Ordered porous materials for emerging applications

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"Space—the final frontier." This preamble to a well-known television series captures the challenge encountered not only in space travel adventures, but also in the field of porous materials, which aims to control the size, shape and uniformity of the porous space and the atoms and molecules that define it. The past decade has seen significant advances in the ability to fabricate new porous solids with ordered structures from a wide range of different materials. This has resulted in materials with unusual properties and broadened their application range beyond the traditional use as catalysts and adsorbents. In fact, porous materials now seem set to contribute to developments in areas ranging from microelectronics to medical diagnosis.

Porous solids are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but throughout the bulk of the material. Not surprisingly, traditional applications of porous materials thus involve ion exchange, adsorption (for separation) and catalysis, and many of these benefit from the high order that can be achieved in solids such as zeolites.

The pores of solids are classified according to size: pore sizes in the range of 2 nm and below are called micropores, those in the range of 2 nm to 50 nm are denoted mesopores, and those above 50 nm are macropores. The distribution of sizes, shapes and volumes of the void spaces in porous materials directly relates to their ability to perform the desired function in a particular application. The need to create uniformity within the pore size, shape and volume has steadily increased over recent years because it can lead to superior applications properties. For example, a material with uniform micropores, such as a zeolite, can separate molecules on the basis of their size by selectively adsorbing a small molecule from a mixture containing molecules too large to enter its pores. Clearly, a distribution of pore sizes would limit the ability of the solid to separate molecules of differing sizes.

In addition to the pore space, the atoms in the solid creating that space can be important. For example, molecular sieves comprising pure silica are hydrophobic and can adsorb organic components from water, whereas molecular sieves comprising aluminosilicate are hydrophilic and can thus adsorb water from organic solvents. Because the control over the uniformity of pore space and the composition of the solid that creates the space is of importance, this review concentrates on porous materials with more ordered structures. Here, I will cover significant issues in microporous materials that have occurred over the last decade or so. In addition to microporous materials, the well-ordered mesoporous solids will be discussed, as they have recently received much attention. The type of materials described here are generally synthesized at low temperatures (less than 473 K) and pressures (a few atmospheres) and in aqueous media. The syntheses do not normally give the thermodynamically most stable product but rather a material that is the result of a kinetically controlled synthetic pathway. Although the starting reagents and compositions and the precise procedures will differ for each type of material, the syntheses are reproducible and thus allow for use in applications. A brief review on zeolites and molecular sieve syntheses that discusses these issues is available[1], as are reviews on microporous and ordered mesoporous materials syntheses and their applications as catalysts[2].

In 1988, the first report of a crystalline microporous material with uniform pores larger than 1.0 nm appeared[3], the ability to syn-thesize well-ordered mesoporous materials was about to be announced[4], and scaffolding-like (but non-porous) structures built from three-dimensional, linked modular molecular units[5] were appearing in the literature. Moreover, zeolite-based membranes with 'molecular sieving' properties were discussed[6], and the inclusion of electro- and photo-active guest molecules in porous host materials[7] gave rise to interesting phenomena. But despite their promise for advanced materials applications, none of these materials led to practical successes. Today, the situation is rather different: our understanding of the structure of ordered porous materials and how to control and tune it has increased considerably and advances have led to practical applications. In fact, the future
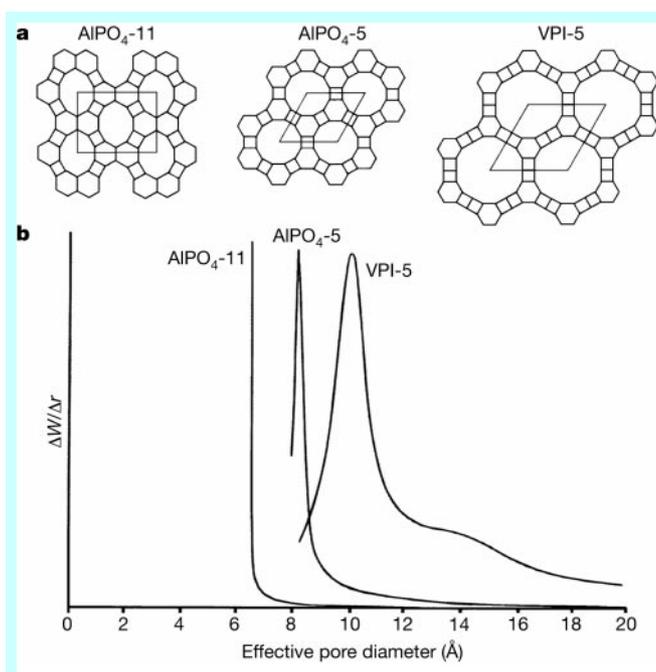
Figure 1 Pore characteristics in the aluminophospates $AlPO_4$-11, $AlPO_4$-5 and VPI-5. **a**, Representations of the pores in the aluminophosphates $AlPO_4$-11, $AlPO_4$-5 and VPI-5. The line segments represent oxygen atoms that bridge between two tetrahedral atoms (intersection points) that are in this case either Al^{3+} or P^{5+} with strict alternation to give a composition of $AlPO_4$. Rhomboids indicate the unit cell. **b**, Measured pore sizes by argon adsorption techniques. Note that VPI-5 shows a pore diameter above 1.0 nm. (ΔW is the change in adsorption mass and Δr is the change in radius of the pore size.)

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uses of ever more sophisticated versions of these materials look very promising.

Microporous materials with large pores

The preparation of the aluminophosphate VPI-5—the above-mentioned crystalline microporous material with uniform pores larger than 1.0 nm—opened up the area of extra-large pore crystalline materials. Extra-large pores are obtained if more than 12 oxygen atoms span the circumference of the pore (see also Fig. 1), and the resultant pore size allows practical applications for which materials with smaller pores are not suitable. In VPI-5, the pores are circular one-dimensional channels that, owing to the crystallinity of the material, have an absolutely uniform diameter of 1.2 nm and endow the material with an approximately 30% void fraction[8]. Following the discovery of VPI-5, numerous extra-large pore materials were synthesized. Table 1 lists typical (though not all) representatives of such materials, all having structures that contain rings made of more than 12 oxygen atoms and most of them phosphate-based. Except for the silicas, these extra-large pore materials exhibit in their as-synthesized form at least one of the following features: (1) mixed metal-ion coordination (such as aluminium in octahedral and tetrahedral coordination), (2) terminal OH groups, and (3) the presence of other non-tetrahedral framework species (such as OH, H_2O, F). These features lower the framework stability relative to that of fully tetrahedrally coordinated materials such as zeolites and their pure-silica analogues. For example, JDF-20 (see Table 1) decomposes upon removal of occluded organic species[9], and exchange of the 1,2-diaminocyclohexane molecules from as-synthesized ND-1 by alkali-metal cations and small alkylammonium cations transforms the material to other products[10].

The diversity in porosity encountered in extra-large pore crystalline materials is strikingly illustrated by the phosphate-based materials listed in Table 1. For example, the pore shape of cloverite resembles a cloverleaf (hence the origin of the name)[11]: the 20-membered ring enclosing the pore contains four terminal OH groups that intrude into the opening to provide the cloverleaf shape. Cloverite is thus unlikely to accommodate molecules of a certain size and shape that can be accommodated in the circular pores of VPI-5. In fact, the role of pore size as well as pore shape in effecting the separation of molecules has recently been demonstrated with ETS-4 (ref. 12): as illustrated schematically in Fig. 2, the pore shape of this material is crucial to discriminate between unsymmetrical N_2 and symmetrical CH_4. This principle, which has led to separation devices that are now commercially available (as Molecular Gate Technology; details available from molecular.gate@engelhard.com), might be extendable to materials with larger pores and the separation of larger molecules.

In addition to pore shape variations, the materials listed in Table 1 also exhibit pronounced differences in the shape and size of their void space. For example, the pore system of cloverite is three-dimensional, containing 3-nm cages that are each accessible through six clover-shaped pores; in contrast, VPI-5 has one-dimensional and uniform pore channels. The fact that cloverite has large cages to which smaller pores provide access allows for the construction of inclusion species and 'ship-in-a-bottle' syntheses, where individual reagents are sufficiently small to enter through the pores, but the assembled inclusion complex is then too large to escape the cages.

The practical value of phosphate-based extra-large pore materials is limited by their relatively poor thermal and hydrothermal stabilities as compared to those of silica-based molecular sieves. Although some of the phosphate materials are sufficiently stable for certain (low-temperature) application areas, concern was raised over whether all extra-large pore materials would lack stability, owing to the presence of extra-large rings in their structures. In the case of VPI-5, the lack of stability has been attributed to the nature of the structural units, rather than to the presence of the extra-large ring (ref. 13 and references therein). This was inferred from VPI-5 and the aluminophosphate $AlPO_4$-H2 being made of the same basic structural units and exhibiting similar instabilities, even though the latter has one-dimensional pores comprising only 10-membered rings. More direct evidence for this interpretation was provided by the successful synthesis of the two extra-large pore silicas UTD-1 (ref. 14) and CIT-5 (ref. 15), which are both crystalline silicas containing 14-membered pore rings (see Table 1). The thermal and hydrothermal stabilities of these materials are comparable to the stabilities of other zeolites containing smaller rings within their structures, thus confirming the view that the presence of extra-large rings does not itself result in destabilization. Rather, the lack of stability seen in phosphate-based materials is due to other structural features, for example, mixed metal-ion coordination, terminal OH groups and the presence of non-tetrahedral framework species such as OH, H_2O or F (as mentioned above).

Given the limited stability of phosphate-based materials, the synthesis of extra-large pore crystalline silicas is a promising advance. Both UTD-1 and CIT-5 (see Table 1) have one-dimensional pore systems, with elliptical (0.75×1.0 nm) and circular (0.75 nm) pore shapes, respectively. These materials provide the precedent for the ability to synthesize extra-large pore crystalline solids and apply them to a greater variety of commercially relevant applications.

Porous metal–organic frameworks

A different approach to preparing microporous solids involves the coordination of metal ions to organic 'linker' moieties, thus yielding open framework structures. In fact, these materials have a long history, and examples include transition metal cyanide compounds (early examples are Hofmann-type clathrates, Prussian-Blue type structures and Werner complexes) and the diamond-like framework bis(adiponitrilo)copper (I) nitrate[16]. Open frameworks comprising metal–organic units gained renewed inerest in the 1990s, but the inability of these solids to maintain permanent porosity and avoid structural rearrangements upon guest removal or guest exchange (some leading to complete collapse of the framework) has been an obvious shortcoming. However, metal–organic frameworks (MOFs) that exhibit permanent porosity have now been prepared[17–19]. The first such solid was MOF-5, which consists of

Table 1 Representative examples of crystalline materials with ring sizes above 12					
Material	Year reported	Main framework composition	Ring size (oxygen atoms)	Pore size (nm)*	Reference
VPI-5	1988	$AlPO_4$	18	1.2	3, 8
$AlPO_4$-8	1990	$AlPO_4$	14	<1.0	131, 132
Cloverite	1991	$GaPO_4$	20	<1.0	11
JDF-20	1992	$AlPO_4$	20	−†	9
ULM-5	1994	$GaPO_4$	16	ND	133
UTD-1	1996	SiO_2	14	~1.0	14
ULM-16	1996	$GaPO_4$	16	ND	134
CIT-5	1997	SiO_2	14	0.8	15
ND-1	1999	$ZnPO_4$	24	ND	10
FDU-4	2001	Ge_xO_y	24	ND	135
NTHU-1	2001	$GaPO_4$	24	ND	136

ND, Not determined.   *By adsorption.   †Structural collapse upon removal of organic.

Zn^{2+} and 1,4-benzenedicarboxylate and has a microporous volume larger than any known zeolite[17]. Another example is a copper-containing framework with pores of 1.64 nm diameter[18]. Recently developed MOF-type solids exhibit the lowest densities reported for any crystalline material ($0.41–0.21\,g\,cm^{-3}$) as well as a high methane storage capacity[19].

Porous metal–organic frameworks are unlikely to compete with zeolites and other oxide-based porous materials in high-temperature applications owing to their limited long-term stability under such conditions and high cost. But the ability to prepare such solids, including frameworks with extra-large pores and high pore volumes, is nevertheless likely to open up many application possibilities in niche areas. For example, the methane adsorption capacity of solids based on copper dicarboxylates and triethylenediamine[20] and of MOF-type solids[19], exceeds that of any other known crystalline material. The functionalization of the organic component of the framework, or incorporation of functional organic groups directly into the framework, may yield porous solids that contain different groups capable of binding guests and/or catalysing chemical reactions involving adsorbed guests. However, organic-functionalized porous oxides are now also available[21] and are likely to compete successfully with metal–organic frameworks in such applications.
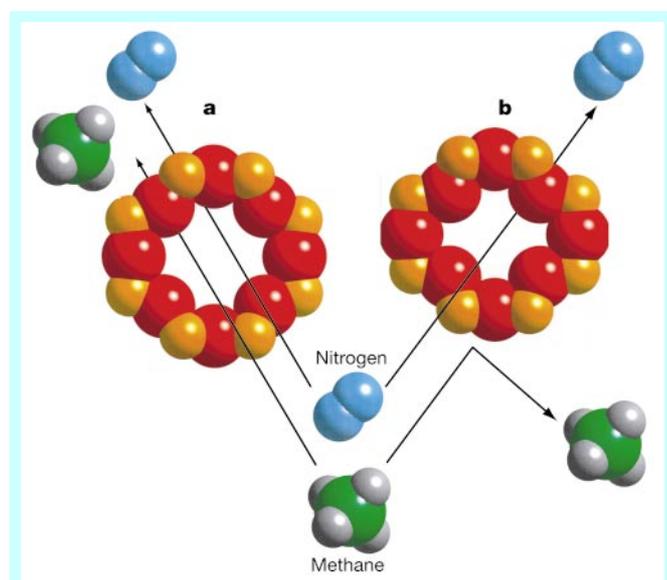
Unique application possibilities may arise from the ability to exploit the metal component and/or its interaction with guest molecules to design porous materials with unusual physicochemical properties, such as redox potentials, light absorption properties or magnetic moments. Moreover, the metal–organic framework approach seems particularly suited to constructing a wide range of chiral porous materials[22,23] for applications requiring enantioselective adsorption and catalysis. In contrast, the formation of chiral porous structures from oxides is proving very difficult, despite one example of enantioselective catalysis and separation using a partially chiral zeolite[1].
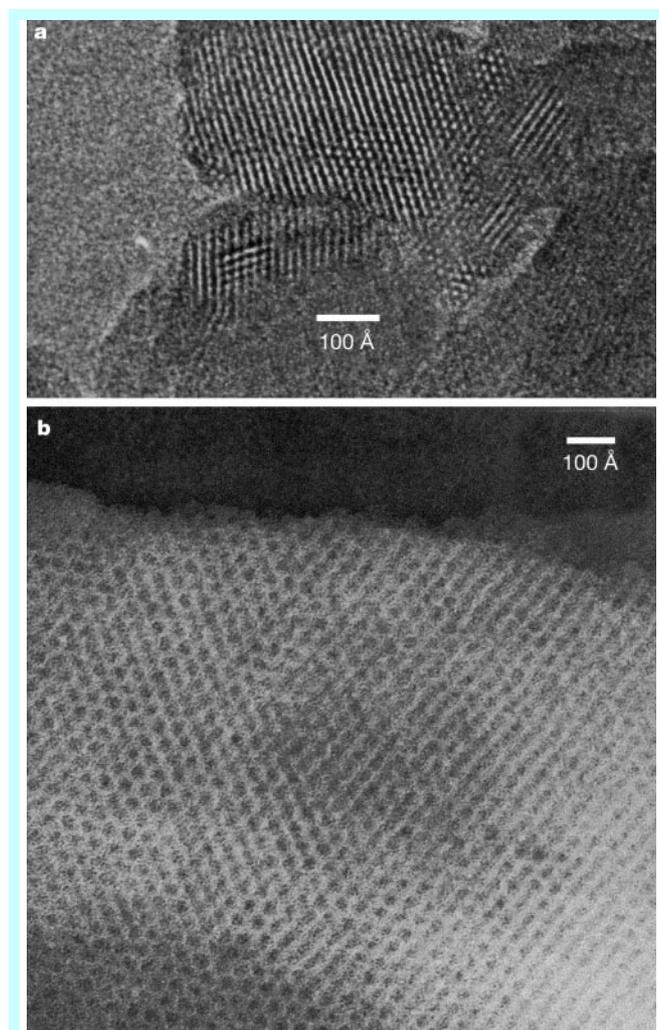
Ordered mesoporous materials

In parallel to the above work on crystalline microporous materials with extra-large pores and on crystalline metal–organic porous solids, the discovery and development of well-ordered, mesoporous materials occurred. Intense focus on ordered mesoporous materials was largely initiated by a report[4] from workers at Mobil in 1992, who described the successful preparation of mesoporous silicas with hexagonal and cubic symmetry and pore sizes ranging from 2 to 10 nm, through the use of surfactants as organizing agents. It was clear that extra-large pore, crystalline materials like VPI-5, $AlPO_4$-8 and cloverite influenced this work, and at that time, no conclusions were drawn as to whether or not the walls of the ordered mesoporous materials had precise atomic ordering[4]. In fact, the hexagonal variant of the material was speculated to be a larger-pore version of VPI-5 (see Fig. 3).

The ^{29}Si nuclear magnetic resonance (NMR) spectrum of Mobil's mesoporous material MCM-41 suggested a disordered wall structure. But this evidence is not conclusive, given that crystalline pure-silica materials with *BEA topology exhibit similar ^{29}Si NMR spectra, owing to a large number of framework defect sites. Proof for the lack of crystallinity of MCM-41 was the subsequent observation[24] that dehydrated samples gave Raman bands indicative of planar 3-membered ring stretch vibrations; crystalline materials containing 3-membered rings do not reveal these vibrations[25] because the rings are no longer isolated when contained within a continuous three-dimensional framework[26]. Moreover, the spectra matched those of amorphous oxides and glasses with 3-membered rings at their surfaces. The lack of precise atomic positioning in these well-ordered mesoporous materials thus suggests that analogous,

Figure 3 Transmission electron micrographs of VPI-5 and MCM-41. **a**, Micrograph of VPI-5; **b**, micrograph of MCM-41; note the difference in scale. Panel **b** is adapted from ref. 24, with permission from Elsevier Science.

Figure 2 Pore size and shape of ETS-10. **a**, Circular pore shape does not discriminate between nitrogen and methane. **b**, Elliptical shape of pore, obtained upon heat treatment, allows nitrogen adsorption only.

well-ordered mesoporous materials can be prepared using element combinations found in other amorphous materials, such as aerogels, xerogels, organic–inorganic hybrid materials, metals and mixed-metal alloys. Indeed, some of these materials are now available in ordered, mesoporous forms[27–29]. Very recently, an ordered, hexagonal mesoporous benzene–silica composite was prepared[30] from the assembly of 1-4-bis(triethoxysilyl)benzene $[(C_2H_5O)_3Si–C_6H_4–Si(OC_2H_5)_3]$ and alkyltrimethylammonium surfactants. This material exhibits periodicity in the hexagonal arrangement of the mesopores obtained upon surfactant removal (5.25 nm lattice constant) and periodicity in the walls along the channel direction with a spacing of 0.76 nm (silica and aromatic units alternate). It will be interesting to see whether this unique arrangement can be generalized to hybrid materials made of other combinations of organic and inorganic units.

Although the report on MCM-41 by Kresge et al.[4] stimulated recent work on ordered materials with uniform mesoporosity, evidence that such materials could be prepared precedes their publication[31,32]. In fact, materials of the type reported by Kresge et al.[4] may have already been made decades ago: in 1971, a material described as low-bulk density silica was obtained through hydrolysing and condensing tetraethylorthosilicate in the presence of cationic surfactants[33]. The porosity and structure of the low-bulk density silica were not reported, but attempts to reproduce the synthesis revealed that it may have yielded ordered mesoporous materials[34]. The first clear demonstration of the successful preparation of a material exhibiting uniform mesoporosity was achieved by Manton and Davidtz[32], who obtained amorphous aluminosilicates with fairly uniform pores, by using quaternary ammonium cations such as tetrabutylammonium and tetrapropylammonium cations during the synthesis. Later, Yanagisawa et al. used cationic surfactants to synthesize silicates with uniform mesoporosity[31].

The work by Kresge et al.[4] was thus not in the absence of earlier claims of having prepared materials with uniform mesoporosity. But it nevertheless constituted a breakthrough because the high degree of order achieved in MCM-41 was unprecedented in the literature; there was little evidence of structural order in the materials reported before. (In fact, controlled-pore glass can have a very uniform mesopore size yet have no structural order in the glass.) Moreover, Kresge et al.[4] identified the connection between the ordering observed in the mesoporous materials and the structure-directing aggregation properties of the surfactants used in their synthesis. (Block copolymers also form mesoscopic assemblies and are now used in the preparation of ordered mesoporous materials.) The combination of these two contributions—the novelty of the new materials, with their unprecedented high degree of ordering, and the introduction of a clear conceptual framework that could guide the design of new materials—stimulated an enormous amount of work. Today, a large number of mesoporous materials of varying composition, pore size and inorganic wall thickness are available.

With the exception of the ordered, hexagonal mesoporous benzene–silica composite prepared by Inagaki et al.[30], ordered mesoporous materials are not crystalline, thus permitting their

synthesis by many different routes, as illustrated by the examples reported in references 35–39. As might be expected, the degree of ordering can depend significantly on the method used to synthesize the mesoporous material, ranging from the high degree of ordering first reported by Kresge et al.[4] to an almost complete lack of ordering. That is, while uniformly sized mesopores are produced, the degree to which they form ordered arrangements within the material shows tremendous variability.

It remains unclear why the vast majority of ordered mesoporous materials cannot be synthesized in crystalline form. The recent example of structural order in the walls of the mesoporous benzene–silica composite[30] may help shed light on this issue. Regarding the inorganic mesoporous materials, their syntheses occur under thermodynamic conditions comparable to those encountered during the syntheses of the more open zeolite frameworks[40], suggesting that thermodynamic barriers in the assembly process are not causing the lack of crystallinity. Ordered mesoporous materials were first prepared using charged organic components, and charge matching between the organic and inorganic components should influence the assembly of ordered mesoporous solids. This aspect of their synthesis may be an impediment to crystallinity[41]. However, the ordered mesoporous materials can now be prepared using non-ionic organic compontents. These assemblies would suggest that charge matching is not the only impediment to crystallinity. Likewise, it is now known that not only ordered mesoporous materials can form through intermediate phases that are layered, but also zeolites (examples include MCM-22 (ref. 42) and ferrierite[43]). The involvement of layered intermediates during formation thus does not seem to be why ordered mesoporous materials do not crystallize.

A plausible explanation for the lack of crystallinity may lie in the correlation between the framework density (FD, the number of atoms per nm^3) and the structural features of porous materials. In 1989, Brunner and Meier revealed that crystalline structures containing tetrahedral atoms (T-atoms) exhibit a correlation between their FD and the parameter MINR, the minimum ring size for every T-atom[44]. (If the structure has T-atoms in rings of different sizes, then a " + " is assigned. For example, MINR = 4+ denotes that some of the T-atoms are in 4-membered rings, while others are in rings of larger size.) All crystalline and 'tetrahedral' materials follow this relationship. In the case of oxide-based solids, most structures have MINR $\geqslant$ 4, which would correlate with a maximum void fraction of about 0.5. The correlation does not hold for crystalline structures built from units containing non-tetrahedral atoms, which have indeed been shown to exceed this void fraction[17–19]. Regardless of the phenomena that are the origin of the correlation between the FD and MINR, they may be the reasons why the ordered mesoporous materials are not crystalline (void fractions violate this relationship).

In order to obey the correlation, ordered mesoporous materials would need to have MINR = 3+; that is, they would need to contain a large number of three-membered rings (3MRs). The recognition that 3MR building units are essential if very open framework materials are to be realized[45] initially focused attention on beryllosilicate materials because many beryllosilicate minerals, albeit dense, have a large number of 3MR. In fact, the successful synthesis[46] of an analogue of the mineral lovdarite illustrated that synthetic materials with a high number of 3MRs could be prepared. However, beryllium is highly toxic, and practically more useful implementations of the '3MR concept' based on the FD-MINR relationship will therefore depend on the development of synthetic routes to 3MR structures using elements other than beryllium[47].

Zinc seems a promising and non-toxic substitute for beryllium, given that some dense zincosilicates have isostructures to beryllosilicates that contain a large number density of 3MRs. Zincosilicate syntheses aimed specifically at the preparation of microporous crystalline solids containing 3MRs have therefore been developed[48,49].

Table 2 Synthetic framework materials with numerous three-membered rings

| Material	Composition	FD (atoms per nm^3)	Pore size	Year	Reference
Lovdarite	Beryllosilicate	18.4	9 MR	1986	46
VPI-7	Zincosilicate	17.1	9 MR	1991	48, 49
RUB-17	Zincosilicate	16.8	9 MR	1995	137
VPI-9	Zincosilicate	16.7	8 MR	1996	138
VPI-10	Zincosilicate	15.3	9 MR	1996	139
RUB-23	Lithosilicate	17.7	8 MR	2000	140
RUB-29	Lithosilicate	17.7	10 MR	2001	141
ASU-15	Ge_2ZrO_6F	9.1	10 MR	2000	142
OSB-1	Beryllosilicate	13.3	14 MR	2001	50
OSB-2	Beryllosilicate	12.7	8 MR	2001	50

FD, framework density; MR, membered rings.

Table 2 lists the synthetic crystalline materials that possess a significant number of 3MRs, which include zincosilicates, lithium silicates and a Ge_2ZrO_6F material. The materials listed illustrate the significant progress in the synthesis of MINR = 3+ materials, which now provides routes to new porous solids. Recently, an extra-large pore beryllosilicate with MINR = 3 has been reported[50], which constitutes a promising extension of the '3MR concept' of Meier[45]. Although beryllium's toxicity precludes practical use of this material, the conversion to a zincosilicate isostructure should be feasible.

As stated above, the reason that ordered mesoporous materials cannot be synthesized in a crystalline form is unknown. Materials with the pore volumes of the ordered mesoporous materials would require MINR = 3+ if they were to be tetrahedral frameworks, so it is possible that the appropriate oxide chemistry that would allow the realization of such materials has not yet been explored. A recently reported ordered mesoporous zincosilicate[51] did not contain sufficient amounts of zinc to facilitate the formation of a significant number of 3MRs, and further exploration of zinc-based materials might thus allow the preparation of ordered mesoporous materials that are crystalline.

Hierarchical structures

Interest in hierarchical porous structures has burgeoned over the past decade. Zeolite particles have been used as building blocks to construct hierarchical porous structures. Pure, crystalline molecular sieves have been produced as free-standing films[52], and films, spheres and fibres have been constructed from nanometre-sized crystals[53–55]. Techniques that use colloidal suspensions to shape ceramic structures are well established, and their extension to microporous colloidal particles for casting gels into designed shapes[56] and for film casting[57] provides flexible synthetic routes to a range of hierarchical microporous structures.

In addition to the use of such 'forming operations', hierarchical structures have also been created through bulk dissolution and structural rearrangement approaches. For example, tubes and fibres of zeolite have been prepared by conversion of pre-existing oxide tubes and fibres[58]. An interesting illustration is the zeolitization of diatoms, which involved conversion of a portion of the diatom silica structure into the zeolite ZSM-5, to yield a micro- and mesoporous hierarchical structure[59]. (Diatoms are single-celled algae enclosed by silica shells that, upon death of the algae, collect on the ocean/lake bed as diatomaceous earth or kieselguhr, a material widely used in filtration applications.).
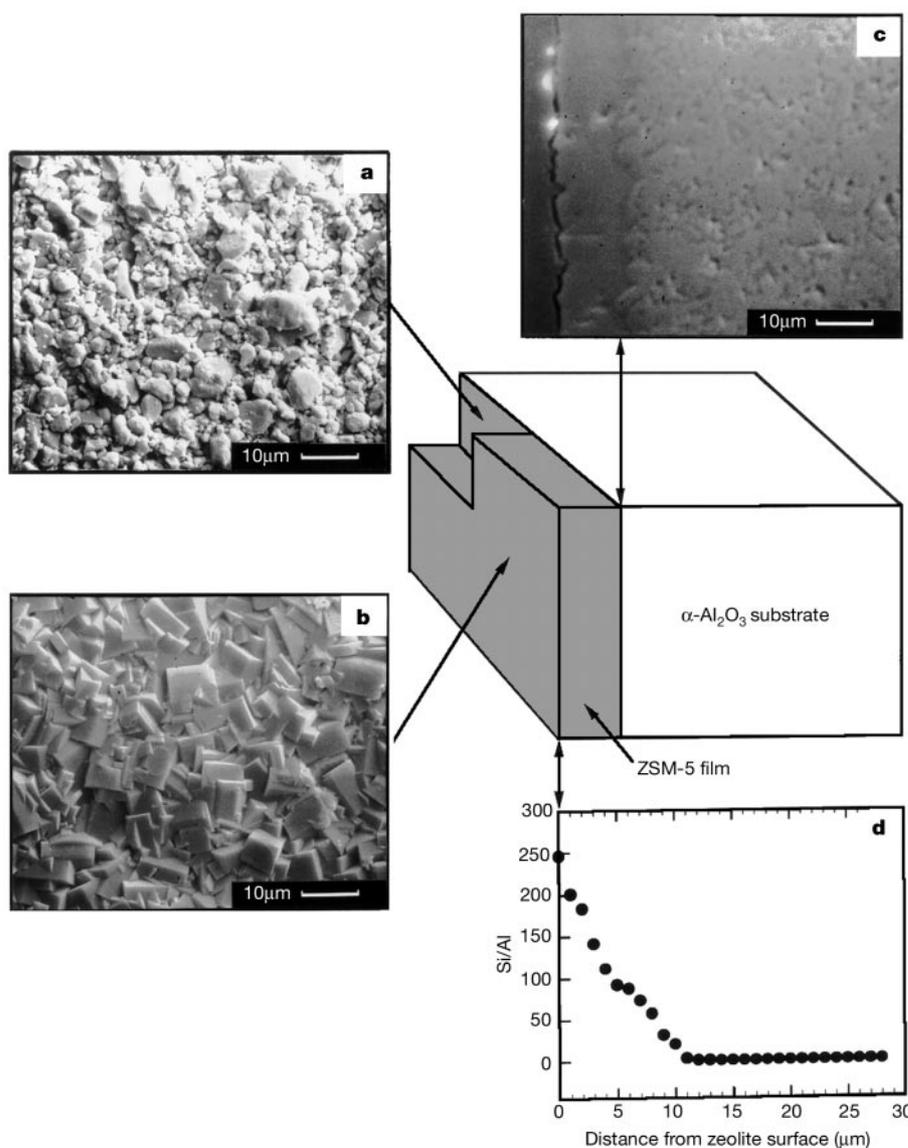
Figure 4 Characteristics of a supported zeolite ZSM-5 film. Shown are scanning electron micrographs of different surfaces (**a**,**b**,**c**) of polycrystalline zeolite ZSM-5 film supported on a porous α-Al$_2$O$_3$ substrate and (**d**) results of electron microprobe analysis showing the zeolite layer to be approximately 10 μm in thickness (consistent with image shown in **c**, which is a view from the top). Adapted from ref. 80; reproduced by permission of The Royal Society of Chemistry.

Hierarchical structures can also be prepared from mesoporous materials. Films, fibres and spheres possessing fairly uniform mesoporosity have been fabricated using surfactants as structure-directing agents, in a manner similar to the synthesis of ordered mesoporous materials[60,61].

Hierarchical porous solids possessing ordered pores on the micro-, and meso- and even macroscale[62,63] have been developed. The hierarchical structure of these materials is expected to open new application opportunities. Until now, most progress has been achieved with films, in terms of both our scientific understanding of their formation and the ability to exploit them for practical applications.

The first zeolite-based films, both supported[6] and freestanding[52], were reported by the early 1990s. Zeolite thin films (Fig. 4) and layers (films and layers refer to continuous and discontinuous structures, respectively; ref. 64 and references therein) are of interest for use as membranes in separations devices and membrane reactors. They can also serve as chemical sensors and hosts for guest species, which in turn impart the material with optical, electrical or magnetic properties.

Early work on zeolite and molecular sieve layers[65–68], including their use as chemical sensors[65,68], yielded layers of randomly oriented materials, while more recent examples contain oriented metallophosphates (zincophosphate, AlPO$_4$-5) and zeolite A. The oriented AlPO$_4$-5 crystals were prepared on alumina membranes[69], while oriented zeolites were obtained using microstructured silicon wafers[70] and metal films[71]. Recently, the heteroepitaxial growth of the zeolites cancrinite[72,73] and chabazite[73] from the surface of millimetre-sized sodalite crystals has been achieved. This break-through in zeolite synthesis opens the way to constructing micro-porous assemblies with precise pore orientation over sufficiently large length scales to be useful for device applications, such as in optics. Oriented layers may find potential use as sensors and other devices, but the lack of continuity precludes their use as membranes. Continuous films have been prepared for use in sensors[74] and as low dielectric constant materials[75], but whether a continuous thin film is indeed required will depend on the particular application[64–68].

In the 1980s, attempts to prepare continuous zeolite films showed little success, but the past decade has seen numerous demon-strations that molecular sieving membranes can be fabricated on ceramic and metal supports in disk and tubular configurations[76–81]. These films usually contained unaligned ZSM-5 zeolite, but con-tinuous and oriented zeolite films have now also been prepared[82–85] and the orientation shown to affect the permeation and molecular sieving behaviour of the membranes[86]. Membranes synthesized

Figure 5 The use of AlPO$_4$-5 as a host for guest molecules. Shown are a micrograph of a AlPO$_4$-5 microcrystal and a schematic representation of its pore structure that can serve as a host for the inclusion of different guest species, to endow the composite structures with new properties.

from other zeolites (such as zeolite A, zeolite Y, mordenite, ferrierite and zeolite UTD-1) and molecular sieves (such as AlPO$_4$-5) are now available as well.

In addition to molecular sieve films and layers, ordered meso-porous materials have been fabricated in these configurations[87–96]. The mesoporous films have been investigated as hosts for materials that act as pH sensors[90,91], shown to function as low dielectric barriers[87–89,92–94] and incorporated as functional elements in photo-nic devices[94]. For some mesoporous materials, orientation of the mesopore system with respect to the supporting substrate has been achieved[95,96].
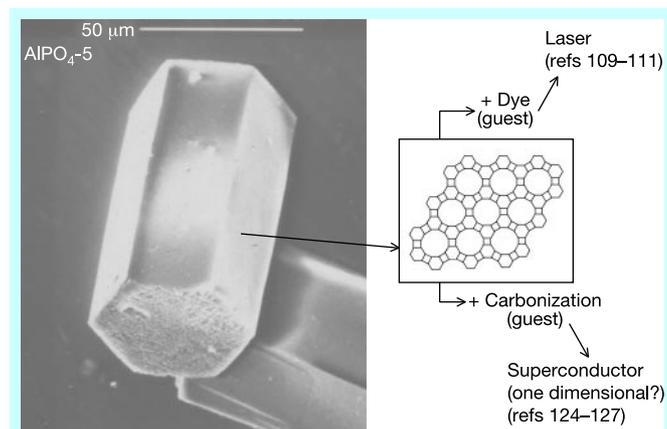
New applications

Over the past decade crystalline microporous materials have con-tinued to find new applications in their traditional areas of use, such as catalysis, separation and ion exchange. Following the discovery of ordered mesoporous materials, these solids have also been regarded as suitable for such applications, with several studies illustrating that they can serve as stationary phases in high performance liquid chromatography[97–99]. Although biomolecule separations have not yet been attempted, the pore size and pore uniformity of mesopor-ous materials may make them suitable for macromolecule separ-ations, which, if accomplished, should lead to commercial use.

In addition, non-traditional applications exploiting the porosity of the material itself, or its ability to host guest species that impart an interesting property, are now also nearing commercialization, or show high potential to do so. For example, microchip device densities continue to increase and feature sizes to decrease, gen-erating much demand for insulators with a lower dielectric constant k than that of dense silicon dioxide ($k = 3.9$–4.2), the currently used insulator material[100]. Porous materials can provide for low-k materials ($k < 2.2$)[101], as demonstrated by the performance of films prepared from ordered mesoporous materials[87–89,92,93] and crystalline pure-silica molecular sieves[75,102]. In fact, one mesoporous silica material, MesoELK, is reported to be targeted for commercial use in 2002, in applications requiring low dielectric constant films (see http://www.schumacher.com/products/DESCRIP/CHEM/Meso.htm for details).

Another promising application area is diagnostic magnetic res-onance imaging (MRI), which relies on administering contrast agents to patients to significantly improve the diagnostic value of MRI. The contrast agents contain high-spin metals that bind water molecules and thereby yield proton spin relaxation times (T_1) that are orders of magnitude faster than those obtained with free water[103]. Gadolinium ions, Gd^{3+}, perform particularly well as contrast agents, but cannot be administered directly owing to their inherent toxicity[104]. However, Gd^{3+} contained in zeolites[105,106] and clays[107,108] has been investigated as contrast agent for the gastro-intestinal tract. In fact, a zeolite containing Gd^{3+} is nearing completion of the regulatory process and is expected to be commer-cially available soon, marketed as Citra Vu by EZM, Canada (K. J. Balkus Jr, personal communication). The zeolite immobilizes the Gd^{3+} and thus mitigates its toxicity (zeolites themselves are not toxic when introduced in the gastrointestinal tract), while still allowing hydration by adsorbed water to allow for NMR T_1 relaxation effects.

Another interesting example among the many uses of porous solids as a host material is the zeolite-dye microlaser: incorporation of organic dyes as guest species in microporous, crystalline AlPO$_4$-5 (Fig. 5) gave the first lasing molecular sieve[109,110], with size, shape and arrangement of the porous crystals affecting the performance of the system[109,111]. The concept has been extended to mesoporous materials acting as the host for laser dyes[112,113], and the use of other guest species as light-emitters, such as complexed Nd^{3+}, is also explored[114].

A somewhat different approach to using porous solids as host material involves the fabrication of porous carbons, which are of

interest as adsorbents, electrode material, and so on. It involves incorporation of organic compounds such as acrylonitrile[115], poly-(acrylonitrile)[116], poly(furfuvyl alcohol)[116,117] or phenolformaldehyde polymers[118] in zeolites such as Y[115–118], mordenite[115], beta[118] or L[118], followed by carbonization and subsequent removal of the inorganic material by acid dissolution. The porous carbons obtained in this manner usually lack uniform pore structure, but one material appears to have structural order with highly uniform porosity[117]. This fabrication method has been extended to using ordered mesoporous materials as hosts[119–123], yielding rigid arrays of nanoporous carbon with pore sizes ranging from 5 to 10 nm. Like the ordered mesoporous oxide-based materials, the mesoporous carbons obtained in this manner can be highly ordered[123]. These carbon-based porous solids are likely to exhibit material properties not encountered in other mesoporous solids.

The pores of a crystalline molecular sieve have also been used as a confining reaction environment to produce single-walled carbon nanotubes (Fig. 5), through the carbonization of occluded tripropylamine[124,125]. These tubes are claimed to be merely 0.4 nm in diameter[124,126] and to show superconductivity[125] that may be one-dimensional[127]. Further work is necessary to understand the precise nature of this composite material, and to establish whether carbon nanotubes can be formed in other porous structures.

Future challenges

As mentioned above, it is unknown why ordered mesoporous materials do not form crystalline frameworks. Crystalline structures containing pores in the size range of 1.0–2.0 nm and exhibiting thermal and hydrothermal stability are highly desirable, especially if the pore system is more than one-dimensional. A major challenge facing the porous materials community is therefore the development of tetrahedral frameworks containing extra-large pores in a multidimensional network. The largely unexplored approach of creating open structures that are based on 3-membered rings might prove successful in this regard. In addition, new types of organic molecules that can act as structure-directing agents are being developed, not least because these costly reagents can often limit the commercial viability of the resultant porous solid. A promising development is the preparation of such organic molecules that can be recycled[128].

The synthesis of an enantiopure, porous tetrahedral framework constitutes another challenge that is not new, but remains unsolved. Among the criteria for synthesizing such a chiral solid[1] is the need for chiral organic molecules as templates. But suitable compounds have not yet been found: the structures obtained when using occluded chiral organic agents exhibit disorder in the organic. Recently, the ordering of fluoride counter ions in a molecular sieve was found to affect the ordering of the organic residing in the porous space of the sieve[129], giving rise to a fluoride-ion–organic arrangement with noncentrosymmetric topological symmetry and thus nonlinear optical behaviour. This effect, in combination with the use of a chiral template, might provide a route to chiral molecular sieves.

Zeolites and other micro- and mesoporous materials are certain to continue to find new uses in catalysis[130] and separation applications[12]. Metal–organic frameworks might also find use in such applications, particularly as they are likely to offer advantages over other porous solids for catalysing chiral transformations that do not require high temperatures. The preparation and characterization of chiral metal–organic frameworks seems therefore particularly promising, especially when aimed at creating pore sizes above 1.0 nm (many useful reactants for chiral transformations are nanometre-sized or larger).

As better and more diverse preparations of hierarchical porous structures become available, an increasing number of porous materials are likely to find use in applications not traditionally associated with such materials. The recent demonstration of hetero-

epitaxial zeolite growth is only one promising example of developments that could lead to new device applications.

Clearly, numerous challenges remain, but the rate of advance in porous materials science over the past decade promises that this area will deliver exciting developments in the early twenty-first century. □

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