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
Nahirsky 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 (tempering) 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 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 form multi dimensional, medium pore size zeolites \( d_p \sim 4-7 \) 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 hexanediampine-mediated syntheses of pure silica zeolites, Burkett and Davis [5] used T-29Si cross polarization (CP) MAS NMR to show that structure direction occurred only when T-29Si 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 TO4 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 x 10A. 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 H2O. 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 size-dependent molecular separation; for example, they observed gas permeation ratios for H2:iso-butane 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 xerogels (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 m² g⁻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 < < cmc2) [27], in the form of cylindrical micelles (cmc1 < < 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, Si₈O₂₆⁻, 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 alkenes, 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-butylphenol 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 C18TMA(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 H2O2, 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. [43] developed phosphine and sulfide 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 wet 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**,52]. 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 radiolarians 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

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

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Figure 3

Synthesis of complex hierarchical 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


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.


This paper presents a comprehensive overview of the factors that influence the formation of zeolites. Particular attention is paid to the relationships between the geometrical and chemical properties of the organic molecules used to direct the crystallization of particular zeolites and the structures of the cages and cavities of the corresponding zeolites in which the organic molecules are occluded.


This paper provides experimental evidence for the existence of pre-organized, inorganic-organic assemblies during zeolite synthesis.


This paper reports on the formation of the first high-silica zeolite prepared with 14-membered rings. The zeolite is shown to be thermally stable and to exhibit strong acidity.


This paper 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.


This article provides a concise review of the current state of the art in zeolite membrane synthesis and characterization.


This paper provides an extensive description of the synthesis and processing conditions required to achieve a continuous ZSM-5 zeolite film that exhibits molecular sieving behavior.


A two-step process to prepare thin zeolite films is described. First, a zeolite L nanosol, containing 60 nm zeolite clusters, is prepared and deposited on a substrate surface by dip-coating or spin-coating of a layer. Then, using a homogeneous potassium aluminoaluminolate solution under hydrothermal conditions the seeds are grown to form a highly intergrown zeolite L layer.


This paper provides a review of several strategies to prepare microporous and mesoporous amorphous silicas, including particle packing, aggregation of fractals, and surfactant templating. It was observed that under certain processing conditions the membrane pore size could be controlled in the approximate range 0.4–0.7 nm simply by varying the composition of the pore fluid during film deposition.


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.


This paper describes the preparation of microporous silica membranes using a template-based approach. Dense hybrid organic–inorganic films are prepared and the organic constituents are pyrolyzed to create a microporous network. Ideal selectivity factors (i.e. ratio of single gas fluxes) of over 1000 are reported for H₂/SF₆.


This paper reviews two organic ‘template’-based strategies for the preparation of porous silicas. Surfactant-templated silicas are discussed, in which the template–matrix interaction is via noncovalent bonds and the pore structure is largely established in the solution stage. This surfactant-template approach is contrasted with a hybrid approach in which silica is templated by organic ligands covalently bound to the silica network.


This paper provides a comprehensive overview of MMSs synthesized by ‘supramolecular’ templating with molecular aggregates of surfactants. Various mechanism pathways are reviewed along with applications of MMSs such as selective adsorbents, catalysts, and host matrices.


This paper presents a comprehensive overview of the applications of modified Al₃⁺, Ti⁴⁺, and V⁵⁺-MMSs in acid-catalyzed reactions and liquid-phase selective oxidation. It is concluded that, because they have large pores, MMSs have decisive advantages over microporous molecular sieves in catalytic applications involving bulky molecules.


This paper reports the templating of silica mesostructures from ordered liquid-crystalline mesophases, the resulting porous silica is in effect a 'cast' of the original organic structure.


This paper describes a new 'ligand-assisted' templating strategy enabling the grafting of an organometallic (titanocene) complex onto the inner walls of an MMS to generate shape-selective catalytic sites. This work has important implications for the synthesis of other mesoporous molecular sieves that are not amenable to electrostatic templating.


This paper reports the formation of MMSs using neutral primary amine bonding interactions between the primary amines and the silica framework. This provides a generalized model of the cooperative organization of inorganic-organic-surfactant and biomimetic assemblies. Science 1995, 267:1136-1143.


This work extends concepts of neutral surfactant templating developed in [35] to include tantalum oxide mesoporous molecular sieves that exhibit high activity and high hydrothermal stability along with high hydrocarbon adsorption capacities.

**34. Biasco T, Corma A, Navarro MT, Perez-Pariente J: Synthesis of a new amino(ethoxy)niobium complex. This paper extends the ligand-assisted templating procedure developed in [43] to include tantalum oxide mesoporous molecular sieves that exhibit good thermal and hydrothermal stabilities along with high hydrocarbon adsorption capacities.**


The result of this paper implies that the condensation of siloxanes and organo silicones in the presence of surfactant templates could provide a general route to the synthesis of hybrid ordered porous silicas with controlled functionality and hydrophobicity.


This paper describes a procedure whereby a preformed aluminosilicate MMS 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 aluminoisolate catalyst and the parent MCM-41 were inactive.

**45. Tanev PT, Pinnavaia TJ: Titanium-containing mesoporous molecular sieves prepared by ionic and neutral surfactant templating: a comparison of physical properties. Chem Mater 1996, 8:2068-2079.**

This paper describes a new 'ligand-assisted' templating strategy enabling the preparation of thermally stable transition metal MMSs. Niobium alkoxide is reacted with tetraethylamine to form a new amino(ethoxy)niobium complex. Assembly of the organometallic surfactants into micellar arrays, accompanied by hydrolysis and condensation of the alkoxide produced well ordered mesopores completely stable during surfactant removal using a careful acid extraction procedure.


This paper reports on the formation of MMSs neutralized by primary amine surfactants. In this case inorganic-organic mesostructures form via hydrogen-bonding interactions between the primary amines and the silica framework. The resulting material was shown to consist of MCM-41 with ZSM-6 structures. Cross-sectional transmission electron microscopy showed that the pore channels were aligned parallel to the silica surface.

**47. Tanev PT, Pinnavaia TJ: Neutrally templated MMS are much more extensively cross-linked than the neutral-templated MMS and that nucleation, growth, and phase transitions may be directed by charge density, coordination, and steric requirements.**


Highly ordered mesoporous silica films were prepared from a cationic surfactant/HCl/TEOS/water solution at 85°C by introduction of a freshly cleaved mica sheet maintained in a horizontal position. It was proposed that the surface structure and reactivity of the mica served to orient the micellar precursors in the mica interface, ultimately imposing order on the resulting solid film. Cross-sectional transmission electron microscopy showed that the pore channels were aligned parallel to the mica surface.


In an extension of the work described in [48], Ozin and co-workers formed free-standing mesoporous silica films at a vapor-liquid interface. It was proposed that the film formation process involves the collective interactions between silicate oligomers, micellar solution species and a surfactant hemimicelle over structure stabilized at the air-water interface.


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 99% and can be prepared as supported thin films.


This paper describes the preparation of a novel class of hybrid aerogels in which the microstructural properties were shown to vary systematically with the alkylene-bridging group length.


This paper described the synthesis of organosilicas that are patterned on the submicrometer-to-millimeter scale using vesicle templates. The resulting materials exhibit morphologies and patterns similar in size and form to those of the siliceous skeletons of diatom and radiolaria.


This paper discloses the development of intricate cellular macrostructures in calcium carbonate by patterned mineralization of oil/water foams.


This paper provides a fascinating account of the formation of complex, hierarchical inorganic materials by pattern replication of self-organized assemblies such as micelles, vesicles, or foams.


This paper provides an example where templating occurs simultaneously on the mesoscale and macroscale. Oil-in-water emulsions were formed containing unhydrolyzed TEOS. Hydrolysis at the interface in the presence of a high concentration of surfactants led to the formation of hollow spheres decorated with mesosstructured porous silicas.


Patents
