# Hybrid Inorganic–Organic Mesoporous Silicates—Nanoscopic Reactors Coming of Age**

By *Andreas Stein,* Brian J. Melde*, and *Rick C. Schroden*

*This review describes methods of preparing hybrid inorganic–organic mesoporous silicates with uniform channel structures, as well as some of their applications. Both reactive and passive organic groups can be incorporated in the porous solids by grafting methods or by co-condensation under surfactant control. Functional groups have been placed selectively on the internal or external pore surfaces or even within the walls of the mesoporous solids. Organic functionalization of these solids permits tuning of the surface properties (hydrophilicity, hydrophobicity, binding to guest molecules), alteration of the surface reactivity, protection of the surface from attack, and modification of the bulk properties (e.g., mechanical or optical properties) of the material. Recent applications of hybrid mesoporous silicates are highlighted, including catalysis, sorption of metals, anions, and organics, reactors for polymerization, fixation of biologically active species, and optical applications.*
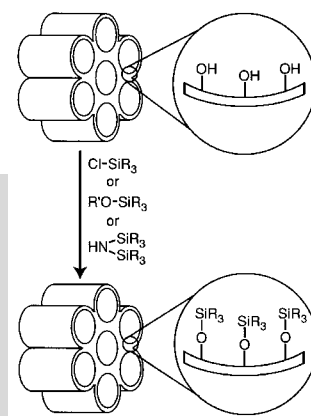
## 1. Introduction

Surfactant-templated mesostructures have played a prominent role in materials chemistry during the last decade. The excitement began with the discovery of hexagonally ordered mesoporous silicate structures by Mobil Corp. (M41S materials)[1,2] and by Kuroda, Inagaki, and co-workers (FSM-16 materials).[3,4] These materials initially appeared to be the holy grail sought after by zeolite chemists of the time. They possessed extremely high surface areas and easily accessible, uniformly sized pores. Most importantly, the pore sizes exceeded those attainable in zeolites and they could be tuned in the nanometer range by choosing an appropriate surfactant templating system, sometimes with a co-solvent or swelling agent. Thus, novel catalysts, sorbents, sensors, and host materials for large guest molecules were envisioned. However, the original mesoporous silicates and aluminosilicates exhibited a number of limitations, including lower hydrothermal stability and lower reactivity than zeolites with comparable compositions. They possessed relatively thin walls, which prevented incorporation of secondary pores within the walls, and they only formed fine particles. Yet, the ability to manipulate structures of porous solids on a nanometer scale in a controlled way proved to be so important to the research community, that many of these limitations have been addressed and overcome in the last few years. For example, the hydrothermal stability of mesoporous silicates has been improved by adding salts to the synthesis mixture,[5] or by producing materials with thicker walls.[6–16] Structures with uniform pore sizes can now be formed throughout most of the mesopore size range, which encompasses 2–50 nm by International Union of Pure and Applied Chemistry (IUPAC) definition.[17]

One important way of modifying the physical and chemical properties of mesoporous silicates has been the incorporation of organic components, either on the silicate surface, as part of the silicate walls, or trapped within the channels.[18,19] Organic modification of the silicates permits precise control over the surface properties and pore sizes of the mesoporous sieves for specific applications, while at the same time stabilizing the materials towards hydrolysis. Bulk properties can also be affected by mixing inorganic and organic moieties in the mesostructures. The inorganic components can provide mechanical, thermal, or structural stability, whereas the organic features can introduce flexibility into the framework, or change, for example,

the optical properties of the solid. Through the development of hybrid inorganic–organic mesoporous solids, much progress has been made in the last few years towards applications of mesoporous solids in a variety of fields. Mesoporous solids have been functionalized at specific sites, and were demonstrated to exhibit improved activity, selectivity, and stability in a large number of catalytic reactions and sorption processes. Mesoporous solids have also been examined for optical applications and as reactors or molds for polymerization processes.

This review focuses on hybrid organic–inorganic mesoporous silicates, synthesized under surfactant control to obtain uniform pore sizes. The emphasis is on recent work describing structures where the inorganic and organic units are bound through covalent Si–C bonds, although a few selected hybrid mesoporous composites in which the organic groups are merely entrapped in the structure are also discussed to dem-

onstrate interesting developments in the field. In the first part of the review, we describe grafting and co-condensation methods used to functionalize mesoporous silicates on the internal and external surfaces or within the walls. The second part highlights recent applications of hybrid mesoporous silicates. A number of designations have been used for mesoporous sieves. For mesoporous silicate structures, some of those relevant to this review include MCM-41 (2D hexagonal, prepared under basic conditions using cationic surfactants),[2] MCM-48 (cubic, basic conditions, cationic surfactants),[2] FSM-16 (2D hexagonal, derived from the layered polysilicate kanemite),[4] HMS (acidic conditions with neutral amine templates),[6] SBA-1 (cubic, acidic conditions, cationic surfactants),[20,21] SBA-3 (2D hexagonal, acidic conditions, cationic surfactants),[20,21] SBA-15 (2D hexagonal, acidic conditions, prepared with block-copolymer templates).[12,14]

*Andreas Stein was born in Germany but his family immigrated to Canada, where he obtained his B.Sc. degree in applied chemistry at the University of Calgary in 1986. He carried out graduate work with Prof. G. A. Ozin at the University of Toronto, specializing in the synthesis and characterization of zeolite materials for advanced application. After earning his Ph.D. degree in 1991, he joined the Advanced Inorganic Materials group at the corporate research labs of Bayer A.G. in Germany as an NSERC postdoctoral fellow, after which he carried out postdoctoral research with Prof. T. E. Mallouk at the University of Texas, Austin, and at Penn State University. In the fall of 1994 he joined the faculty at the University of Minnesota, where he is currently an Associate Professor of Chemistry. Professor Stein's research interests are in the field of solid-state chemistry, in particular porous materials.*

*Brian J. Melde was born in St. Paul, Minnesota, in 1974. He obtained a B.A. degree in chemistry from Concordia College in Moorhead, Minnesota in 1996. He is currently pursuing his Ph.D. degree under the supervision of Prof. A. Stein.*

*Rick C. Schroden was born in St. Cloud, Minnesota, in 1975. He obtained a B.S. degree in chemistry from St. Cloud State University in 1997. He is currently pursuing his Ph.D. degree under the supervision of Prof. A. Stein.*

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## 2. Mesoporous Silicates with Organic Surface Groups

### 2.1. Grafting Methods

Grafting, in this context, refers to post-synthesis modification of a pre-fabricated mesoporous support by attachment of functional molecules to the surface of the mesopores, usually after surfactant removal (Fig. 1). Mesoporous silicates possess surface silanol (Si–OH) groups that can be present in high con-
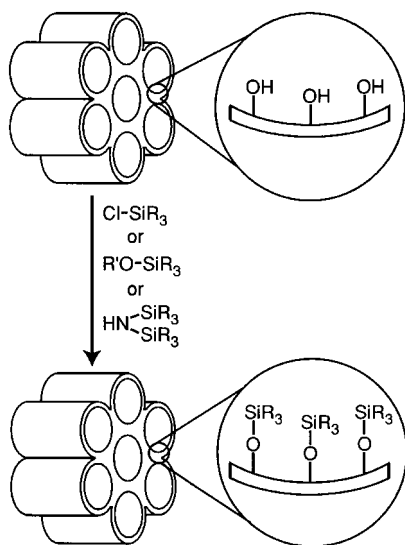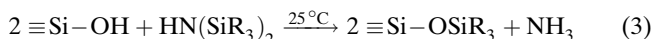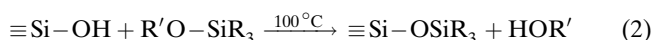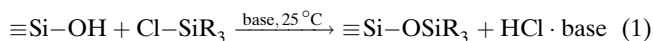


Fig. 1. Functionalization of mesoporous silicates by grafting.

centration and, like in amorphous silica, act as convenient anchoring points for organic functionalization.[22–24] Surface modification with organic groups is most commonly carried out by silylation, although modification of silanol groups is also possible by esterification, e.g., with ethanol.[25,26] Typically, silylation is accomplished by one of the following procedures:[27]

$$\equiv Si-OH + Cl-SiR_3 \xrightarrow{\text{base, 25 °C}} \equiv Si-OSiR_3 + HCl \cdot base \quad (1)$$

$$\equiv Si-OH + R'O-SiR_3 \xrightarrow{100 °C} \equiv Si-OSiR_3 + HOR' \quad (2)$$

$$2 \equiv Si-OH + HN(SiR_3)_2 \xrightarrow{25 °C} 2 \equiv Si-OSiR_3 + NH_3 \quad (3)$$

Silylation occurs on free ($\equiv Si$–OH) and geminal silanol ($=Si(OH)_2$) groups, but hydrogen-bonded silanol groups are less accessible to modification because they form hydrophilic networks among themselves.[28] The original structure of the mesoporous support is generally maintained after grafting.

If a high surface coverage with functional groups is desired, it is important to maintain a large number of surface silanol groups after removal of the surfactant. Surfactant removal is carried out either by calcination or by appropriate extraction methods. Calcination promotes condensation of unreacted silanol groups, and many surface groups are lost at typical calcination temperatures (400–550 °C). The surface can be rehydrated by boiling calcined mesoporous silicate in water and

removing excess water by azeotropic distillation, e.g., with toluene[29] or benzene.[30] The surface of calcined MCM-41 can also be rehydroxylated by acid hydrolysis[31] or by steam treatment.[22] Extraction processes (e.g., with acid/alcohol mixtures for cationic surfactants or with alcohols for neutral surfactants) minimize loss of surface silanols, although post-extraction thermal treatments can increase the surface reactivity for silylation and strengthen the walls through additional condensation. Zhao and Lu determined that, for MCM-41 samples in which the surfactant was removed by extraction, optimal outgassing temperatures appeared to be between 400–450 °C.[28] At lower temperatures, a large number of silanols remain inaccessible to grafting because of hydrogen bonding between them; at much higher calcination temperatures, many silanol groups are lost due to condensation reactions.

Recently, supercritical fluids have been used as a reaction medium to deliver siloxanes to channel surfaces.[32] This method is particularly suited for smaller pore materials due to the low density, viscosity, and surface tension, and the high diffusivity of supercritical fluids, such as $CO_2$. When this technique was applied to mesoporous silica, a high degree of crosslinking was observed, resulting in an increase of the hydrolytic stability of the surface groups.

### 2.1.1. Grafting with Passive Surface Groups

Grafting of the mesopore surfaces with groups that exhibit low reactivity, such as alkyl chains or phenyl groups, can be used to tailor the accessible pore sizes of mesoporous solids, increase the surface hydrophobicity, passivate silanol groups, and thereby protect the framework towards hydrolysis. In their early work, Mobil researchers demonstrated that the pore sizes of MCM-41 could be reduced by trimethylsilylation.[2,33] Similar pore size tuning was carried out with FSM-type mesoporous silicas,[3,4] which contain fewer geminal silanols than MCM-41.[34] The pore diameters could be progressively decreased using longer alkyl chain lengths of chloroalkyldimethylsilanes. Alternatively, the apparent pore size of ordered mesoporous materials could be adjusted by varying the amount of grafted long-chain silylating agent.[34] It should be noted that pore size values, which are determined by gas adsorption measurements (typically nitrogen adsorption), depend strongly on the adsorption model that is used and also on the identity of the functional group. Jaroniec and co-workers demonstrated that low-pressure adsorption data are influenced by the presence of organic groups on mesoporous silica surfaces, making it possible to detect and sometimes quantify the organic species by gas adsorption techniques.[35,36]

Zhao and Lu recently carried out a systematic study of the surface coverage obtained by silylating an MCM-41 surface with trimethylchlorosilane (TMCS).[28] The maximum degree of surface coverage obtained was ca. 85 %. Silylation increased the hydrophobicity of the surface and strongly influenced the degree of water adsorption. Tatsumi et al. showed that trimethylsilylation of MCM-41 and MCM-48 improved their stability to moisture and mechanical compression.[37] It

is remarkable that the additional siloxane groups protected the walls of the mesoporous solid even after removal of the methyl groups by calcination.

Anwander et al. functionalized the surface of MCM-41 with disilazane agents of the type $HN(SiR^1R_2^2)_2$ ($R^{1,2}$ = H, Me, Ph, vinyl, $^nBu$, $^nOct$).[27,38] The size of the silylating groups affected the degree of silylation and the concurrent surface hydroxyl consumption. Best surface coverage was obtained with the sterically less demanding silyl groups. Hexamethyldisilazane functionalization was used to quantify the number of surface silanols, passivate surface silanols, and depolarize the surface for selective adsorption experiments. Multiple functionalization was carried out by consecutive or competitive silylation. The competitive silylation reactions demonstrated that the grafting rate depended on the steric bulkiness of the silyl groups of the silylamine, with preferential grafting of smaller groups.

### 2.1.2. Grafting with Reactive Surface Groups

A number of silane-coupling agents, such as those with olefins, nitriles, alkylthiols, alkyl amines, alkyl halides, epoxides, and some other surface groups, are reactive, permitting further functionalization. Olefins, such as vinyl groups, can be modified, e.g., by bromination[39] or hydroboration.[38] Nitriles can be hydrolyzed to form carboxylic acids, and alkylthiols can be oxidized to sulfonic acids,[40,41] which can be further employed as electrostatic anchoring points, e.g., for amino acids.[42] Surface amines may be derivatized, for example, by alkylation, nucleophilic aromatic substitution, or formation of amides or imines.[43] Functionalization of alkyl halides is possible by nucleophilic replacement of the halogen atom.[44] An example is given by Sutra and Brunel,[45] who attached a $Mn^{III}$ Schiff-base complex (Mn–salen) to an MCM-41 surface modified with 3-chloropropylsilane moieties. In this type of reaction, HCl is produced and quaternization of the amine can occur as a side reaction. A milder method that is particularly suited to attachment of basic surface groups involves the reaction of oxirane surface groups (from 3-trimethoxylsilylpropoxymethyloxirane) with amines.[46]

Balkus and co-workers functionalized MCM-41 with cobalt-complexing ligands (ethylenediamine, diethylenetriamine, and ethylenediaminetriacetic acid (EDT)).[47] The uniform, large pores of the MCM-41 support limited coordination of cobalt to adjacent ligands, avoiding random ligation, which may occur on amorphous silica. The EDT-complexed metal centers were shown to be redox active on the mesoporous silicate supports.

Anwander et al. developed a mild grafting method for chelating complexes using yttrium bis(dimethylsilyl) amide complexes as the anchoring groups.[48] These complexes were attached to the surface of MCM-41 by metal siloxide bond formation after elimination of the amine groups. The products acted as catalysts in a hetero Diels–Alder cyclization reaction.

### 2.1.3. Site-Selective Grafting

Multiple grafting has also been demonstrated. For example, if uncovered areas remain after silylation (e.g., leaving hydro-

philic sites) they can be passivated by trimethylsilylation.[28,37] Such passivation changes the hydrophobicity of the surface and thereby controls adsorption of polar/non-polar molecules.

In grafting reactions, the external surface is more easily accessible and is functionalized predominantly over the internal mesopore surface.[49] The functional groups on the external surface are again more accessible in subsequent reactions, leading to reduced selectivities in processes that benefit from pore confinement. To minimize involvement of the external surface in reaction processes and to optimize selectivity, it is possible to passivate these surfaces first, before functionalizing the internal silanol groups. Controlled dual functionalization has been achieved by two different methods (Fig. 2).
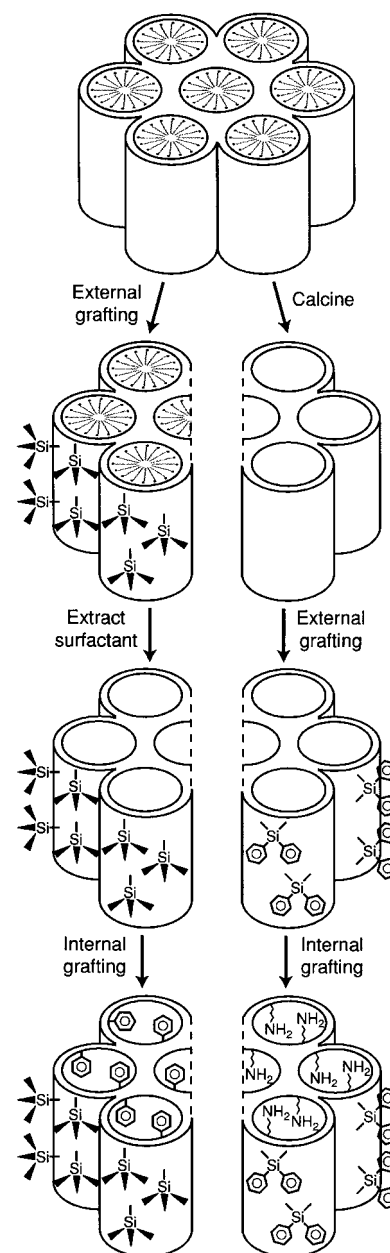


Fig. 2. Methods of selective grafting on external and internal surfaces of mesoporous silicates.

Shephard et al. assumed that silanol groups on the external surface of a calcined MCM-41 sample are kinetically more accessible for functionalization.[50] Calcined MCM-41 was modified first with $Ph_2SiCl_2$ to passivate the external surface and then with $(MeO)_3SiCH_2CH_2CH_2NH_2$ as an anchor for a redox-active ruthenium cluster. This cluster acted as a stain in high-resolution transmission electron microscopy (HRTEM) by which the authors concluded that the amine tethers were present almost entirely on the internal surface of MCM-41. De Juan and Ruiz-Hitzky employed an alternate approach for selective functionalization of external and internal MCM-41 surfaces.[51] The first (external) grafting step was carried out with the as-synthesized mesoporous sieve whose pores were still filled with the surfactant template. Exposure of this support to a solution of trimethylsilyl chloride resulted in functionalization mainly of the external surface due to steric restrictions in the surfactant-filled mesochannels. The template was then extracted and the internal pore surfaces were functionalized with phenylpropyldimethylchlorosilane.

Aronson et al.,[52] as well as Antochshuk and Jaroniec,[53] demonstrated that one needs to be cautious in assuming that silylating agents are excluded from the channels of as-synthesized MCM-41, in particular when high concentrations of silylation reagents are used. Antochshuk and Jaroniec[53] carried out simultaneous grafting and extraction of template molecules by modification of uncalcined MCM-41 with trialkylchlorosilanes. As-synthesized MCM-41 was refluxed in the neat trialkylchlorosilane, first by itself, then with added anhydrous pyridine, followed by multiple washing with different solvents, leading to surfactant-free mesoporous products. The loading of surface groups exceeded that on calcined supports that were otherwise treated in a similar way. Several advantages were noted for this procedure: more surface hydroxyl groups were present by eliminating the calcination step; the reduction in pore size was minimized by eliminating shrinkage during calcination or during formation of smaller channels in a direct synthesis. This method was demonstrated for short and long alkyl groups (trimethyl- and octyl-dimethylchlorosilyl groups).

### 2.2. Coating

In the grafting processes noted above, silylation reagents were typically added under dry conditions to avoid hydrolysis and condensation away from the pore walls. Under anhydrous conditions the hydrophilic portion of the silica surface is preserved during silylation[54] and surface groups are relatively isolated. However, by employing just enough water in the process to form a monolayer on the pore surface, more continuous coats of organosilanes may be obtained, leading to a high concentration of organics in the product (Fig. 3). Excess water must be avoided, because it can lead to uncontrolled polymerization of the silylation reagents within the channels or external to the mesoporous sieve. Water-controlled coating has been employed with mercaptopropyl functions on MCM-41 and HMS type structures.[30,55]
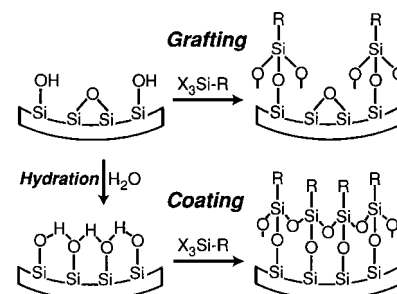


Fig. 3. Comparison of coating and grafting processes.

Dai et al. recently described an interesting imprint coating method.[56] They coated the mesoporous surface of MCM-41 with complexes of ligands and target metal ions rather than just with the free ligands. When the metal ions were removed, the ligands were already positioned for complexation with metal ions of the same type. The selectivity to binding the original metal ion in competitive binding experiments was greater than in randomly functionalized mesoporous sieves. The material's performance remained high after repeated absorption and elution of metal ions. The effects of imprint coating on selectivities were observed only with mesoporous sieves as supports but not with amorphous silica gel. The different behavior was attributed to the curvature of the mesopores and the confinement of guest species.

### 2.3. Co-condensation Reactions

Co-condensation of a tetraalkoxysilane and one or more organoalkoxysilanes with Si–C bonds is an alternative method of producing inorganic–organic hybrid networks by sol–gel chemistry.[57] Such co-condensation reactions (also called "one-pot" syntheses) have also been applied to surfactant-templated syntheses (Fig. 4). Since the early work by the research groups of Mann,[58,59] Macquarrie,[60] Stucky,[61] and Stein,[39] co-condensation reactions have been used to prepare hybrid mesoporous silicates under a wide range of reaction conditions. Some common criteria in the choice of the co-condensation reaction system include the need to avoid phase separation of the precursors to obtain uniform distributions of functional groups and the need to avoid Si–C bond cleavage during the sol–gel reaction and during surfactant removal. Examples of co-condensation reactions are summarized in Table 1. The discussion of "one-pot" reactions will be subdivided here by reaction pathway.
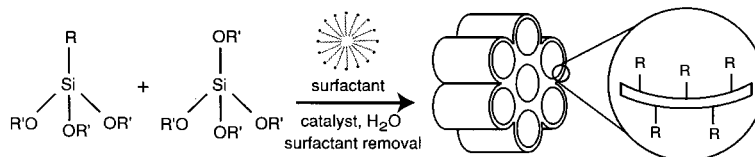


Fig. 4. Preparation of hybrid mesoporous silicates by co-condensation.

Table 1. List of mesoporous co-condensation products.

| Functional group | Surfactant | Mesophase | Author, year, reference |
|---|---|---|---|
| 3-aminopropyl-, 2-cyanoethyl- | *n*-dodecylamine | HMS | Macquarrie 1996 [60] |
| 3-aminopropyl- | $C_{16}$TABr | MCM-41 | Mann 1997 [64] Walcarius 1999 [123] |
| 3-chloropropyl- | *n*-dodecylamine $C_{16}$TABr | HMS Ti-MCM-41 | Macquarrie 1999 [78] Tatsumi 2000 [87] |
| 4-[(4-dimethyl-aminophenyl)azo]benzoic acid, sulforhodamine B (with aminopropyl linkages) | $C_{16}$TABr | MCM-41 | Wöhrle 2000 [133] |
| 3-(2,4-dinitrophenylamino)propyl- | $C_{16}$TABr | MCM-41 | Mann 1998 [77] Mann 1999 [74] |
| ethyl-, propyl-, *n*-hexyl-, *n*-octyl-, 3-butenyl- | *n*-dodecylamine | HMS | Nakajima 1998 [82] |
| 3-(2,3-epoxypropoxy)propyl-, 3-imidazole- | $C_{16}$TABr | MCM-41 | Mann 1997 [64] |
| 3-mercaptopropyl-, propyl-$SO_3H$ | $C_{16}$TABr *n*-dodecylamine | MCM-41 HMS | Stein 1998 [40] Jacobs 1998 [55] Jacobs 1998 [55] |
| 3-mercaptopropyl- | Tergitol 15-S-12 Triton-X100 | MSU-1 MSU-2 | Mercier 1998 [83] Mercier 1998 [83] Mercier 2000 [84] |
| | *n*-octylamine | HMS | Mercier 2000 [81] |
| 3-mercaptopropyl-, allyl- | $C_{16}$TABr | MCM-41 | Mann 1997 [64] |
| methyl- | $C_{16}$TABr | Ti-MCM-41 | Corma 1998 [86] Tatsumi 2000 [87] |
| methyl-, ethyl-, *n*-octyl- | $C_{16}$TABr | SBA-3 | Babonneau 1999 [72] |
| $CH_3HN(CH_2)_3$-, $(CH_3)_2N(CH_2)_3$-, $H_2N(CH_2)_2NH(CH_2)_3$- | *n*-dodecylamine | HMS | Macquarrie 1999 [78] |
| phenyl- | $C_{16}$TABr | MCM-41 | Mann 1996 [58] Mann 1996 [59] Mann 1998 [129] |
| | | SBA-1 SBA-3 | Babonneau 1999 [63,73] Babonneau 1999 [63,72,73] |
| | | Ti-MCM-41 | Tatsumi 2000 [87] |
| | $C_{16}$TACl | MCM-41 MCM-48 | Slade 1998 [130] Mann 1999 [69] |
| | *n*-octylamine | HMS | Mercier 2000 [81] |
| phenyl-, methyl- | *n*-dodecylamine | HMS, Ti-HMS | Nakajima 1998 [82] |
| phenyl- with allyl-, 3-aminopropyl-, or 3-mercaptopropyl- | $C_{16}$TABr | MCM-41 | Mann 1999 [69] |
| $Ph_2P(CH_2)_3$-, $Ph_2P(S)(CH_2)_3$-, $Ph_2P(CH_3)(CH_2)_3$- | *n*-hexadecylamine | HMS | Corriu 1999 [80] |
| *n*-propyl-, *n*-butyl-, *n*-octyl- | *n*-octylamine | HMS | Mercier 2000 [81] |
| vinyl- | $C_{16}$TABr | MCM-41 SBA-3 | Stein 1997 [39], 1999 [49] Babonneau 1999 [72] |
| | *n*-dodecylamine | HMS | Nakajima 1998 [82] Macquarrie 1999 [78] |
| vinyl-, allyl-, *n*-pentyl- | $C_{16}$TABr | Ti-MCM-41 | Tatsumi 2000 [87] |

### 2.3.1. Co-condensation by an $S^+I^-$ Pathway

The $S^+I^-$ pathway is the method used to prepare the original MCM-41 and related structures. Here, $S^+$ refers to cationic surfactants, such as alkylammonium surfactants, and $I^-$ to anionic silica precursors, which are obtained under basic reaction conditions. When organic groups are incorporated in the mesoporous sieve by this pathway, the surfactants are normally extracted with HCl/alcohol mixtures,[39,62] although with phenyl surface groups the surfactant can be removed by calcination at 350 °C.[63] The first studies by Mann and co-workers involved mixtures of cetyltrimethylammonium bromide (CTAB) surfactants with tetraethylorthosilicate (TEOS) and organosilanes chosen from the following set: phenyltriethoxysilane (PTES), octyltriethoxysilane (OTES), allyltrimethoxysilane (ATMS), 3-mercaptopropyltrimethoxysilane (MPTMS), 3-aminopropyltriethoxysilane (APTES), 3-(2,3-epoxypropoxy)propyltrimethoxysilane, or 3-imidazolyltriethoxysilane.[58,59,64] In selected systems hexagonal order was obtained when up to 20 mol.-% of the organoalkoxysilane was used.[65] Based on $^{29}$Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra, the distribution of organic groups in the silica network appeared to be uniform.[65] The upper limit of organoalkoxysilane incorporation into the hybrid mesostructured materials has been estimated to be less than 40 %, because some fully linked $Q^4$ silicate groups are necessary to form stable wall structures.[58]

At about the same time, Stucky and co-workers investigated several long-chain alkoxysilanes as surfactant precursors in mesostructure syntheses.[61] MCM-41 and MCM-48 type structures were synthesized using *n*-tetradecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride as a covalently bonded surfactant–silica source. They surmised that the surfactant was part of the inorganic framework of the product.

Stein and co-workers prepared hybrid MCM-41 structures with reactive vinyl groups by co-condensation of vinyltriethoxysilane (VTES) with TEOS.[39] The highest hexagonal order was obtained with VTES/TEOS mole ratios below 1:4. The surfactant could be extracted without affecting the vinyl functionalities. A difficult

**ADVANCED MATERIALS**

question in many surface modifications of porous materials is whether the functional groups are located on the internal pore surface, the external particle surface, or within the walls. Stein and co-workers employed a bromination reaction of vinyl-MCM-41 to probe the functional group location. During bromination in dichloromethane, a very slow reaction rate indicated that most vinyl groups were present within the mesopore channels. The bromination rate increased with increasing pore diameter. A strong dependence of the reaction rate on the presence and type of solvent molecules was observed. Gas-phase bromination was complete within 40 min. These results provide evidence for attachment of most vinyl groups to the accessible surface within the mesopore channels. This conclusion was corroborated by small angle neutron scattering experiments using contrast matching techniques.[66] Bein and co-workers co-condensed 3-methacrylpropyltrimethoxysilane and tetramethoxysilane (TMOS) in an MCM-41 type structure and also found that the C=C double bonds could be completely brominated.[67]

Similarly, mercaptopropyl-functionalized porous silicates were synthesized by the co-condensation of 3-mercaptopropyltriethoxysilane (MPTES) and TMOS in the presence of a cationic surfactant under basic conditions (Fig. 5).[40] Ordered hexagonal arrays of channels, similar to those of MCM-41
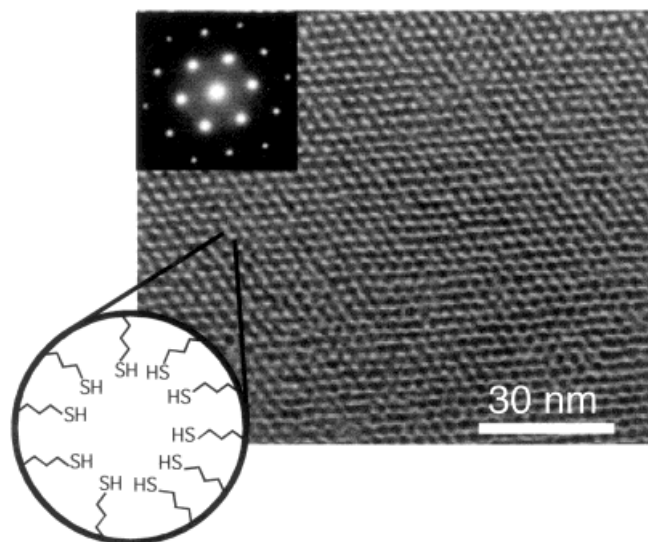


Fig. 5. Transmission electron micrograph of a region of 3-mercaptopropyl-MCM-41. The inset shows the selected area electron diffraction pattern from this region. Adapted from [40].

mesoporous sieves but with smaller pore diameters, were obtained with MPTES/TMOS ratios as high as 1:2.5 and a thiol content up to 5 mmol S/g silica. The extracted solids were microporous, with an average pore diameter of ca. 14 Å. The thiol surface groups could be oxidized to sulfonic acid functionalities, creating a solid acid ion exchanger with the advantages of the ordered porous support, including high surface area, controlled pore size, mechanical stability, as well as reduced swelling or contraction upon ion exchange, compared to polymeric sulfonic acids.[40] Similar mercaptopropyl-MCM-

41 structures were prepared by Jacobs and co-workers[55] and Laha et al.[68] A cubic phase, phenyl-MCM-48, was prepared by Mann and co-workers.[69] This phase could not be prepared with amino, thiol, or allyl groups.

In co-condensation reactions involving the $S^+I^-$ pathways it is commonly observed that, as the concentration of organoalkoxysilane increases, both the $d_{100}$-spacings and the pore sizes of the channels are significantly reduced, even when the same surfactant is used.[49,59] At the same time, the apparent wall thickness increases, partly because organic groups extend into the channels. One possible reason for the shrinkage in cell dimensions may be a stronger interaction between nonpolar organic groups and the tails of the surfactant molecules, which draw the organic precursors further into the micelles.

The co-condensation reaction has now also been applied to incorporate covalently attached organic groups within zeolite cages.[70,71] The organic groups were incorporated directly during the synthesis of zeolite beta and other zeolites, using phenethyltrimethoxysilane as one of the precursors. The intrapore phenyl rings were subsequently sulfonated to produce sulfonic-acid sites within the zeolite cages. Shape-selective catalysis involving formation of a cyclic ketal was demonstrated.

### 2.3.2. Co-condensation by an $S^+X^-I^+$ Pathway

This mechanism involves cationic silicate precursors ($I^+$), which are obtained under acidic reaction conditions. The $I^+$ species interact with cationic surfactant molecules via anions ($X^-$) present. Under these conditions, Stucky and co-workers obtained a lamellar phase from an aqueous reaction mixture containing $C_{16}H_{33}Si(OEt)_3$, TEOS, and HCl. A lamellar phase was also formed with this surfactant in the absence of any other silica source.[61]

Babonneau and co-workers studied co-condensation reactions of a series of hybrid mesoporous sieves under acidic conditions, incorporating methyl, ethyl, octyl, vinyl, and phenyl surface groups in the structure.[72] Hexagonally ordered structures were obtained only with the phenyl groups. Due to the weaker interactions between the surfactant and the silicate surface under acidic conditions, the surfactant could be extracted with ethanol, although some structural disordering was observed after this process. Calcination at 350 °C, on the other hand, preserved the ordered structure as well as the phenyl groups. Most other organic groups cleave or decompose during this heat treatment. A 2D hexagonal phase analogous to SBA-3 and a cubic phase analogous to SBA-1[20,21,61] were prepared by co-condensation of a mixture of phenyltriethoxysilane and TEOS under acidic conditions templated by CTAB.[72,73] The hexagonal phase was obtained when the precursors were pre-hydrolyzed before addition of the surfactant, while the cubic phases resulted when the pre-hydrolysis step was left out. It is notable that the cubic phase also retained its structure after removal of the surfactant by calcination at 350 °C and even after removal of the phenyl groups by calcination at 600 °C.

Compared to basic conditions, acid conditions are more amenable to the formation of mesostructured monoliths and films, which can be of interest, for example, in optical applications. Mann and co-workers prepared transparent yellow thin films and millimeter thick monoliths of silica mesostructures[74] by slow solvent evaporation from an aqueous precursor solution containing TEOS, 3-(2,4-dinitrophenylamino)-propyltriethoxysilane, and CTAB surfactant following the acid synthesis procedure of Brinker and co-workers.[75,76] In prior work carried out under basic conditions, the product was in powder form.[77]

### 2.3.3. Co-condensation by an $S^0I^0$ Pathway

Uncharged silica precursors ($I^0$), such as TEOS, can also form mesostructures with neutral amine surfactant micelles ($S^0$), e.g., octylamine or dodecylamine. Because of the weak interaction between the neutral surfactants and the wall, removal and recovery of the surfactant is possible by extraction with ethanol. This approach was first used by Macquarrie for hybrid materials with 3-aminopropyl and 2-cyanoethyl groups[60] and was subsequently extended to other functional groups, including vinyl and chloropropyl groups,[78] 3-imidazole,[64] and mercaptopropyl groups.[55,79] As with pure silica HMS structures,[6] the products have disordered, worm-like channels with narrow pore size distributions. Corriu et al. included phosphorus centers in hybrid mesoporous solids by co-condensing TEOS and $R'Si(OEt)_3$ ($R'$ contains P atom) in the presence of *n*-hexadecylamine.[80] The resulting mesopore structure was maintained even after subsequent sulfuration or quaternization of the phosphorus centers.

A detailed investigation of co-condensation reactions involving the $S^0I^0$ assembly was carried out by Mercier and Pinnavaia who considered octyl-, butyl-, propyl-, mercaptopropyl-, and phenyl groups.[81] This study differentiated between template substitution pathways and direct addition pathways. Template substitution refers to partial replacement of the surfactant and TEOS by an equivalent amount of organoalkoxysilane whose organic component is comparable in length to the surfactant. With greater incorporations of the long-chain precursors the pore volume and surface area of the mesoporous products decreased systematically. The direct addition pathway was applied to organoalkoxysilanes with relatively short organic moieties, which replaced equivalent amounts of TEOS. Very short ethyl groups apparently became trapped in the walls, leading to reduced order and porosity of the products. In these processes the pore volumes and surface areas did not vary systematically with loading, but as in materials prepared by the $S^+I^-$ pathway, smaller pore sizes were observed with increased loading of the organic component. This behavior was also noted by Koya and Nakajima for HMS structures containing alkyl, alkenyl, and phenyl groups.[82] They also noted that the absorption capacity for water was less in the hybrid materials than in the pure silica samples, and it decreased with increasing alkyl chain length.

### 2.3.4. Co-condensation by an $N^0I^0$ Pathway

Mercier and co-workers investigated an $N^0I^0$ pathway, employing a non-ionic surfactant ($N^0$), such as alkylpoly(ethylene oxide) (Tergitol 15-S-12 [$CH_3(CH_2)_{14}(OCH_2CH_2)_{12}OH$] or Triton-X100 [$(CH_3)_3C(CH_3)_2CCH_2C_6H_4(OCH_2CH_2)_{10}$-OH]), as the structure-directing agent.[83,84] This synthesis was carried out at neutral pH and surfactant extraction was possible with ethanol. With TEOS and organotrialkoxysilanes, worm-like channel structures were obtained with lattice spacings that became smaller with higher loadings of organics.[83] A product from co-condensation of TEOS with MPTMS exhibited a high capacity for the absorption of mercury ions (2.3 mmol/g).[84]

### 2.3.5. Multifunctional Surfaces

Incorporation of two or more functional groups in a one-pot synthesis is also possible, although the location of functional groups is not as controlled as by the grafting processes described earlier; the functional groups are randomly distributed in the product. Published examples include mixtures containing phenyl and aminopropyl, phenyl and mercaptopropyl, phenyl and allyl, and methyl and aminopropyl groups.[69,85] Typically an excess of TEOS (at least 80 mol.-%) was used and loadings of the organic groups were in the range 1–5 mmol/g.

### 2.3.6. Co-condensation of Hybrid Mesoporous Silicates with Inorganic Heteroatoms

Incorporation of inorganic heteroatoms, such as titanium, is feasible during co-condensation reactions. Corma et al. prepared an active epoxidation catalyst, methyl-tethered-Ti-MCM-41, in a one step synthesis using mixtures of TMOS, methyltriethoxysilane, and titanium tetraethoxide as precursors with CTAB as the template (Ti/Si: 0.0075–0.0166).[86] Bhaumik and Tatsumi synthesized a whole range of organically modified Ti-MCM-41 samples by co-condensation of TEOS, organo-triethoxysilane (methyl, vinyl, allyl, 3-chloropropyl, pentyl, phenyl), and titanium tetrabutoxide and tested the materials as epoxidation catalysts.[87] A higher Ti content could be obtained than in the absence of the organic groups. Unlike for organically modified silica MCM-41 samples, in the Ti-doped analogs the pore sizes and *d*-spacings increased slightly upon incorporation of $C_1$–$C_3$ groups. With pentyl and phenyl groups the pore sizes and *d*-spacings decreased. Enhanced selectivity for epoxide in epoxidation reactions compared to Ti-MCM-41 without organic surface groups was attributed to the greater hydrophobicity of the modified surface.

### 2.4. Comparison Between Grafting and Co-condensation Methods

Lim and Stein compared the relative distribution of surface groups in vinyl-functionalized MCM-41 samples prepared by

**ADVANCED MATERIALS**

either a post-synthesis grafting process or a direct co-condensation synthesis.[49] Based on powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and bromination kinetics data, the vinyl groups appeared to be non-uniformly distributed in samples prepared by the grafting process, with a large proportion of vinyl groups on the external surface of the crystallites or inside channels but near the channel openings. In products from a direct co-condensation reaction, the vinyl groups appeared to be more uniformly distributed throughout the channels.

Each of the two functionalization methods has certain advantages. If uniform surface coverage with organic groups is desired in a single step synthesis, the direct method may be the first choice. It also provides better control over the amount of organic groups incorporated in the structure. However, products obtained by post-synthesis grafting are often structurally better defined and hydrolytically more stable than samples from the direct synthesis method. Although pore sizes can be controlled to some extent by both methods, pore size control is more easily achieved by grafting.

## 3. Hybrid Wall Components

A recent development in the field of hybrid materials has been the study of mesoporous materials with wall structures that consist of covalently bonded hybrid inorganic–organic networks. The surfactant-templated syntheses of these materials use a precursor that has two trialkoxysilyl groups connected by an organic bridge. Such precursors have already been used in the production of hybrid materials,[88,89] specifically the synthesis of bridged polysilsesquioxanes.[90] Shea and co-workers prepared hybrid polysilsesquioxane xerogels employing bis(triethoxysilyl)alkane, alkylene, and aryl derivatives either alone or with TEOS.[90–92] Even without surfactant templating, arylene bridged polysilsesquioxanes are porous and have high surface areas.[90] Alkylene-bridged polysilsesquioxanes with short, stiff alkylene bridges are also mesoporous—the pore size depending on the length of the alkylene chain.[93]

If surfactants are added to these types of syntheses, the uniformity of channels can be improved, and sometimes high structural order is obtained. Three independent groups have recently described mesoporous hybrid inorganic–organic framework structures formed by surfactant templating methods, with publications occurring nearly simultaneously.[94–97] The procedures are similar to those used to synthesize MCM-41. The double trialkoxysilyl precursors are hydrolyzed and condensed in the presence of amphiphilic surfactant micelles. The surfactant can be removed by ion exchange, leaving a high surface area framework with channels of regular diameter (Fig. 6). The technique permits stoichiometric incorporation of organic groups in silicate networks, resulting in higher loadings of organic functional groups than by grafting methods or by direct synthesis of mesoporous silicates with organic surface groups. One can envision further tunability of the me-
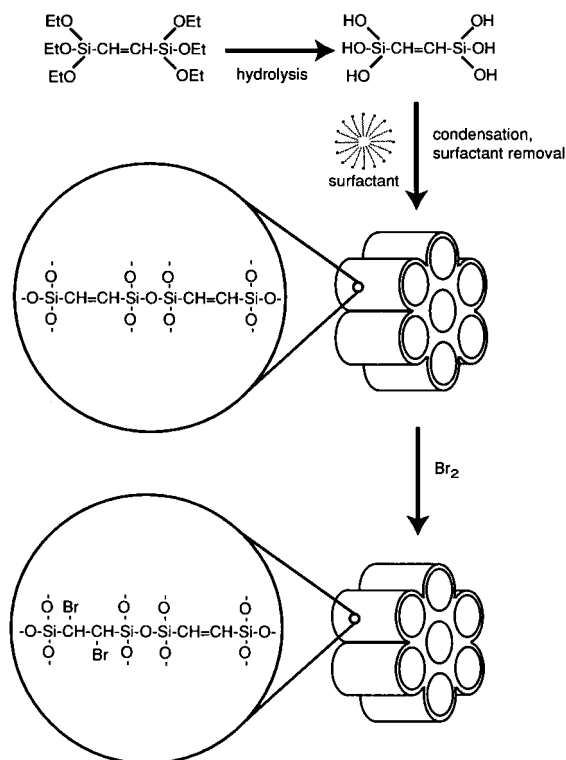


Fig. 6. Preparation of mesoporous hybrid framework solids, showing an example with reactive ethene bridges in the walls. These groups can be further brominated.

chanical, surface chemical, electronic, optical, or magnetic properties of the hybrid composite by introducing suitable functional groups into the walls.

The first report of these new materials was from Inagaki et al. who used 1,2-bis(trimethoxysilyl)ethane (BTME) as the framework precursor and octadecyltrimethylammonium chloride (ODTMA) surfactant.[94] Depending on reaction conditions, they obtained a highly ordered 2D hexagonal phase consisting of rod-like particles with hexagonal cross sections, or a 3D hexagonal mesophase consisting of spherical particles. The surfactant-extracted products contained accessible mesopores with pore sizes of 3.1 nm and 2.7 nm for the 2D and 3D materials, respectively. The bridging ethane components decomposed at 400–700 °C, temperatures higher than those required to decompose ethyl groups grafted onto a solid support. In hydrothermal stability tests, XRD patterns did not change significantly after boiling the materials in water for 8 h. The authors also describe a cubic hybrid mesophase, which forms decaoctahedral crystals.[98]

The formation of a 3D mesophase using an alkyltrimethylammonium surfactant is unusual. Surfactants with large head groups or non-ionic alkyl poly(ethylene oxide) oligomers are typically required to induce such a phase in inorganic oxide networks.[11,14] Hydrolyzed BTME has a lower charge density than a precursor such as TEOS, the silyl groups being separated by ethane. This may enlarge the effective head group area of the surfactant, resulting in higher curvature at the surfactant–BTME interface and the formation of a 3D phase.

Stein and co-workers used 1,2-bis(triethoxysilyl)ethane (BTSE) and CTAB to synthesize a mesoporous hybrid framework designated UOFMN-1 (unified organically functionalized mesoporous network).[95] The precursor was prehydrolyzed with acid before the pH was raised by adding base. A material designated UOFMN-2 was made by a similar procedure using 1,2-bis(triethoxysilyl)ethylene (BTSEY) as the precursor. The products consisted of fine particles with no regular shape. They contained uniform pores (pore size: 2.2 nm for UOFMN-1, 2.4 nm for UOFMN-2). In contrast to Inagaki's structures, the channel systems of UOFMN-1 and UOFMN-2 were worm-like, lacking long-range order.

The organophilicity of UOFMN-1 was visibly demonstrated by adding some powdered sample to a vial containing water and chloroform. Most of the sample floated on top of the aqueous phase until the vial was shaken, upon which it mixed with the chloroform. This behavior differed from that of pure silica gel, which, though hydrophobic, seemed to only coat the organic phase with little mixing. The hydrophobic nature of UOFMN-1 and thicker pore walls contributed to its greater hydrothermal stability compared to that of a pure silica MCM-41 made under similar conditions using TEOS and CTAB. Boiling UOFMN-1 in water for 17 h caused only a slight decrease in XRD peak intensity, and even after refluxing for another three days, a low-angle XRD reflection remained. UOFMN-2 could be partially brominated, with no deleterious effect on the material's mesostructure. The brominated UOFMN-2 was itself reactive as a source of bromide. A sample stirred in aqueous AgNO$_3$ produced crystalline AgBr.

Ozin and co-workers also used BTSEY or mixtures of BTSEY with TEOS to synthesize hexagonal hybrid frameworks, which they labeled PMOs (periodic mesoporous organosilicas).[96] The intensity of powder XRD reflections of the resulting products increased upon adding larger proportions of TEOS to the hybrid precursor. This effect could be due to greater product order as well as increased electron density in walls as the ratio of Si/C in the walls increased, demonstrating that organic groups were part of the framework. The pore diameter of the ordered product (3.94 nm) was significantly larger than those of UOFMN materials and of Inagaki's materials, which made use of an C$_{18}$ chain surfactant. Like UOFMN-2, the ethene bridges in a PMO material made with BTSEY were proven to be reactive. The PMO sample was refluxed in CH$_2$Cl$_2$ with Br$_2$ for 8 days. All alkene groups were consumed according to $^{13}$C cross polarization (CP) MAS-NMR. However, based on chemical analysis, it was estimated that only ca. 10 % of the ethene groups were brominated and the others had reacted with solvent.

The choice of precursor has a strong influence on the structure of mesoporous hybrid framework solids, as investigations using the precursors 1,4-bis(triethoxysilyl)benzene, 2,5-bis(triethoxysilyl)thiophene, 1,1′-bis(triethoxysilyl)ferrocene, bis(triethoxysilyl)bithiophene, and bis(triethoxysilyl)acetylene showed.[97] The precursors were hydrolyzed and condensed under basic conditions in the presence of CTAB surfactant. It was observed by $^{29}$Si CP MAS-NMR that Si–C bond cleavage

occurred for the benzene and thiophene precursors. Acidic conditions resulted in less Si–C bond cleavage for these precursors and the formation of products that exhibited some hexagonal order on XRD patterns. An optimized procedure was developed for the benzene and thiophene compositions to minimize bond cleavage and induce hexagonal order, using cetylpyridinium chloride with the bis(triethoxysilyl)organo precursor in acidic aqueous solution and gradual neutralization with sodium bicarbonate and ammonium fluoride. The other precursors were more difficult to utilize in a PMO synthesis. The Si–C bond in the acetylene precursor was too labile under aqueous conditions and use of the bithiophene precursor resulted in poorly ordered products. A synthesis involving the ferrocene precursor resulted in a material with low order and partial Si–C cleavage, but much of the ferrocene remained intact in the framework according to NMR.

## 4. Applications

### 4.1. Catalysis

During the last few years, hybrid mesoporous solids have been considered for a wide range of heterogeneous catalysis reactions.[43] Heterogenization of active centers can improve the overall efficiency of the catalytic processes because: 1) it is easier to retain the solid catalyst in the reactor or to separate it from the liquid process stream by filtration (compared to extraction or distillation requirements for homogeneous processes); 2) often the catalyst can be regenerated and recycled; and 3) confinement of the catalyst within mesopores provides a means of introducing size and/or shape selectivity and thus greater specificity to a reaction. In contrast to organic polymers, mesoporous silicates used in organic solvents do not swell or dissolve. If functional groups are covalently attached to the surface, leaching is minimized.

Typically, mesoporous supports are initially functionalized with relatively inexpensive organotrialkoxysilanes to incorporate surface amines, alkyl halides, alkenes, nitriles, or thiols. These moieties can be further modified by the methods mentioned earlier. Reactions that have been studied using functionalized mesoporous solids include acid catalysis,[40,41,55,79] base catalysis,[46,85,99–105] oxidations,[106–109] reductions,[110,111] enantioselective catalysis,[54,112–114] stereospecific polymerizations,[115] and other catalytic reactions that produce fine chemicals.[44,100,116–118]

It has been noted that mesoporous catalysts differ significantly in many respects from their post-functionalized, amorphous silica counterparts.[102] In several investigations, confinement of the catalyst in the mesoporous solid improved the activity compared to attachment to amorphous or non-porous silica, either due to enhanced selectivity in a sterically homogeneous environment or due to higher catalyst turnover brought about by stabilization of the catalyst within the channels. In other instances the performance of the mesoporous catalyst was worse than for a catalyst attached to a non-po-

rous support, due to limited accessibility of the active sites in the mesopores. In the latter studies, the pores were typically smaller than 4.0 nm, and improved performance would be expected with larger mesoporous hosts. For example, in an enantioselective reaction (asymmetric diethylzinc addition to benzaldehyde), using a proline-derived ligand attached to the surface of MCM-41 or SBA-15, the best performance was observed with SBA-15, which had larger pores (8.4 nm) than MCM-41 (2.3 nm), although both materials exhibited significantly better performance than functionalized amorphous silica.[113] Other advantages exist; for example, mesoporous silicates with highly acidic surface groups are relatively safe to handle, since most of the acidic groups are confined within the channels.

## 4.2. Environmental Applications

Several environmental issues are being addressed, employing hybrid mesoporous materials either for the generation of desired products without formation of waste, or for waste clean-up, including sorption of toxic heavy metal cations and anions, radionuclides, and organic solvents.[85,99] The characteristics of suitable mesoporous sieves for environmental remediation include their high adsorption capacity and specificity for certain contaminants.

### 4.2.1. Heavy Metal (Cation) Removal

Mesoporous sieves of interest for the removal of toxic heavy metals, such as mercury, cadmium, and lead, are based mostly on mesoporous silicates functionalized with mercaptopropyl surface groups. The thiol functionalities, which exhibit a high affinity for these metals (Fig. 7), have been incorporated either by grafting or by co-condensation techniques. Much of the development has been carried out by the groups of Liu, Pinnavaia, and Mercier.

Feng et al. attached MPTMS to large-pore MCM-41 by a wet coating technique, achieving a relative surface coverage
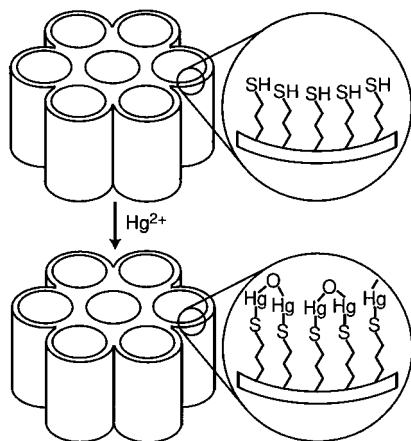


Fig. 7. Heavy metal adsorption by thiol-functionalized mesoporous silicates. Adapted from [30].

up to 76 %.[30] A distribution coefficient for $Hg^{2+}$, $K_d$ (defined as the mass of adsorbed metal [μg] per gram of adsorbing material, divided by the concentration of metal [μg/mL] remaining in the processed effluent), up to $3.4 \times 10^5$ was obtained, with the mercury uptake exceeding 5.2 mmol per gram of silica. Later, $K_d$ values up to $10^8$ for $Hg^{2+}$ were reported.[29] Adsorbed $Hg^{2+}$ could be subsequently removed by washing with concentrated HCl, although the loading capacity of regenerated sorbents was less than half of its original value. It was possible to vary the population density of surface functional groups by controlled hydration of the grafting mixture with enough water to wet the silica surface with 2–2.5 monolayers of water.[29] By extended X-ray absorption fine structure (EXAFS) and NMR spectroscopies it was determined that at low surface coverages (25 %), the channel surfaces were covered mostly with terminal groups connected to single neighboring siloxane groups, although a significant number of crosslinked groups bound to two neighboring siloxanes and some isolated groups were also observed. As the surface coverage was increased (76 %), more surface groups had nearest neighbors and extended approximately at right angles with respect to the channel surface. Mercury atoms adsorbed to the thiolated surface were connected by oxygen bridges between adjacent sites. The materials exhibited fast mercury binding kinetics and high selectivity, outperforming existing commercial resins for mercury removal.[119] These materials could selectively remove mercury from different types of waste streams, including water, oil, acidic, neutral, and basic solvents. Effective removal of $Pb^{2+}$, $Ag^+$, $Cd^{2+}$, and $Cu^{2+}$ was also demonstrated, even in the presence of $Ba^{2+}$, $Zn^{2+}$, $Na^+$, and $NO_3^-$ ions. It was pointed out that trapped mercury should be protected from attack by bacteria, which are much larger than the pore dimensions.

Mercier and Pinnavaia grafted MPTMS onto an HMS support under dry conditions.[120] The product contained one MPTMS molecule per ca. 2.3 surface silanol groups, or 1.5 mmol SH per gram of material, and exhibited an uptake of 1.5 mmol $Hg^{2+}$ per gram of material (i.e., one $Hg^{2+}$ per surface SH). In a comparison between MPTMS-functionalized MCM-41 and HMS,[31] more thiol groups could be attached to the surface of HMS, presumably because removal of the neutral surfactant template from HMS by solvent extraction preserved more surface silanols than high-temperature calcination (650 °C) of MCM-41. The material effectively reduced the mercury level to 5 ppb in a simulated waste stream containing 1.1 ppm $Hg^{2+}$ as well as other ions commonly found in waste streams. The better accessibility of the immobilized metal complexation ligands in the uniform channels, especially in larger pore samples, led to improved performance over similarly functionalized amorphous silicas, clays,[121] and organic polymers (Fig. 8).

Thiol-functionalized HMS supports prepared by co-condensation of TEOS and MPTMS using a neutral amine template were equally effective.[122] $Hg^{2+}$ was selectively adsorbed in the presence of other metal ions ($Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Co^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Ni^{2+}$). This selectivity is remarkable, as thiol ligands can
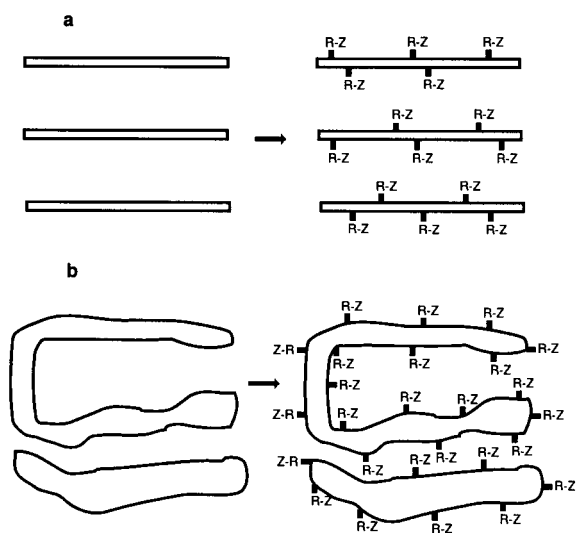
Fig. 8. Comparison of pore accessibilities in functionalized ordered mesoporous silicates (a) and functionalized amorphous supports (b). Adapted from [120].

bind strongly to most of these metal ions. It was tentatively proposed that $d^{10}$ ions other than $Hg^{2+}$ were not strongly adsorbed by thiol groups in the mesopore channels due to their inability to coordinate within the confined spaces. Thiol-derivatized MCM-41 samples prepared by co-condensation were also demonstrated to be efficient adsorbers of mercury ions.[40]

The effective sorption of copper ions on MCM-41 grafted with aminopropyl groups was utilized by Walcarius et al. to preconcentrate and detect trace $Cu^{II}$ in natural water by electrochemical methods.[123] A modified carbon paste electrode prepared with functionalized MCM-41 material exhibited higher sensitivity for copper detection than composite electrodes with analogous amorphous materials, due to the higher number of accessible binding sites in the ordered mesoporous sieve.

### 4.2.2. Anion Removal

Mesoporous silicate supports functionalized with metal-chelated ligands (an ethylenediamine-terminated silane binding to $Cu^{2+}$ ions) were capable of adsorbing up to 1.12 mmol chromate/g or 1.00 mmol arsenate/g.[124] These results are comparable to earlier work by Stein and co-workers involving a purely inorganic mesoporous anion exchange material.[125,126] The hybrid sorbents were effective at removing low concentrations of chromate and arsenate even in the presence of higher sulfate ion concentrations, making the materials useful for remediation of drinking waters.

### 4.2.3. Radionuclide Removal

Mesoporous silicates whose surfaces were derivatized with hydroxypyridonates (HOPO) might be of interest for cleanup of nuclear waste sites to convert high level radioactive waste to low level radioactive waste. These materials act as se-

questering agents for actinides ($Am^{III}$, $Np^V$, $Pu^{IV}$, $Th^{IV}$, $U^{VI}$), showing $K_d$ values for $Am^{III}$ up to $4.5 \times 10^5$.[127] Thiol-MCM-41 has also been examined for uptake of actinides.[127]

### 4.2.4. Sorption of Organics from Aqueous Waste Streams

It is possible to change the wettability of mesoporous silicates by specific surface functionalization. This process can be used to separate liquids of different polarity. Mobil Oil Corp. has patented a sorption separation process using modified MCM-41 for purification of water.[128] Lim and Stein showed in a qualitative way that vinyl-modified MCM-41 exhibited interesting sorption properties (Fig. 9).[49] Because of their hydrophobic surface and small particle size (a few micrometers),
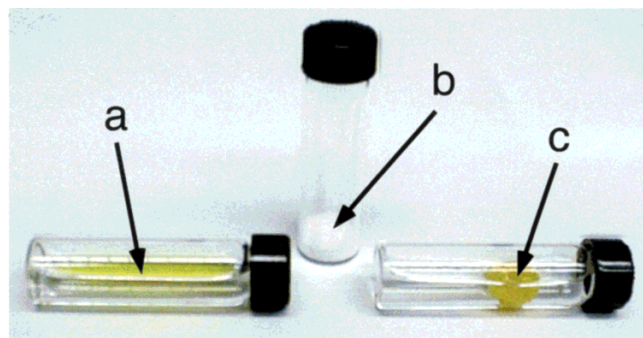


Fig. 9. Illustration of the sorption effect exhibited by vinyl-MCM-41 for toluene. a) Vial containing a water/toluene mixture. The toluene has been dyed with azobenzene for clarity. b) Vial containing vinyl-MCM-41 powder. c) Vial containing the mixture from (a) after it had been shaken with the vinyl-MCM-41 powder (b). The dyed toluene fraction has been soaked up by the hybrid mesoporous sieve. (Photo: courtesy of M. H. Lim and A. Stein.)

vinyl-MCM-41 particles tended to float on the surface of water. However, when the samples were shaken with a mixture of chloroform and water, the solids sank to the bottom of the flask as they absorbed the denser organic solvent. In emulsions of toluene and water, toluene was absorbed by vinyl-MCM-41, and the filled solids tended to form clumps. On the basis of their affinity for non-polar solvents, vinyl-MCM-41 and related materials may be useful for removing small amounts of organic fractions from water or for carrying out "dry" chemical reactions within the channels. Similar observations for UOFMN-1 materials have already been mentioned above.[95]

Zhao and Lu have carried out a systematic study of the sorption properties of silylated MCM-41 to develop selective adsorbents for the removal of volatile organic compounds present in high-humidity gas streams or waste water.[28] MCM-41 modified with trimethylsilyl groups is very hydrophobic, exhibiting a good adsorption capacity for non-polar organic compounds while excluding water in the whole vapor pressure range.

Mann and co-workers quantified benzene and water sorption of phenyl-MCM-41.[129,130] For small pore samples, a type I isotherm was observed with benzene sorption, consistent with the sample's microporosity, while a type V isotherm for water sorption illustrated the hydrophobicity of the sam-

ple due to the influence of the phenyl groups and the low number of surface silanol groups present in the sample. For larger pore samples, obtained by including trimethylbenzene as a swelling agent during the co-condensation reaction, a type IV isotherm resulted from benzene sorption. Corma et al. exploited the increase in hydrophobicity and increased stability of trimethylsilylated Ti-MCM-41 to improve the catalytic activity and selectivity in the epoxidation of olefins.[131]

### 4.3. Optical Applications

Suitably functionalized hybrid mesoporous silicates are promising candidates for optical applications, including lasers, light filters, sensors, solar cells, pigments, optical data storage, photocatalysis, and frequency doubling devices. Stucky and co-workers demonstrated that mesoporous silica fibers can function as optical waveguides.[132] Modification of the mesoporous fibers by incorporation of appropriate dyes would allow tuning of the optical properties. A number of dyes have been integrated in mesoporous solids.[74,77] Schulz-Ekloff and co-workers incorporated a photochromic azo dye or a fluorescent laser dye (sulforhodamine B) in MCM-41 by co-condensation of TEOS with (3-aminopropyl)triethoxysilane coupled to the dye.[133] The reaction was carried out in a microwave oven, reducing the reaction time to 20 min. The dye molecules were anchored to the surface and could not be extracted, either during or after surfactant removal.

Kinski et al. investigated the nonlinear optical properties and polarization of *para*-nitroaniline (*p*-NA) entrapped in MCM-41 via the vapor phase or from alcoholic solution.[134] One-dimensional ordering of guest molecules depended on the sorption procedure, post-treatment, and annealing of the sample. Samples that were freshly loaded with *p*-NA showed no second harmonic generation (SHG). After gas-phase loaded samples were aged in air for several weeks, an increasing SHG signal was observed, indicating polar alignment of *p*-NA molecules within the channels. Coherent domains were disrupted by exposure to water.

Zhou and Honma incorporated photosensitive copper phthalocyanine (CuPc) or the photosynthetic chlorophyll molecule (Chl) in mesoporous silicates as well as mesostructured $V_2O_5$, $WO_3$, or $MoO_3$.[135–140] In some of their experiments a specially functionalized surfactant (11-ferrocenyltrimethylundecylammonium bromide) was used to synthesize hexagonal and lamellar mesostructured silicates with redox-active micelles. The ferrocenyl dye encapsulated in the channel structure provided optical absorptions in the visible wavelength region, corresponding to the oxidized and reduced states of the dye. Air oxidation led to an increase in the intensity ratio of the corresponding states (oxidized/reduced). Other examples of encapsulated dyes involving porphyrins and phthalocyanines are listed below in Section 4.5. Several pyridine, phthalocyanine, phenanthroline, and quinoline complexes in mesoporous solids were mentioned in the recent review by Moller and Bein.[18]

### 4.4. Polymer Syntheses

Mesoporous silicates have been used as hosts or reactors for a variety of polymerization reactions. Although no Si–C bonds are formed in many cases studied, the hybrid intermediates or products exhibit such interesting properties that we chose to highlight them in this review.

Nano-sized conductors encapsulated in mesoporous sieves were studied relatively early in the development of MCM-41. Wu and Bein synthesized conducting filaments of polyaniline in aluminosilicate MCM-41.[141] The channels were loaded with aniline vapor and the material was oxidized with $(NH_4)_2S_2O_8$ in solution. The conductivity of the encapsulated polymer filaments was demonstrated by contactless microwave absorption. The same group also synthesized polyacrylonitrile (PAN) by radical initiation from acrylonitrile adsorbed in MCM-41 channels.[142] Pyrolysis converted the occluded PAN into conducting carbon wires. Tolbert and co-workers incorporated the conjugated semiconducting polymer poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) in the channels of MCM-41.[143] In order to increase the uptake of the polymer by increasing interactions between the polymer and the host, the surface of the mesoporous support was first grafted with phenyldimethylchlorosilane or trimethylchlorosilane. The polymer was then introduced from solution at elevated temperature. It was proposed that each nanopore (free diameter of the functionalized pores: 15–17 Å) could only contain one polymer chain and that the chains were isolated and oriented in the channels. This configuration permitted controlled energy transfer in these composites.[144]

When mesoporous silicates are used as polymerization reactors, the resulting polymer properties are often different from bulk polymers. Llewellyn et al. studied the gas phase polymerization of vinyl acetate, styrene, and methyl methacrylate within MCM-41 and noted several confinement effects, including an increase in chain length of poly(methylmethacrylate) (PMMA) with decreasing pore size due to less facile termination processes. The glass transition temperature ($T_g$) of poly(vinyl alcohol) (PVA) was higher than in the bulk but decreased for smaller mesopore size.[145] Aida and co-workers observed that MMA polymerization in MCM-41 leads to a larger molecular weight of PMMA than in the bulk.[146] Frisch and Mark noted that $T_g$ of polystyrene polymerized in the channels of hexagonal mesoporous silica was affected by inclusion of the polymer.[147] Bein and co-workers found that after polymerization of MMA via radical initiation in MCM-41 (30 Å pores) and MCM-48 (35 Å pores) the glass transitions normally observed in bulk polymers were suppressed due to strong host–guest interactions.[24,148] The absence of this transition indicated that the long-range motion of the polymer strands was restrained. No bulk polymer was detected on the external mesoporous sieve when the monomers were introduced via the gas phase. With methacrylate groups present on the channel surfaces, PMMA could be directly coupled to the silica walls.[67]

Ozin and co-workers employed the channels of MCM-41 as a mold to form ca. 20 Å thick poly(phenolformaldehyde) fibers with aspect ratios >1000.[149] Aida and co-workers provided an exciting demonstration of extrusion polymerization by a nanofabrication process (Fig. 10).[150] They modified the channels (27 Å diameters) of mesoporous silica fibers[132] with
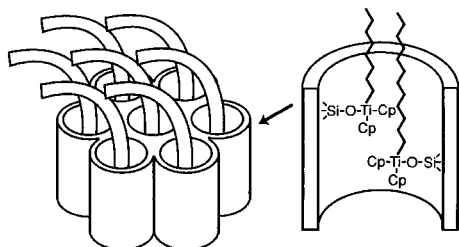


Fig. 10. Extrusion polymerization in mesoporous silica fibers. Adapted from [150].

titanocene and used these materials as nanoscopic reactors to grow linear polyethylene fibers.[150] Methylalumoxane was employed as a cocatalyst. The polymerization product consisted of crystalline fibers with high molecular weights (6 200 000) and diameters between 30 and 50 nm. The authors proposed that polymer chains formed inside the mesopores at the activated titanocene sites and were then extruded into the solvent phase where they grew into longer crystalline fibers. It is likely that confinement within the mesopores prevented the polymer chains from folding. These types of crystalline fibers were not obtained with similarly functionalized amorphous silica supports under corresponding reaction conditions.

Tudor and O'Hare grafted MCM-41 with *rac*-ethenebis(indenyl)zirconium dichloride and used this material to carry out a stereospecific propene polymerization.[115] In comparison with a homogeneous system and with a layered clay system, the activity was lowest in MCM-41 due to diffusion-limited access to the metal centers deeper within the channels, but the isotacticity of the polypropene and its melting point were high in the MCM-41 system. The product morphology was also influenced by confinement in the mesoporous sieve. The same group functionalized the walls of calcined MCM-41 and FSM-16 with ferrocenyl end groups by a ring-opening reaction of strained metallocenophanes, such as $[Fe(\eta-C_5R_4)_2SiMe_2]$ (R = H or Me), in a pentane solution.[151,152] This organometallic guest remained intact within the mesopores, where it was attached to the surface via Si–O linkages. Both single ferrocenyl and short-chain oligo(ferrocenyl) units were present in the products. The ferrocenyl groups in these materials remained redox active and oxidized in air to ferrocenium species. Ozin, Manners, and co-workers carried out a thermal in-situ ring-opening polymerization of a silaferrocenophane inside the channels of MCM-41.[153] The polymerization products remained predominantly inside the pores.

### 4.5. Fixation of Biologically Active Species

The mesopores in M41S, HMS, SBA, and related structures are sufficiently large to incorporate molecules with biological activity. Díaz and Balkus immobilized globular enzymes, cytochrome c (a heme protein), papian, and trypsin (both proteases) in MCM-41 by physical adsorption and then entrapped them within a "fence" of adjacent 3-aminopropyltriethoxysilane groups that were attached to accessible surface silanols.[154] Entrapment of trypsin enhanced its stability by isolating individual enzymes from each other, and minimized leaching of this protease from the mesoporous support. The entrapped trypsin enzyme exhibited some activity in the hydrolysis of $N$-$\alpha$-benzoyl-DL-arginine-4-nitroanilide, although it was less active than expected for the loading.

Holland et al. incorporated a water-soluble porphyrin *meso*-tetrakis(5-trimethylammoniopentyl)porphyrin (TMAP)) in MCM-41 directly during a hydrothermal synthesis or by a surfactant ↔ porphyrin ion-exchange reaction with as-synthesized MCM-41.[107] Both methods permitted encapsulation of the porphyrin within the mesoporous channel system. Even after extraction of the surfactant, TMAP remained in the structure. UV-vis absorption spectra indicated that the porphyrin molecules remained isolated in the channels of hydrothermally prepared samples, producing spectra closely resembling those of solution species. Acid extraction of the surfactant converted the encapsulated free-base porphyrin to the dication TMAP-$H_2^{2+}$, which could be further metallated with $Cu^{2+}$, $Ni^{2+}$, or $Fe^{2+}$ without leaching porphyrin from the mesoporous sieve. The copper-loaded porphyrin was stabilized by the support in an oxidative bleaching reaction of an azo dye. Isolation of the porphyrin molecules within the MCM-41 channels prevented their mutual oxidation. In contrast, during a solution-phase oxidation reaction, mutual oxidation of nonsupported porphyrin molecules resulted in their decomposition.

Porphyrin molecules were also incorporated in the mesopores of FSM-16 by sublimation in an evacuated sealed glass tube at 350–500 °C.[155] The porphyrin/FSM-16 complex exhibited enhanced oxygen adsorption capabilities, but the oxygen could be desorbed by UV irradiation. In an even more complex system, metalloporphyrins and fullerene were both encapsulated in FSM-16 by sublimation.[156] While neither the FSM-16 support nor a powder of the metalloporphyrin exhibited any significant oxygen uptake, the entrapped porphyrins acted as effective, reversible oxygen carriers. Encapsulation kept the porphyrins isolated and prevented formation of a $\mu$-oxo-dimer.

Kevan and co-workers trapped manganese 2,2′-bipyridine complex cations in silicate and aluminosilicate MCM-41 by incipient-wetness impregnation or by ion exchange.[157] The maximum loading of the complex was greater in the aluminosilicate mesoporous sieves with higher framework aluminum content. It was possible to cycle the encapsulated manganese complexes between $Mn^{2+}$ and $Mn^{4+}$ oxidation states, a transformation that does not occur in solution.

In a series of papers, Schulz-Ekloff and co-workers studied complex mesoporous structures involving zinc phthalocyanine (ZnPc) complexes or rhodamine B as guest molecules.[158–160] These guests were encapsulated during the hydrothermal syn-

thesis of Ti-MCM-41 or by impregnation of the calcined mesoporous support, in order to bring titania and dye molecules close enough to each other that photoinduced charge transfer could occur.[159,160] When the guests were introduced by the hydrothermal route, monomeric ZnPc was embedded in the micelles, whereas rhodamine B was exclusively located outside the micelles or aggregated at the external surface. Monomeric ZnPc was also found after impregnating Ti-MCM-41 samples that contained well-dispersed monomolecular $TiO_x$ centers at the surface of the channels. However, aggregation occurred in samples with titanium located in the pore walls. As anticipated, the close contacts between titanium oxide centers (electron acceptor) and ZnPc (electron donor) permitted electron transfer and quenching of the dye fluorescence. To examine possible leaching of guest molecules, Ganschow et al. incorporated substituted ZnPc complexes with negative, positive, or no charge in the mesopores of MCM-41 during the hydrothermal synthesis.[158] The phthalocyanines could not be extracted with water, although the negatively charged and neutral phthalocyanines were extractable with ethanol.

## 5. Conclusion and Future Opportunities

During the last decade much progress has been made in controlling the architecture of porous inorganic solids by using organic molecules or molecular aggregates as structure directors, space fillers, or templates. Functional porous nanostructures can now be designed with a high degree of complexity by combining processes from a number of fields, including sol–gel chemistry, zeolite chemistry, surfactant chemistry, colloid chemistry, and polymer chemistry. Structuring can be carried out on multiple length scales.[161–165] For example, co-condensation methods combined with colloidal crystal templating have been applied to produce organically functionalized silicates with pore sizes of a few hundred nanometers.[166] In the future one can expect increasingly complex structures that combine hierarchical pore sizes with multiple organic or inorganic functional groups that are strategically placed on the internal or external surfaces and may provide synergistic influences on bulk properties and host–guest interactions. Surface functionalization will make it easier to interface the mesoporous sieves with substrates that may be necessary in device applications (e.g., silicon substrates in the electronics industry).

Morphological properties will also be addressed in similar ways as they have been tackled for pure silica mesoporous solids. In typical syntheses of M41S type materials, fine powders with particle sizes between 0.05 and 2 μm are obtained.[2,167] Several procedures have been developed to control the product morphology and to produce larger uniform particles for chromatographic packing materials, shaped particles, fibers, and films for membranes or sensor applications.[75,132,168–189] With few exceptions these syntheses involve acidic conditions (<pH 2, the isoelectric point of silica) where interfacial inter-

actions are weaker and the product structure is more closely related to the structure of the pure organic phase. Many of these techniques can probably be adapted to analogous co-condensation reactions, or else, the shaped mesoporous products can be functionalized with organic groups after their synthesis. Introduction of organic moieties within the silicate framework may increase the flexibility of mesoporous films and fibers and reduce the brittleness of monoliths.

The flexibility in choosing organic, inorganic, or hybrid building blocks and combinations of templates allows one to control the material's properties and to optimize them for each desired application. In the next few years one can expect new developments, not only in the nanometer architecture of porous materials, but also in the design of macroscopic shape, morphology, and interfaces with other materials. As the surfaces in the mesoporous solids become more complex, it will be increasingly important to understand the interactions of confined guest molecules with the functionalized host. Issues that will need to be addressed include the transport of guest molecules in the hybrid mesoporous solids, stabilization effects of the host on the guest (and vice versa), and the influence on sorption properties. One can be confident that new surprises in materials properties will emerge and that the excitement of the field will continue in the upcoming years.

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