A double-barrelled zeolite

TEMPLATING on lipid aggregates and their ilk may be the new trend, as Davis's News and Views article describes, but there is life in the old molecular templating method yet — the remarkable zeolite created by J. M. Thomas and colleagues at the Royal Institution testifies to that

pores, 1.6 nm across and large enough to accommodate multiply branched alkanes or other large molecules. The A channels are linked to each other through shorter 10-ring pores, and to the B channels by 8-ring pores (free diameter ~ 0.39 nm). The organic 'template' used in this

in the channels. The template can be removed by calcination in dry oxygen at 610 °C to yield the acidic form of the material, thus opening up the possibility that it may be used in acid-catalysed reactions.

The structure looks much like a hybrid between the two most widely used zeolitic catalysts, zeolite Y (with the structure of the natural mineral faujasite) and zeolite ZSM-5, shown in Davis's figure. Zeolite Y, used for catalytic cracking in gasoline manufacture, has a three-dimensional network of pores in which 12-ring windows (free aperture ~ 0.74 nm) open into larger cavities, ~ 1.2 nm across. ZSM-5, which is used in xylene isomerization and methanol conversion, contains two different channels of similar size to the A channels in DAF-1, but in this case the channels intersect. Because of its family resemblance to zeolites Y and ZSM-5, it is expected that DAF-1 should also be useful for shape-selective hydrocarbon conversions.

But that is not all. The complex architecture of non-intersecting pores offers, at last, a real prospect of molecular 'traffic control' (E. G. Deruane, *J. Catal.* 100, 541–544; 1986). The hope is that two types of large molecules, such as the branched alkanes essential to the petrochemical industry, could be preferentially accommodated in the A or B channels. Small molecules, such as methanol, would be free to nip between the channels and react with the imprisoned molecular juggernauts.

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The hexagonal crystal structure of DAF-1, showing a space-filling model viewed down the unique axis with the B channel (at the centre) surrounded by a hexagon of A channels, and side views of the A (left) and B (right) channels, with iso-octane molecules located at their respective energy minima (courtesy of P. A. Wright).

(P. A. Wright *et al.* *J. chem. Soc. chem. Commun.* 633–635; 1993).

The new material, known as DAF-1 (Davy–Faraday-1), is the first zeolite with two large, but different, non-intersecting channels (see figure). Each of the channels has 'windows' made up of 12 tetrahedrally coordinated aluminium or phosphorus atoms, linked by oxygen bridges. The smaller channel (A) has a uniform free diameter of only ~ 0.61 nm because of puckering of these 12-rings, whilst the wider channel (B), of free diameter 0.74 nm, opens into bulbous

case is decamethonium hydroxide, $\{(-(\text{CH}_2)_5\text{NMe}_3)_2(\text{OH})_2\}$, which is incorporated into the channels of the final product. In chemical terms, the system is a metal-containing aluminium phosphate, otherwise known as a MeAPO molecular sieve. The metal (magnesium, for example) substitutes for aluminium in the aluminium phosphate framework (E. M. Flanigen *et al.* in *New Developments in Zeolite Science and Technology*, 103–112 (Kodansha, Tokyo, 1986)) so charge-compensating cations, in this case the template, are required

possibility of designing new materials will really be with us. Chemistry libraries overflow with information on synthesizing specific organic microstructures, whether by employing new amphiphiles, counterions, cosurfactants or mixtures thereof. With a little ingenuity, we should be able to adapt this to the design of composite (organic–inorganic) structures.

In fact, even lipid tubules can be used to organize silicon⁸ and iron¹ oxides. As Archibald and Mann show, lipid-iron oxide composites can be synthesized as tubes or lamellar disks depending on the synthesis conditions¹, showing how flexible this new method can be. Moreover, the inorganic portion need not be inorganic oxides. Clever choices of inorganic precursors should allow a broad spectrum of inorganic materials to be formed.

The concept of self-assembled microstructures serving as structure-directing agents, new as it is, is not limited to inorganic materials. For example, biconti-

nous phases can be used to organize organic species which are then photopolymerized; after extraction of unpolymerized components, what are left are porous organic monoliths^{11–13}. These materials, with pores in the size range 2–50 nm, are useful for separations technology, and for soft contact lenses and other biological and medical applications. These materials can readily be made biocompatible, as they are in many ways similar to biological membranes. In fact, biomineralization in living organisms^{14,15} may well resemble this organization of inorganic materials by self-assembled molecular aggregates.

The importance of these new synthetic efforts is that three-dimensional structures with prescribed architectures — regularly spaced pores, thin sheets or scaffolding-style structures — containing order on the 2–100 nm length scale can be formed through self-assembly processes. Order on this size offers opportunities for

synthesizing novel catalysts, electronic materials and the like. For example, the material MCM-41^{5,6,10} would be formed from the hexagonal phase illustrated in the figure where the aqueous region is

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