Writing on the Wall with a New Synthetic Quill

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Abstract: A new class of periodic mesoporous organosilicas (PMOs) with organic groups incorporated inside the channel walls of the material is discussed. In particular, the unique properties and chemistry exhibited by periodic mesoporous methylenesilica, an isoelectronic analogue of periodic mesoporous silica, are highlighted. Finally, some of the advances made in our group and others, as well as future directions that we envision in the field are described.

Keywords: mesoporosity · methylene · organic–inorganic hybrid nanocomposites · solid-state chemistry · supramolecular chemistry

Introduction

In 1992, the discovery of a self-assembly synthetic pathway to periodic mesoporous silica, called Mobil Composition of Matter 41 (MCM-41), was recognized as a significant intellectual breakthrough in materials synthesis.[1, 2] For the first time, siliceous materials with hexagonal close-packed arrangements of single-size channels with tunable diameters over the 2–10 nm mesoscopic size range were available through surfactant-templated hydrolytic polycondensation of silicate precursors, such as $Si(OEt)_4$. Since then, a periodic table of inorganic compositions have been incorporated into the structure of mesoporous materials, including metals, metal oxides, metal chalcogenides, and metal phosphates. As a consequence of their uniform arrangement of mesopores and narrow mesopore size distributions, these materials are attractive for applications in chromatography, host–guest chemistry, and catalysis.

While inorganics alone may be suitable for some applications, researchers quickly realized that the properties of the mesoporous materials could be modified by including organic groups in the channel spaces.[3] These first appeared as terminal organic groups "dangling" inside the voids of the channels by either incorporating organosiloxane precursors such as $RSi(OEt)_3$ in the preparation, or by grafting the organic group onto the walls of the inorganic channels in a post-synthesis route.[4, 5] This has created materials with many interesting properties; for example, mesoporous silica with terminal alkanethiol $SiCH_2CH_2CH_2SH$ groups inside the channel space has a large surface area for removing lead, mercury, and other heavy metal contaminants from the environment—effectively a high surface-area "sponge" for toxic metal pollutants.

Although a large number of organic groups may be grafted into the mesoporous silica, they suffer from many difficulties inherent with the preparations.[4a,c] First, they lead to an inhomogeneous distribution of organic groups in the mesoporous materials, often located in the vicinity of the pore opening. Second, if the organic groups are incorporated in the initial synthesis, there is a limit of about 25 % organic groups [$RSiO_3$] before the material loses its long-range order and structurally collapses. Third, the organic groups are housed within the pore space, occupying the channel volume in the mesoporous material.

Discontinuity

It is clear that the combination of organics and inorganics inside well-ordered hybrid mesostructures will lead to new materials with novel properties and functions, and potentially important applications. Last year, our group and two others independently reported a brand new class of organic–inorganic hybrid materials, which we dubbed "periodic mesoporous organosilicas" (PMOs).[6–9] Also formed by a surfactant-templated mechanism, these nanocomposites had a structure based upon periodic arrays of hexagonal close-packed channels akin to MCM-41, but for the first time contained organic groups as an integral part of the structure. In essence, MCM-41 is the pure silica "end-member" of a whole new world of periodic mesoporous organosilica materials. While MCM-41 has a nondescript silica channel wall with limited function and utility, the bridging organics inside the channel wall of periodic mesoporous organosilicas offer a diversity of function and potential uses. The PMOs can be prepared with a wide variety of organic and organometallic groups, R, by the surfactant-templated hydrolytic polycondensation of $(R'O)_3Si{-}R{-}Si(OR')_3$ precursors (see Scheme 1). So far,

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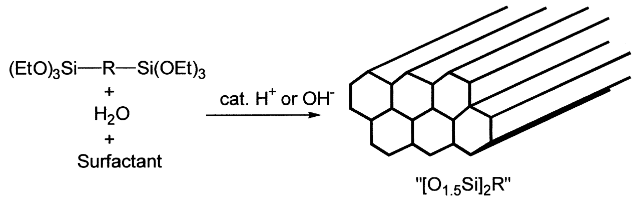
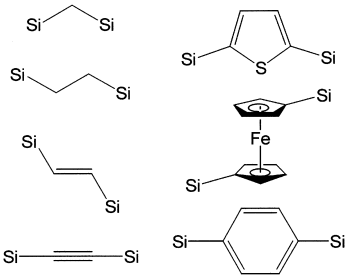


Scheme 1. General synthetic route to periodic mesoporous organosilicas.

ethane, ethylene, methylene, ferrocene, thiophene, acetylene, and phenylene (Scheme 2) have been incorporated into the PMOs to give structurally well-ordered materials. In the case of ethylene spacers, the alkenes situated inside the channel wall are accessible for chemistry, such as bromination.[6, 8] Details of the self-assembly synthesis, structure, and properties of these PMOs can be found in the original papers; only an overview of these materials will be presented in the following paragraphs.[6–9]



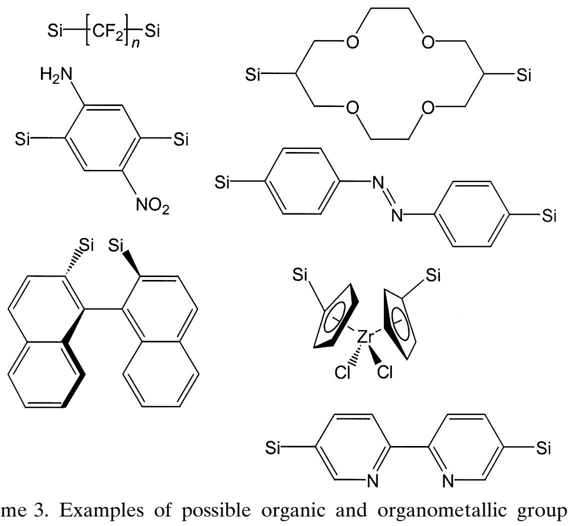
Scheme 2. Examples of organic and organometallic bridging groups that have been incorporated into PMOs.

Like MCM-41, the mesopores in these materials are very well organized in hexagonal symmetry arrays. They are stable to surfactant removal and display surface areas and pore volumes that are similar to siliceous MCM-41. Moreover, we have shown that the composition can be continuously tuned between the pure SiO_2 end-member and $[SiO_2]_m[O_{1.5}Si–R–SiO_{1.5}]_{1-m}$ ($0 \leq m < 1$) for R = ethylene, giving organic groups homogeneously dispersed in the hexagonal mesoporous silica matrix.[6]

What is so special about these new materials is that organic functionality has been integrated "*inside*" the channel walls of a silica-based material, which exhibits crystalline mesoporosity. The incorporation of "*bridge-bonded*" organic groups within the walls of periodic mesoporous silica is considered a breakthrough for several reasons:

- It allows the composition, hydrophobicity – hydrophilicity, and chemical properties of the mesoporous host to be tuned using chemistry.
- There is potential to chemically change the mesoporous material to modify the physical and mechanical properties of the host.
- The functional groups do not hinder space inside of the channels, as do terminally grafted organic groups.
- It permits a greater fraction (100%) of organosilicate sites [$RSiO_3$] to be placed inside the framework of the material than other routes, which put organic groups within the channel spaces and are restricted to about 25% before all order is lost.
- It ensures a homogeneous distribution of organic groups inside the channel walls of the materials.

Having reactive organic groups integrated "*within*" the wall of periodic mesoporous silica, rather than simply "*hanging*" in the channel, may be advantageous for many applications. For example, chemical reaction with the organic groups in the wall could result in changes in the dimensional, mechanical, chemical, and physical properties of the materials. Detection of the changes (by methods such as diffraction, electrical conduction, or fluorescence) could constitute the basis of new chemical sensors. Chiral organics inside the walls could enable molecular recognition in a size tunable channel space and permit new kinds of enantioselective separations and asymmetric syntheses. Redox active organics within the walls may lead to electrically tunable molecular filters or vehicles for the controlled delivery of chemicals. Photoisomerizable organics within the walls could lead to smart channels that change their diameter reversibly when irradiated with light of the right wavelength. Metallocene polymerization catalysts housed in the channel walls may provide a route to oriented polymer fibers in what is effectively a nanoextrusion process.[10] Modified crown ethers inside the wall may be very effective for removing alkali metals from solutions. Organic groups with acidic functionality may facilitate fast proton conduction along the channel walls and new proton-conducting mesostructured membranes for use in hydrogen/methanol-oxygen fuel cells. Coordinating ligands, such as bipyridine, may be inserted into the structure to generate mesoporous materials with "*channel ligands*" that strongly bind transition metals. Some of these examples are illustrated in Scheme 3. Clearly, many opportunities abound for PMOs with appropriately designed functional organics "*inside*" the framework.



Scheme 3. Examples of possible organic and organometallic groups to incorporate into PMOs.

Moreover, there are additional advantages that may arise from the incorporation of organics into the "*backbone*" of the material. Due to the flexibility of many organic spacers, monoliths may be less prone to cracking, a problem that has plagued research into monoliths of mesoporous silica. Amorphous organic polymer/inorganic oxide hybrid materials have shown rubberlike elasticity, which suggests that the incorporation of organic groups into the walls of mesostructured silica may impart similar mechanical properties.[11] This flexibility may also be advantageous to film formation and, as Ianagaki et al. have noted,[7] to achieving excellent structural order in the resulting mesostructured material. Additionally, the toughness, hardness, and density of the bulk mesoporous organosilica may be tuned by changing the organic groups present in the framework. This provides a route to lightweight, mechanically tailorable mesoporous materials.

To put the work on PMO materials into context, it is useful to contrast them with prior reports of organosilica composites.[12] They are considered to be distinct from organosilica-based xerogels, which are amorphous materials containing a random array of broadly distributed pore sizes. While xerogels have attracted attention for potential application in catalysis, their lack of size and shape selectivity has limited their use in this regard. Although xerogels have incorporated organic groups since their conception,[13, 14] there are few reports of periodic mesoporous silica hybrid materials containing a terminally bound organic moiety located in the channel space[4, 5] and, before last year,[6–9] none for a bridge-bound organic moiety as an integral part of the inorganic structure. By analogy with polymer science, our synthetic strategy puts organic and organometallic species into the "*backbone*" of the framework where they can have a more dramatic effect on structure–property relations than do grafted or "*sidechain*" groups.

As the PMOs can be prepared with a variety of organic and organometallic spacers, it is expected that mesoporous organosilica materials with interesting electronic, optical, mechanical, catalytic, and chromatographic properties will emerge from this research. Furthermore, PMOs with mixed organic functional groups and/or terminally bound functional groups may give rise to multifunctional mesoporous materials.

Periodic Mesoporous Methylenesilica

Recently, we described the simplest PMO, periodic mesoporous methylenesilica, with CH_2 spacers incorporated inside the structure (Figure 1).[15] Although the material is deceptively simple, it has generated some unique chemistry that may lead to new ways of thinking about materials synthesis and new applications possibilities.

Periodic mesoporous methylenesilica was prepared by the base-catalyzed hydrolytic polycondensation of $(EtO)_3SiCH_2Si(OEt)_3$ in the presence of a surfactant template. After surfactant removal, the materials contain a well-defined hexagonal array of channels (Figure 1), surrounded by methylenesilica, an isoelectronic analogue to SiO_2. It is intriguing to consider the effect of replacing oxide by methylene in a silica-based mesostructure. Not only is this the simplest substitution imaginable, but also the restricted tetrahedral angle of the latter compared with the flexible angle of 90–180° of Si-O-Si may affect structure–reactivity relations.

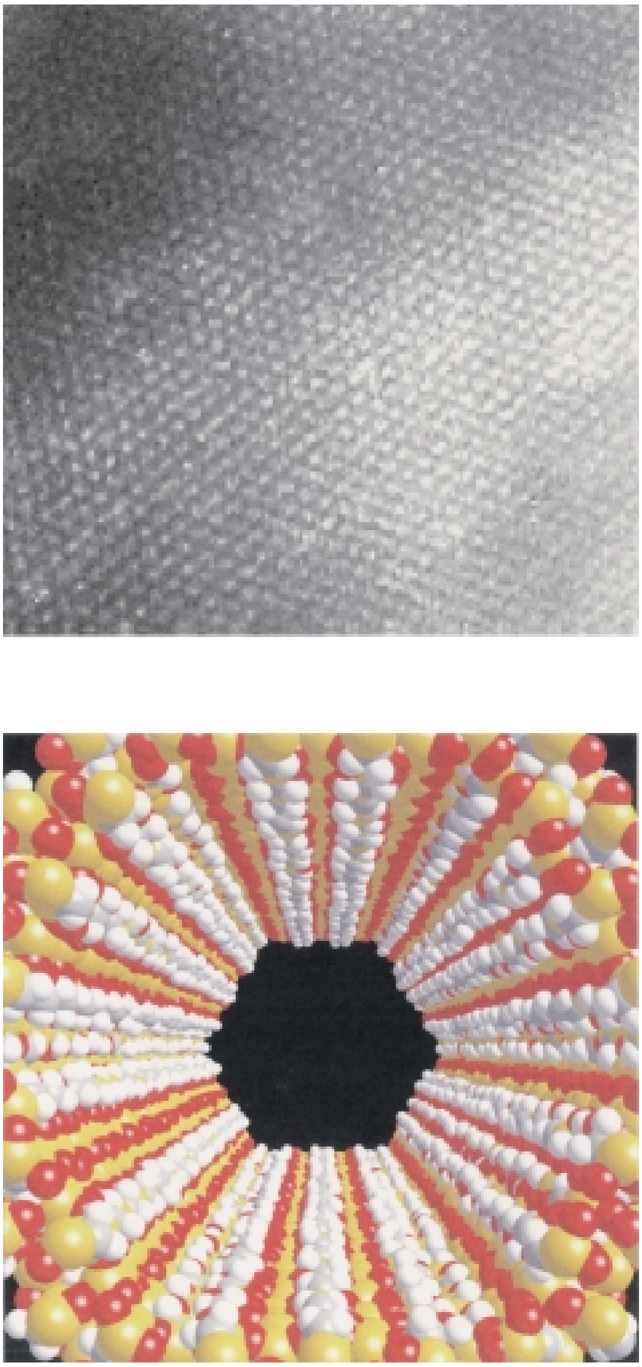
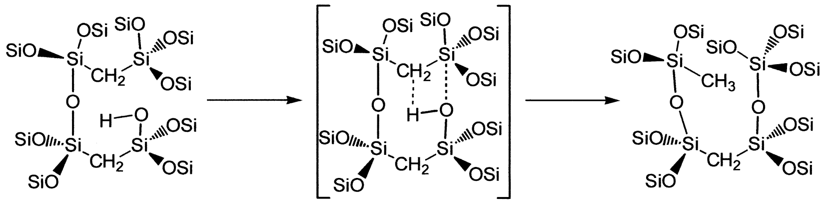


Figure 1. Top: Transmission electron micrograph of a sample of mesoporous methylenesilica shows the highly ordered structure of the material. Bottom: Graphical illustration shows an ideal representation of a single channel of hexagonal mesoporous methylenesilica, in which bridge-bonded methylene groups and isoelectronic oxygen atoms respectively occupy alternating $O_3Si\text{-}\mathbf{CH_2}\text{-}SiO_3$ and $O_3Si\text{-}\mathbf{O}\text{-}SiO_3$ sites "*inside*" the channel walls of the structure. The color of the graphical image is red: silicon, yellow: oxygen, gray: carbon of bridge-bonded methylene, white: hydrogens of bridge-bonded methylene. Disorder has been built into the channel wall to represent the glassy microstructure that has been established by diffraction, microscopy, and polarization micro-Raman spectroscopy studies of the material.

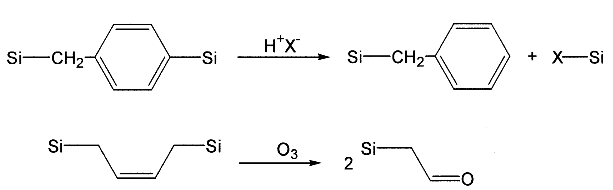
Surprisingly, the mesostructure of the material is thermally stable to over 900 °C! Although complete elimination of methylene groups is observed by about 700 °C, the periodic mesoporous methylenesilica heals to form periodic mesoporous silica, with smaller diameter channels. By incorporating larger organic spacers in the PMO, controlled thermal treatment may lead to materials with channel diameters smaller than those accessible with a liquid crystalline template. Significantly, it may be possible to *span the scientifically and technologically relevant microporous-mesoporous two nanometer size regime* by using this synthetic strategy. Designer "*pore-shrinking*" of this type could provide a new class of silicas with hexagonal close-packed channels in the challenging size range between zeolites and mesoporous materials that may be useful in diverse application areas from chromatography to catalysis.

The elimination of methylene groups from periodic mesoporous methylenesilica was monitored during thermal post-treatment to identify the mode of transformation of the bridging organic group inside the silica channel wall. Using a combination of techniques, we unequivocally identified a "*bridging-methylene to terminal-methyl*" transformation that occurred "*inside*" the channel walls of the mesoporous material. This is a new type of "*chemistry of the channels*" and is considered distinct to the bromination of ethylene groups housed inside the channel walls of periodic mesoporous ethenesilica. As the periodic mesoporous methylenesilica is heated at 350–600 °C, the bridging methylene groups transform to terminal methyl groups by O–H addition to a bridging Si–CH_2 bond, as indicated in Scheme 4. It is worth noting that similar chemistry has been observed in poly(dialkoxysilylenemethylene), $[(RO)_2SiCH_2]_n$, a polymeric analogue of the methylenesilica PMO.[16] Upon hydrolysis and thermal treatment, Si–O/Si–C scrambling results in methyl sidegroups formed from the methylene groups initially in the backbone of the polymer.



Scheme 4. The thermolysis of the channel walls of periodic mesoporous methylenesilica leads to terminal methyl groups.

In essence, the organosilica channels of the as-synthesized methylene PMO undergo *metamorphosis* from one structure to another while maintaining the integrity of the mesostructure intact. This provides a new route to periodic mesoporous silica materials with a microscopically distinct channel structure and terminal organic groups in the channels rather than in the walls. Since the as-synthesized periodic mesoporous methylenesilica contains a homogeneous distribution of 100% bridging organic groups inside the channel walls and did not collapse during the thermal transformation, it may be possible for the first time to achieve high populations of terminal organic groups (Si–R) without loss of mesostructural order. This lies in contrast to typical syntheses of periodic mesoporous silica materials with terminally bound organic groups, from $(EtO)_3SiR$ precursors, which give a maximum of 25% terminal groups before loss of mesostructural order and structural collapse.[4a,c] By choosing unsymmetric organic spacers in which one Si–R bond is more likely to cleave, it may be possible to readily form a mesoporous silica material with 50% terminal groups. Thus, treatment of a PMO prepared from $(EtO)_3Si-CH_2C_6H_4-Si(OEt)_3$ under mild acidic conditions is expected to generate a mesoporous silica material with terminal $Si-CH_2C_6H_5$ groups, since Si–aryl bonds are more readily cleaved than Si–alkyl bonds under acidic conditions. Alternatively, with bridging organic groups that can be cleaved in the middle, it may be possible to create mesoporous materials with 100% terminal functional organic groups. For example, channel wall ozonolysis of a PMO formed from $(EtO)_3Si-CH_2CH{=}CHCH_2-Si(OEt)_3$ may give a material with 100% terminal acetaldehyde groups available for further chemistry (see Scheme 5).



Scheme 5. Potential routes to selectively convert bridging organic groups into terminal organic groups in the PMO.

The incorporation of organic molecules in the channel walls also conjures challenging and fundamentally interesting questions not relevant to the pure inorganic materials. For example, how are the organic groups organized in the channel wall and can $(EtO)_3SiR-Si(OEt)_3$ precursors be chosen that spontaneously organize amongst themselves as well as with the surfactant micellar template, effectively a "double co-assembly" process? How do the difference in the restricted bond angles present in organic molecules change the structural and mechanical properties of periodic mesoporous silica, in which Si-O-Si angles can vary between 90–180°? How do the properties of the channels and the overall structure vary between geometric isomers of the organic component? How might chiral bridging groups influence the environment inside the channel? How does the reactivity of functional organic groups in the PMO differ from those in molecular species? Is there electronic communication through the channel walls of PMOs with electroactive bridging groups? Is it possible to create reactive intermediates from the channel wall that undergo reaction in a confined space?

Seeing the Writing on the Wall

It will be interesting to watch as this new area of solid-state chemistry, which fuses the strength of organic synthesis with the power of solid-state materials chemistry, unfolds in the future. The synthetic strategy enables access to a wide range of organic functionality "*inside*" the channel walls of a periodic mesoporous silica, which is likely to lead to the development of "*smart channels*" with "*intelligent*" functions and utility. As the properties of PMO materials can be modified by incorporating a broad spectrum of organic and organometallic moieties within the channel wall, new materials with potential applications in non-linear optics, chemical sensing, electro-and photocatalysis, chemical delivery, filtration, and chromatography may arise. There are at least nine evident key areas that should be pursued in order to expand upon and enrich what we currently know about PMOs:

- Expanding the synthetic approach to elemental compositions beyond organosilicas. As an example, semiconducting mesoporous organotin sulfides could arise from the condensation of $(EtO)_3SnRSn(OEt)_3$ precursors with sulfide-based reagents.
- Exploring new templates, such as cubic lyotropic phases, block copolymers, and colloidal crystals, to expand the size regimes and phases of PMOs. Inagaki et al. have prepared PMOs with 3-D hexagonal symmetry, a phase rarely observed in mesoporous silicas.[7] Stein et al. have reported PMOs with wormhole structures.[8]
- Creating PMOs with new bridging organic groups, such as those illustrated in Scheme 3.
- Determining the spatial distribution of bridging organics inside the channel walls of PMOs.
- Search for PMOs with organized arrays of bridging organics inside the channel walls.
- Establishing the effect of head group dimensions of surfactant or tri-block copolymer templates on the size of bridging organic groups that can be successfully assembled into a PMO before loss of periodicity and collapse of the mesostructure to an organosilica glass or xerogel.
- Morphology control of PMOs as fibers, films, spheres, monoliths, and patterns.
- Measuring the mechanical and physical properties of the PMOs as a function of their organic component.
- Further investigations of the reactivity, chemistry, thermal stability, and transformations of PMO materials.

Periodic mesoporous organosilicas with bridging organic groups inside the channel walls open a new area of chemistry with research opportunities for organic, inorganic, and materials chemists alike.

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