Porous inorganic materials
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The field of porous, inorganic materials is experiencing explosive growth, as is shown by more than 6000 literature citations since 1994 along with numerous recent symposia and workshops that have been devoted to this topic. Much of the recent interest has been fueled by new synthetic strategies, such as 'supramolecular templating', that have enabled precise engineering of pore size, shape, and connectivity on the mesoscopic scale. In general, template-based approaches involving the cooperative organization of organic–inorganic assemblies as intermediates are emerging as a promising conceptual basis for future developments in the field of porous inorganic materials, such as the synthesis of hierarchical morphologies that mimic the intricate structures found so often in nature.

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Abbreviations
cmc	critical micelle concentration
CP MAS	cross polarization magic angle spinning
LC	liquid crystalline
MCM	Mobil composition of matter
MMS	mesoporous molecular sieve
SDA	structure directing agent
TEOS	tetraethylorthosilicate
UTD-1	University of Texas at Dallas number 1
XRD	X-ray diffraction

Introduction

In an attempt to briefly review recent advances in porous inorganic materials, I have limited the scope of this article to include mainly papers published since January 1995 and to exclude porous carbons, which from my point of view may be considered organic. This article is organized according to pore size, in agreement with the three classes of porous materials as defined by IUPAC [1]: firstly, microporous materials, in which the pore diameter d_p is less than 2 nm; secondly, mesoporous materials, in which 2 nm $\leq d_p \leq$ 50 nm; and, thirdly, macroporous materials, in which $d_p >$ 50 nm. Following a brief discussion of the corresponding energetics, these classes of porous materials are discussed in turn with respect to new materials, new understanding, and new applications.

Energetics

Navrotsky et al. [2•] recently reported the enthalpies of formation of a series of high silica content zeolites and several mesoporous silicas prepared with pore diameters in the range 3–5 nm. They found these materials to be only 8–14 kJ/mol^{-1} less stable energetically than crystalline quartz, despite their appreciable differences in molar volume and in related parameters, such as framework density and pore size. This finding was considered 'good news for synthesis', for it implied that there are no stringent energetic limitations to the myriad possible structural types that can form. This energetic parity sets the stage for new synthetic efforts in the development of porous inorganic materials: as there are no large thermodynamic biases, synthesis strategies to develop new porous materials are limited only by the 'ingenuity of the chemist in identifying appropriate kinetic pathways for their formation [2•]'. Indeed, much of the recent progress in porous inorganic materials has involved the development of new classes of structure-directing (templating) agents, that induce the formation of a particular structure through noncovalent electrostatic, van der Waals, or hydrogen-bonding interactions.

Microporous inorganic materials

Microporous inorganic materials comprise crystalline zeolite molecular sieves and related solids (in which the porosity is defined by a periodic crystalline framework) along with amorphous materials such as 'imprinted' silicas and inorganic gels, typically formed by sol-gel processing techniques. Current interest in microporous materials continues to lie in molecular separation, via size-dependent filtration or sieving, along with shape-specific molecular recognition, adsorption, and catalysis.

Much progress in the area of microporous materials has resulted from an improved understanding of the roles of structure-directing agents (SDAs) in zeolite synthesis. Lobo et al. [3••] summarize the general correlation between use of SDAs and high silica zeolite structures as follows: first, in the absence of SDAs (hydrothermal) silicate syntheses form dense crystalline or layered materials; second, small molecules — amines in particular — direct the formation of clathrasils (cages of polyhedra that can be considered zeolites with zero-dimensional pores); third, linear molecules usually form 1 D, 10-ring molecular sieves; fourth, branched molecules form multi dimensional, medium pore size zeolites (d_p ~4–7 Å); and fifth, large polycyclic molecules produce large pore 1D zeolites. According to studies by Burkett and Davis [4•,5•] and Zones and co-workers [3••], key features of SDAs are moderate hydrophobicity and the ability to form strong inorganic–organic complexes via noncovalent interactions (such as van der Waals contacts). Moderate hydrophobicity favors the restructuring of water to form a hydrophobic hydration sphere that accommodates the SDA, while maintaining a fully hydrogen bonded network of water. Replacement of water

in the hydration sphere with inorganic (e.g. silicate) species generates the inorganic–organic assembly that translates the geometry of the SDA into the zeolite pore architecture. The concomitant release of ordered water along with the establishment of intermolecular van der Waals interactions provides the thermodynamic driving force to form the inorganic–organic assembly. The strength of intermolecular interactions between the SDA and framework precursors largely governs the efficacy of the SDA in inducing the formation of a prescribed structure. For example, in studies of tetraalkyl ammonium- and hexanediamine-mediated syntheses of pure silica zeolites, Burkett and Davis [5•] used ^1H-^{29}Si cross polarization (CP) MAS NMR to show that structure direction occurred only when ^1H-^{29}Si CP NMR signatures were observed, implying close association of the SDA and silica framework. When such signatures were not observed, the occluded organic molecule served to create a cavity, but there was no structure direction effect, that is no unique relationship between the template molecule and the resulting crystal phase.

A significant advance in the preparation of high-silica zeolites with large pore size is the synthesis of UTD-1 (University of Texas at Dallas number 1) by Balkus and co-workers [6••,7,P1]. The structure of UTD-1 can be described as a fully condensed $TO_{4/2}$ network containing a 1D pore system built of extra large elliptically shaped pores circumscribed by 14-membered rings ([7]; see Fig. 1). The approximate free diameter of the large pore is $7.5 \times 10 \text{Å}$. UTD-1 was synthesized using a novel organometallic complex, bis-(pentamethyl-cyclopentadienyl)-Co(III) hydroxide, as an SDA, although it was concluded [6••] that there was not a perfect match between the shape of the pore and the complex (evidence of the fact that the understanding of SDAs in zeolite synthesis is in its infancy). Importantly, UTD-1 exhibits exceptional thermal and hydrothermal stability compared with large pore aluminophosphates such as VPI-5, AlPO4-8, and cloverite. High temperature XRD showed no loss of crystallinity in UTD-1 below 1000°C, even in the presence of 23 torr H_2O. In addition, the aluminum-containing form of UTD-1 possesses Brønsted-acid sites comparable in strength to those of other high-silica zeolites.

Zeolites exhibit precise control of pore size by virtue of their crystalline structures and thus can be considered ideal candidate materials for the preparation of inorganic membranes. Progress in the development of zeolite membranes has been slow, mainly because of difficulties in processing zeolites as ultra thin, defect-free films on porous supports. Bein [8•] and Jansen and Coker [9] have recently reviewed this topic. The current status is that zeolitic membranes of ZSM-5 and silicalite-1 (the all-silica form of ZSM-5) have been fabricated on a small scale (several square centimeters) and tested (mainly) by single gas permeance measurements [10•,11,12]. Yan et al. [10•] and Noble and Falconer [11] have shown evidence for

Figure 1
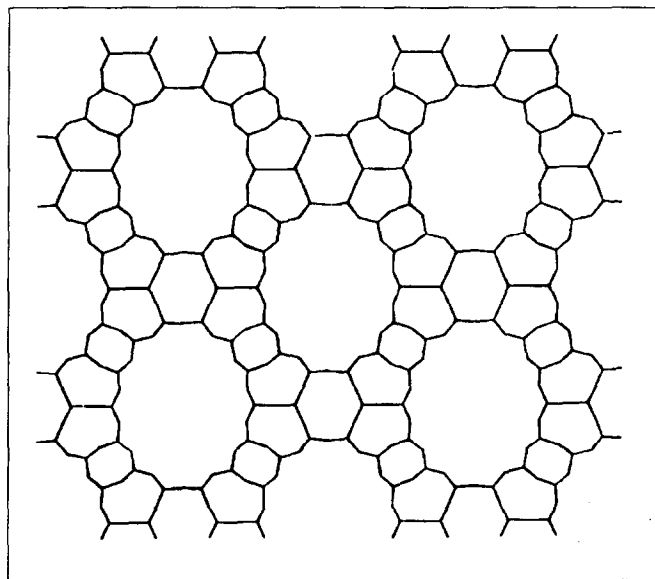
Topology of the organometallic-free UTD-1 zeolite as viewed along the large 14-membered ring channels (<010>zone axis). The main structural building unit within the pore walls consists of one six-membered ring surrounded by four five-membered rings. These units are linked via 4-membered rings to create infinite two-dimensional layers parallel to the a–c plane. Reproduced with permission from [7].

size-dependent molecular separation; for example, they observed gas permeation ratios for H_2:isobutane and n-butane:iso-butane of 151 and 18 at 303K, and of 54 and 31 at 458K, respectively. It was proposed [10•,11] that at low temperature, transport is dominated by adsorption and at higher temperatures by diffusion. Although supported films of zeolite A [13] and zeolite L [14•] have been reported, permeance data are lacking. In general more thorough studies of zeolite thin film processing, such as those performed by Jansen et al. [15•], are sorely needed.

Despite having a pore size distribution, rather than a fixed pore size like zeolites, amorphous microporous materials formed by sol-gel processes have several advantages for applications in membranes, sensors, and catalysis. First and foremost, compared to zeolites it is easy to prepare defect-free, ultrathin films on porous supports [16•]. Second, the extraordinary flexibility of the siloxane backbone should enable precise molding of the framework by template molecules or ligands. Recent progress in molecular imprinting of amorphous silicas has been reviewed by Davis et al. [17••], who concluded that, although there are indications for the use of amorphous silicas in molecular recognition and catalysis from imprinted sites [18], site heterogeneities are prevalent and limit reaction selectivities. In related papers, Raman and I [19], Cao et al. [20•], and Raman et al. [21••] report on template-based approaches to prepare microporous silica membranes wherein covalently bonded organic ligands are

occluded in a dense silica matrix and removed (pyrolyzed) to create a microporous network. It was concluded that due to the amphiphilic nature of the covalently bonded hybrid framework, only under a limited set of conditions (that depend strongly on [template] ligand–framework–solvent interactions) is phase separation suppressed enabling the faithful replication of the template ligands (pore size ≈ ligand size). It was also observed that, depending on the extent of condensation and viscosity of the silica matrix at the pyrolysis temperature, pyrolysis might be accompanied by considerable shrinkage, resulting in a reduction of pore volume and size. My colleagues and I [16•] have also used noncovalently bonded templates to create amorphous, microporous membranes. We observed that under certain (sol-gel) processing conditions, the membrane pore size was related to the size of the solvent molecules (water, methanol, ethanol, propanol etc.) and suggested a solvent templating mechanism to explain this observation.

Mesoporous inorganic materials

Mesoporous inorganic materials comprise inorganic xero-gels (e.g. the common silica desiccants), pillared clays, and the mesoporous molecular sieves (MMSs) recently discovered by researchers at Mobil, referred to in the literature as the MCM (Mobil composition of matter) family of materials. MMSs have received enormous attention from the research community since their announcement by Kresge et al. in 1992 [22], and there have been numerous recent reviews of this subject [21•,23,24•,25•]. In the past two years advances have been made in understanding and exploiting the supramolecular templating process used in MMS formation, developing new synthesis procedures, extending the compositional range beyond silicas, and processing MMSs as thin films.

MMSs are high surface area amorphous solids (up to 1400 m²g⁻¹) characterized by monosized cylindrical pores, ranging from 20 to 100 Å in diameter, organized into periodic arrays that often mimic the liquid crystalline phases exhibited by surfactants [22,26]. MMS synthesis procedures typically require four reagents: water, surfactant, a soluble inorganic precursor, and catalyst. MMSs form (as precipitates) in seconds to days [26,27] at temperatures ranging from 180°C to as low as –14°C, depending on the inorganic precursor. Pure silica MMSs exhibit three structure types: hexagonal (referred to as H or MCM-41), a 1D system of hexagonally ordered cylindrical pores; cubic (C), a 3D, bicontinuous system of pores; and lamellar, a 2D system of silica sheets interleaved by surfactant bilayers [22,26].

Over the past several years various MMS synthetic pathways have been elucidated [24•]. Experimentally, it has been shown that MCM-41-type phases form under conditions in which the surfactant — before the addition of the silica source — is in any of the following forms: free (where the surfactant concentration, c, is less than

the critical micelle concentration cmc1) [28]; in the form of spherical micelles (cmc1 < c < cmc2) [27], in the form of cylindrical micelles (cmc < c < LC [liquid crystalline]) [29], or in the form of liquid crystalline phases such as H₁ (c = LC) [30•,31] (see Fig. 2). These findings indicate that silica does not in general simply petrify a pre-existing LC array but instead cooperatively co-assembles with the surfactant to form LC phases during the course of the synthesis. Specific details of the co-assembly mechanism are still controversial. Three models have been postulated: a puckering layered model [32], a silicate rod assembly model [30•], and a cooperative charge density matching model [33]. Regardless of the specifics, it has been shown that silica condensation is not essential to the assembly process. Using anionic cubic octamers, $Si_8O_{20}^{8-}$, Firouzi et al. [34••] demonstrated reversible lamellar → hexagonal phase transformations. Electrostatic interactions are also nonessential to the assembly process. Tanev and Pinnavaia [35••] and Bagshaw et al. [36•] have demonstrated the formation of MMS using two neutral routes based on hydrogen bonding and self-assembly of nonionic primary amine [35••] or polyethylene oxide [36•] surfactants and neutral oligomeric silica precursors. Tanev and Pinnavaia [37•] compared MMSs prepared with ionic and neutral surfactant templates. They concluded that, although the ionic surfactant templated MMSs usually have greater order, the neutral surfactant templated MMS has thicker walls, a greater extent of condensation, improved thermal stability, and greater textural mesoporosity and therefore might perform better in applications requiring thermal stability and rapid diffusion, like catalysis. In addition, the combination of a neutral framework and extensive condensation permits template removal by solvent extraction.

In the past few years considerable effort has been put into synthesizing multicomponent and nonsilica MMSs [27] for catalytic applications, as a result of their higher surface areas and greater accessibility of active sites compared to zeolites [25•]. Particular attention has been paid to titanium incorporation in silica MMSs, based on expectations that, by analogy to the ability of TS-1 (titanium-doped high silica ZSM-5) to selectively oxidize alkanes, alkenes, and alcohols [38], titania–silica MMS (Ti-MMS) may perform shape-selective oxidation of larger organic molecules. Ti-MMS have been synthesized by incorporation of titanium into the silica framework [39,40] or by grafting titanocene complexes on preformed silica MMS [41•], the latter procedure providing higher surface concentrations and accessibility of catalytic sites. Oxidation studies have confirmed the ability of Ti-MMS to oxidize large molecules. For example, selective epoxidation of norborene using tertbutylhydroperoxide as an oxidant could be achieved with Ti-MMS but not with TS-1, due to the bulky nature of the reactants [40]. Additionally, shape-selective conversion of 2,6-di-tert-butyl phenol has been demonstrated [39] along with enhanced activity when titanium is grafted as a pendant catalyst on the pore interior [41•]. In contrast, when comparing oxidation

Figure 2
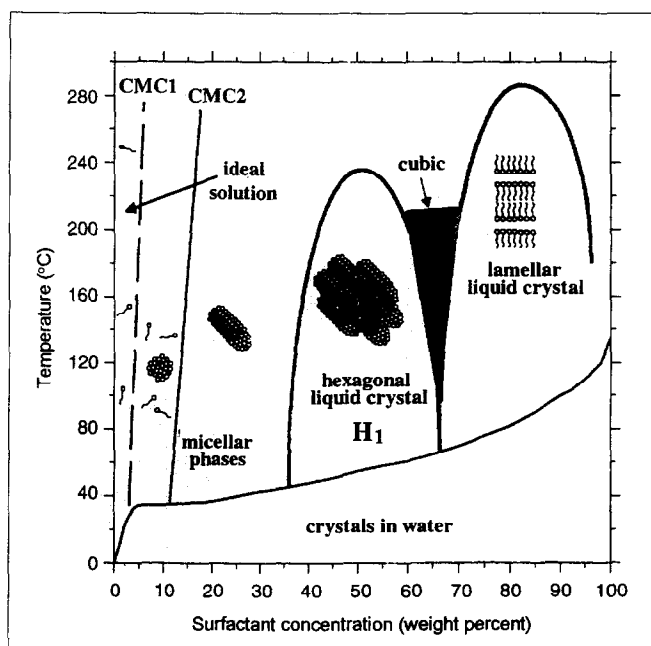
Schematic phase diagram for C_{16}TMA(tetramethylammonium) Br in water. Critical micelle concentration 1 (CMC1) is exaggerated to higher concentration. Reproduced with permission from [21•].

reactions for small molecules, such as the epoxidation of hexene by H_2O_2, TS-1 exhibits much higher activity than Ti-MMS [42], and reactions that occur readily with TS-1, such as primary amine oxidation, practically do not occur over Ti-MMS [25•]. The reasons for these differences in reactivity are presently unclear but altered framework crystallinity, hydrophilicity, and titanium redox potential may be contributing factors [25•].

With regard to nonsilica frameworks and hybrid structures, several recent reports are noteworthy. Antonelli and Ying [43••,44•] developed a ligand-assisted templating scheme to prepare pure niobium and tantalum oxide MMSs that were stable to surfactant removal and hydrothermally stable to temperatures ranging from 300–800°C. Neutral primary amine surfactants were pre-reacted with metal alkoxides to form new metal organic surfactant molecules, which were hydrolyzed in a second step to produce pure niobium or tantalum MMS. The surfactant was removed by acid washes that cleaved the metal–nitrogen bond. Ciesla et al. [45] developed phosphate and sulfate complexation schemes to stabilize zirconium oxide MMSs. Phosphate and sulfate ions assisted in the formation of zirconia–surfactant composites and promoted further cross-linking of the zirconium oxo species, stabilizing the porous structure to 500°C. Using tetraalkoxysilane and substituted organoalkoxysilane precursors, Burkett and Mann [46•] prepared hybrid inorganic–organic MMSs containing covalent Si-phenyl and Si-n-octyl bonds. Kloetstra et al. [47•] hydrothermally treated calcined, aluminosilicate MMSs with tetrapropylammonium hydroxide and formed

Al–Si MMSs containing zeolitic ZSM-5 micro-domains. These composite materials were shown to be able to crack hexane under conditions where commercial aluminosilicate catalysts and the parent Al–Si MMS were not.

For potential applications in separation technology or catalysis, MMS have been prepared as both supported and free-standing films. Yang et al. [48••] described approaches to prepare ordered MMS films at crystal (mica)/liquid interfaces or air/liquid interfaces [49•]. In each case it was proposed that surfactant ordering at the interface conferred structure on the developing film. The pore channels were observed to be oriented parallel to the interface, which may prove problematic for applications in membranes. Ogawa [50] reported a simple sol-gel procedure for preparing MMS films. Sols were prepared by surfactant addition to prehydrolyzed tetramethoxysilane and deposited by spin-coating to form thin films. No detail was provided concerning the mechanism of film formation.

Aerogels and macroporous inorganic materials

Aerogels are highly porous materials normally formed from wets gels by extraction of the pore fluid above its critical temperature and pressure in an autoclave. Drying therefore is accomplished in the absence of drying stress (capillary stress), preserving the hierarchical (often fractal) structure of the wet gel. A major recent breakthrough in aerogel processing has been the development of an ambient temperature/pressure drying procedure that dispenses with autoclaves altogether [51••,P2]. The ambient drying procedure involves derivatization of the hydroxylated surface of an elastic, wet gel with alkylsilanes (e.g. trimethylsilane). Subsequent evaporative drying initially causes the gel to shrink as it is subjected to capillary stress. The methylated surface prevents further condensation reactions from occurring, however, so at the final stage of drying, when the capillary stress vanishes, the gel 'springs back', re-creating the porosity of the wet gel state. The final dried gels exhibit densities, pore volumes, and surface areas comparable to those of conventional aerogels. Other advances in aerogel processing include the synthesis of multicomponent, nonsilica (see e.g. [52,53,54]), and hybrid organic–inorganic aerogels [55,56].

Macroporous materials contain pores larger than 50 nm in diameter, the same as the dimensional scale of many natural materials, such as the mineralized exoskeletons of radiolaria and diatoms. Ozin and co-workers [57••] recently synthesized lamellar aluminophosphates exhibiting bowl-shaped and honeycomb patterns on the same macroscale and with much the same subtlety as those seen in nature. The synthetic procedure extended concepts of micellar and LC templating to larger vesicle templates. Introduction of a tetraethylene glycol cosolvent was proposed to induce a lamellar→vesicular phase transition. Further mineralization of the vesicles and the sticking of

Table 1

Pattern replication in inorganic morphosynthesis.

Process	Pathway	Examples
Transcriptive synthesis	Self-assembly→Transcription→Replication	Tubular/lamellar/mesoporous silica, thin films, CdS arrays
Synergistic synthesis	Coadaptation→Coassembly→Replication	Mesoporous silica, metal oxides
Metamorphic reconstruction	Coassembly→Replication→Reconstruction	Microskeletal calcium phosphate, silica
Microphase separation	Coassembly→Evolution→Replication	Mesolamellar aluminophosphate, cellular calcium carbonate
Systems synthesis (in general)	Molecular assembly→Supramolecular assembly→Microphase assembly→System assembly	

*Reproduced with permission from [59••].

vesicles to growing aluminophosphate spheres accounts for bowl-shaped features decorated with concentric rings and platelets. Similarly, Walsh and Mann [58•] used biliquid foams as patterned assemblies to synthesize cellular calcium carbonate (aragonite) in a manner superficially analogous to the packing of areolar vesicles in the biomineralization of diatoms.
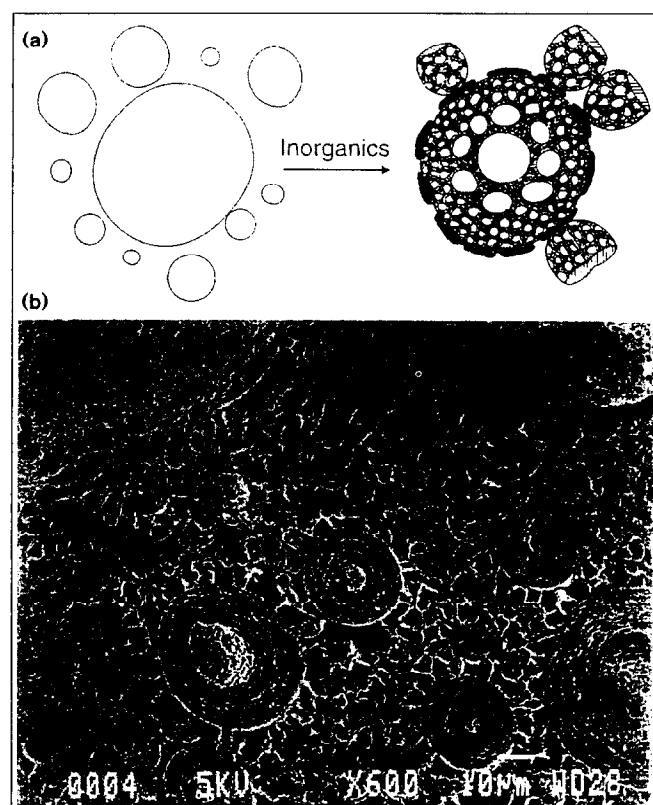
Future directions: hierarchical inorganic materials

Beyond improving the synthesis and processing of microporous, mesoporous, and macroporous inorganic materials, future directions in porosity engineering will inevitably arise from the synthesis of complex, hierarchical microstructures designed with controlled porosity on several length scales. Such structures are common in nature, but synthetic pathways to their efficient preparation in the laboratory are lacking. Recently Mann and Ozin [59••] delineated four processes for pattern replication during inorganic 'morphosynthesis' (see Table 1). The idea is to use appropriate templating agents, namely, molecules, polymers (e.g. block copolymers), micelles, vesicles, and foams, to orchestrate the positioning, interconnection, and stabilization of inorganic building blocks at the microscale, mesoscale and macroscale. Such organic templating strategies could in principle be combined with physical phenomena such as fractal aggregation [16•], ionic strength-, temperature-, or solvent induced shrinking and swelling (observed for organic and hybrid gels [16•]), capillary stress-induced collapse (and re-expansion) induced by capillary stress [51••], and surface patterning (using, for example, self-assembled monolayers or microlithography) to create multifunctional complex materials. The challenge will be to devise concurrent or sequential processing strategies that induce the progressive evolution of structure in a predetermined manner. To date some fascinating examples of hierarchical materials exist [57••,59••,60•,61•] (see Fig. 3), but our abilities to pre-design the structure and then engineer the construction are at a developmental stage.

Acknowledgements

Figure 3

Synthesis of complex hierarchial materials. **(a)** Illustration of vesicle templating of a hierarchical inorganic material. Mesolamellar aluminophosphate vesicles undergo fusion, fission, reshaping and collapse to form synthetic patterns with complex form. **(b)** Scanning electron microscopy image showing complex surface patterns formed by mesolamellar aluminophosphate vesicles during hydrothermal synthesis. Scale bar=10 μm. Reproduced with permission from [57••].

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

• of special interest
•• of outstanding interest

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The enthalpies of formation of a series of high-silica zeolites, MMSs, and other microporous materials are reported. It is found that for microporous and mesoporous materials in general, enthalpies of formation are only 8–14 kJ mol^{-1} less exothermic than that of crystalline quartz. This suggests that there are no stringent energetic limits to the possible porous structures that can form. What is necessary is the development of the appropriate structure-directing synthesis scheme that selects the target structure from many others of similar energy.

3.   Lobo RF, Zones SI, Davis, ME: **Structure-direction in zeolite**
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This paper provides experimental evidence for the existence of pre-organized, inorganic–organic assemblies during zeolite synthesis.

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Bein provides an excellent review of various synthesis and processing strategies used to create supported zeolite and microporous films on a variety of substrates. Three general methods are discussed: first, the deposition or embedding of preformed crystals on a substrate; second, transport of colloidal or polymeric precursors to a surface, followed by hydrothermal treatment; and third, direct nucleation on the substrate, followed by growth. The use of self-assembled monolayers to orient crystal growth is also discussed.

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16.   Brinker CJ, Wallace S, Raman NK, Sehgal R, Samuel J, Contakes
•   SM: **Sol-gel processing of amorphous nanoporous silicas: thin film and bulk.** In *Access in Nanoporous Materials.* Edited by Pinnavaia TJ, Thorpe MF. New York: Plenum Press; 1995:123–139.
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••   **imprinted nanostructured materials.** *Chem Mater* 1996, 8:1820–1839.
This paper provides an extensive review of imprinting (or templating) of amorphous metal oxides and zeolites along with organic polymers. These three classes of imprinted materials are compared with respect to their structures and corresponding catalytic properties.

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21.   Raman NK, Anderson MT, Brinker CJ, **Template-based**
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This paper describes a procedure whereby a preformed aluminosilicate MMS is reacted with tetrapropyl ammonium hydroxide under hydrothermal conditions. The resulting material was shown to consist of MCM-41 with ZSM-5 substructures. These composite materials were active in hexane cracking at mild conditions, whereas a commercial aluminosilicate catalyst and the parent MCM-41 were inactive.

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Aerogels are normally prepared from 'wet' gels by supercritical solvent extraction, which eliminates drying shrinkage induced by capillary stress. This paper describes a new approach in which a wet gel is derivatized with trimethylsilyl groups prior to drying (by evaporation). The gel initially shrinks, but because the trimethylsilyl groups prevent further condensation reactions from occurring, the gel 'springs back' at the final stage of drying, when the capillary stress vanishes. The final dried gels have porosities of up to 98% and can be prepared as supported thin films.

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Patents

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