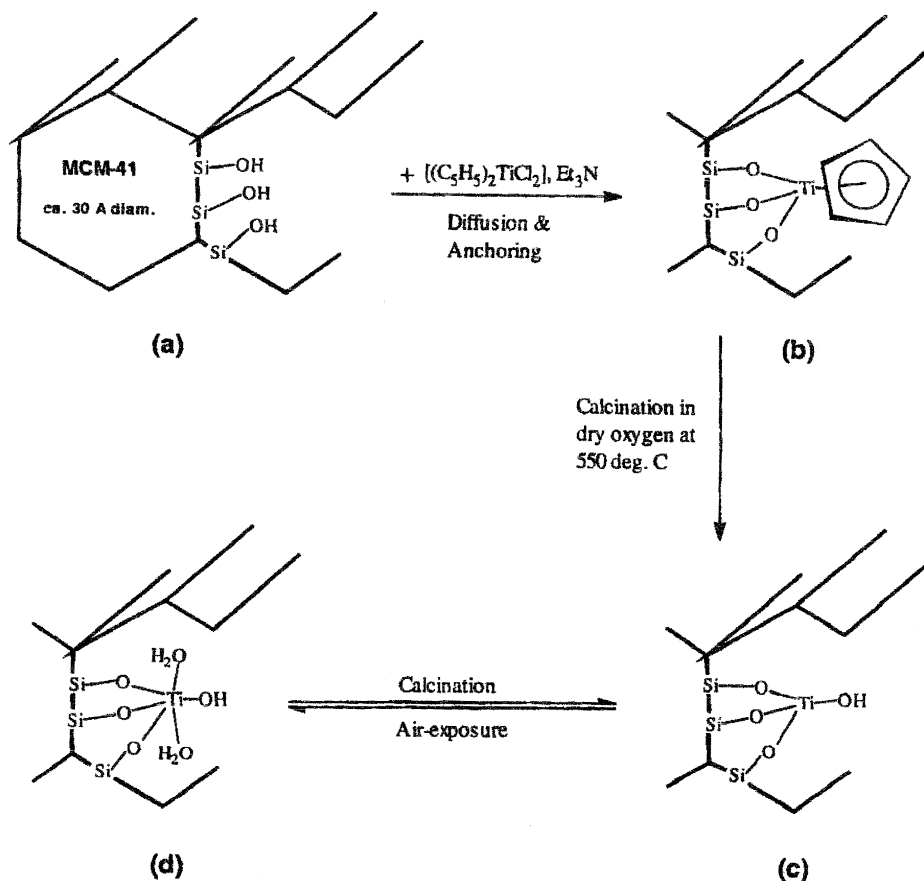


Fig. 8. Schematic representation of the preparation of the grafted catalyst: (a) the support, (b) anchoring reaction, (c) calcination, and (d) reversible reaction of the organometallic-derived Ti-MCM-41 epoxidation catalyst with water upon exposure to the atmosphere.

plexes and organometallic moieties onto the inner walls of their high-surface areas (typically $1000 \text{ m}^2 \text{ g}^{-1}$). This opens routes to the preparation of novel catalysts consisting of large concentrations of accessible, well-spaced and structurally well-defined active sites. Maschmeyer et al. [26] in this laboratory have described the production of titanocene-derived catalyst precursors anchored to the inner walls of the MCM-41 silica (where there are forests of pendant $-\text{Si}-\text{OH}$ groups) and its conversion (monitored by X-ray absorption spectroscopy) to a powerful catalyst for the epoxidation of cyclohexene as well as of even bulkier species such as pinene. Furthermore, this catalyst is also potentially suitable in the oxidation of these ethers (to sulphones and possibly sulphoxides) and possibly of other terpene molecules of relevance in the world of perfumery [27]. X-ray absorption spectroscopy not only helps (as does in situ FTIR) to identify key intermediates in the epoxidation catalysts, but also reveals that, in the activated state of the precursor, Ti is four coordinated with no evidence for a titanyl ($\text{Ti}=\text{O}$) bond. During catalytic reaction, EXAFS analysis shows that the Ti(IV) ion is in six-fold coordination — see Fig. 8.

With MCM-41-based catalysts it is possible not only to anchor a reactive (catalytic) centre, designed to order according to the principles of organometallic chemistry, but also to tether them as schematised in Fig. 9. Here the active site is situated at the extremity of the tether, and is free to flutter in the molecular breeze during the process of catalytic conversion. By deliberately restricting the spatial freedom in the vicinity of the active centre it should be possible to design highly stereo-selective (enantiomeric) catalysts. Such possibilities are now under active investigation in numerous laboratories including this one.

Already my colleagues and I know [28] that oxo-centred tricobaltic acetate, tethered on to the inner walls of an MCM-41 silica support, is a very good catalyst for the selective oxidation of cyclohexane to cyclohexanone and cyclohex-

anol, which are valuable precursors for the production of nylon. In situ monitoring of the catalyst by X-ray absorption and diffraction enables the intermetallic ($\text{Co}-\text{Co}$) and other distances to be charted in the passage from the prepared to the active catalyst.

Numerous other investigations involving the design of grafted and tethered active sites on mesoporous silicas are underway in this laboratory.

Acknowledgements

I thank EPSRC for its continued support and also Unilever plc for many grants of a largely unrestricted nature. My senior postdoctoral colleagues, Drs. G. Sankar and T. Maschmeyer, are gratefully thanked for their collaborative efforts on many fronts.

References

- [1] I.E. Maxwell and M.E. Davis (Eds.), *Curr. Opin. Solid-State Mater. Sci.* (1996).
- [2] M.E. Davis, *Acc. Chem. Res.* 26 (1993) 111.
- [3] J.M. Thomas, *Angew. Chem. Int. Ed.* 33 (1994) 913–937.
- [4] J.M. Thomas, *Intercalation Chemistry*, A.J. Jacobson and M.A. Whittingham (Eds.) (1982) pp. 56–99.
- [5] J.M. Thomas and C.R.A. Catlow, *Progress in Inorganic Chemistry*, S.J. Lippard (Ed.), Vol. 35 (John Wiley, 1987) ch. 1, pp. 1–49.
- [6] J.M. Thomas and P.L. Gai-Boyes, *Nature* 364 (1993) 478.
- [7] L. Smith, A.K. Cheetham, L. Marchese, J.M. Thomas, P.A. Wright and J. Chen, *Catal. Lett.*, 41 (1996) 13.
- [8] J.M. Thomas, *J. Chem. Commun., Faraday Trans.* 100 (1995) C9–C27.
- [9] K.I. Zamaraev, *Top. Catal.*, 3 (1996) 1.
- [10] M. Taramasso, G. Perego and B. Notari, *U.S. Patent*, 4410501 (1983).
- [11] Y. Xu, P.J. Maddox and J.M. Thomas, *Polyhedron* 8(6) (1989) 819–826.
- [12] P.A. Barrett, R.H. Jones, J.M. Thomas, G. Sankar, I.J. Shannon and C.R.A. Catlow, *J. Chem. Soc., Chem. Commun.*, submitted.
- [13] P.A. Wright, R.H. Jones, S. Natarajan, R.G. Bell, J. Chen, M.B. Hursthouse and J.M. Thomas, *J. Chem. Soc., Chem. Commun.* 7 (1993) 633–635.
- [14] D.W. Lewis, C.R.A. Catlow and J.M. Thomas, *Chem. Mater.* 8(5) (1996) 1112–1118.
- [15] D.W. Lewis, D.J. Willock, G.J. Hutchings, C.R.A. Catlow and J.M. Thomas, *Nature*, 382 (1996) 604.

- [16] D. Akporiaye, S.D. Pickett, A.K. Nowak, J.M. Thomas and A.K. Cheetham, *Catal. Lett.* 1 (1988) 133–140.
- [17] J.M. Thomas and G.N. Greaves, *Science* 265 (1994) 1675–1676.
- [18] J. Chen and J.M. Thomas, *J. Chem. Soc., Chem. Commun.* (1994) 603–604.
- [19] J.W. Couves, J.M. Thomas, D. Waller, R.H. Jones, A.J. Dent, G.E. Derbyshire and G.N. Greaves, *Nature* 354 (1991) 465–468.
- [20] Q. Huo, R. Xu, S. Li, Z. Ma, J.M. Thomas, R.H. Jones and A.M. Chippindale, *J. Chem. Soc., Chem. Commun.* 12 (1992) 875–876.
- [21] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartali and J.S. Beck, *Nature* 359 (1992) 710.
- [22] Q. Huo et al., *Nature* 368 (1994) 317.
- [23] I.E. Maxwell and M.E. Davis, *Curr. Opin. Solid-State Mater. Sci.* 1 (1996).
- [24] J.M. Thomas, *Nature* 368 (1994) 289–290.
- [25] F. Rey et al., *Top. Catal.* 3(1, 2) (1996) 121–134.
- [26] T. Maschmeyer, F. Rey, G. Sankar and J.M. Thomas, *Nature* 378 (1995) 159–162.
- [27] A. Corma, F. Rey, J.M. Thomas, G. Sankar, G.N. Greaves, A. Cervilla, E. Llopis and A. Ribeiro, *Chem. Commun.*, in press.
- [28] T. Maschmeyer, R.J. Oldroyd, G. Sankar, J.M. Thomas, I.J. Shannon, J. Kleptko, A.F. Masters and C.R.A. Catlow, *Science*, submitted for publication.