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There has been a growing interest in the extension of the microporous molecular sieve synthesis and applications to mesoscopic dimensions. Typical areas for the application of mesoscopic zeolite-type structures are in separation (e.g., protein separation and selective adsorption of large organic molecules from waste waters) and catalysis (e.g., processing of tar sand and of the high distillates of crude oils to valuable low-boiling products). Another is in the supramolecular assembly of molecular arrays and polymers for electronic and optical applications. In a new concept in the synthesis of porous material the templating agent is no longer a single, solvated, organic molecule or metal ion, but rather a self-assembled molecular array. This template leads to mesoporous materials with adjustable pore sizes between 16 and > 100 Å, covering well the mesoporous range of greatest interest. The periodic arrangement of pores is very regular, and the pore size distribution measured by absorption is nearly as sharp as that of conventional zeolites.

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## Ordered Molecular Arrays as Templates: A New Approach to Synthesis of Mesoporous Materials

By Peter Behrens\* and Galen D. Stucky

During the past decade, physicists have discovered a new world in mesoscopic systems, in which classical models collide with quantum effects. It is a world in which electronic transport becomes a coherent process and any change in phase leads to a macroscopic change in conductance. Similarly, small changes in atomic structure or externally applied electromagnetic fields can cause large changes in absorption edges, polarization, optical transparency, and general nonlinear response. Using electrooptic interconnects in this dimension offers the possibilities of decreasing processing times in optical computers, increasing our capabilities to manipulate and store visual images, and a host of other potential applications.

The physicist's and engineer's approach to the mesoscopic world<sup>(1)</sup> has been by way of molecular beam (MBE) and atomic layer epitaxy on substrate with an ordered two-dimensional lattice to fabricate ultra-thin (monolayer) semiconductor epitaxial layers. Quantum wires in which carriers and electronic wave functions have only one degree of freedom can be formed in the MBE approach by corrugation of quantum layers or by lateral structuring, but are still a challenge in the field of materials below diameters of about 100 Å.

The chemist's interest in the mesoscopic world has been equally intense, based on a long-held recognition that ultimately all materials and living organisms have their origins in the collective assembly of a small number of atoms or molecules. Whether it be the beginning of life, crystallization, or the natural formation of a complicated biological nanocomposite like a sea shell, the inherent future properties such as shape, mechanical strength, color, conductivity, etc. of an extended structure are established very early as the molecules or atoms assemble and make the critical transition from few units with nanoscale dimensions to mesoscopic arrays. It is at this metamorphosis that macroscopic collective properties are defined and have their birth.

Two chemical approaches to the micro- and mesophase manipulation of atoms and molecules have been most extensively used. The first, in which considerable progress has been made, is the assembly of microcluster atomic arrays. Examples include small chunks of metal<sup>(2a)</sup> that are solubilized and protected by a coating of ligands, such as  $[\text{HNi}_3\text{Pt}_6(\text{CO})_{44}]^{3-}$ <sup>(2b)</sup> and  $[\text{Au}_{25}(\text{PPh}_3)_{12}]^{6+}$ <sup>(2c)</sup> as well as the use of competitive core cluster growth and surface capping (which terminates the cluster growth) of semiconductor clusters.<sup>(3)</sup> A limitation has been the difficulty to subsequently ordering these clusters into three-dimensional supramolecular lattices.

A second approach has been to use two-dimensional, structure-directing surfaces and three-dimensional porous media for molecular recognition. The chemical growth from solution of superlattice layered structures, giving a periodic array of planes of atoms or molecules with confinement in one dimension (perpendicular to the epitaxial grown layers) has been beautifully developed by the research groups of Malouk, Marks, and Katz for applications such as enantioselective synthesis and nonlinear optical devices.<sup>(4)</sup> The separation of the layers in these nanophase materials is generally less than 20 Å.

Microporous phases with three-dimensional framework

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structures are now routinely synthesized on molecular units or hydrated alkali or alkaline earth cations as templates. Their well-defined pore structures and pore sizes (3 to 13 Å) reflect the template dimensions. Chronologically the development of this microporous synthesis chemistry has evolved from zeolites that possess crystalline aluminosilicate frameworks to pure silicate phases, and more recently to compounds that exhibit similar framework structures but have compositions in which Al and/or Si are substituted by other elements as Be, B, Ga, Ge, Zn, and P. The aluminosilicate and silicate microporous solids have found extensive application in the fields of ion exchange (consider the use of zeolite A as water softener in detergents), desiccation, sorption (e.g., gas separation and purification), and catalysis. Especially for the latter two applications, the geometric restrictions imposed by the porous framework are of importance in differentiating between molecules of different size (size exclusion from intraporous sorption) and, in performing the control over starting materials, transition states, and products of catalytic processes ("shape-selective catalysis").<sup>[9]</sup>

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In the last five years, new applications of the precisely defined void structure of zeolite-type microporous solids have been envisaged. In an approach to "supramolecular architecture"<sup>[6]</sup> and "nanoscale inclusion chemistry"<sup>[7]</sup> based not on molecular ensembles but on extended solid state structures, they serve as a versatile host medium for assembling and maintaining controlled microstructures of quantum dots and wires,<sup>[8]</sup> organic molecules and polymers,<sup>[9]</sup> metal carbonyls and organometallic molecules,<sup>[8a, 8b]</sup> redox systems and electron-transport chains,<sup>[11]</sup> as well as nanosize reaction vessels.<sup>[12a]</sup> This type of host-guest chemistry results in synthetic nanocomposite materials that can be described as "expanded" metals and semiconductors, stabilized arrays of aligned molecules or spatially organized redox systems for which applications in optoelectronics,<sup>[8a, 8b]</sup> nonlinear optics,<sup>[9a, 9b]</sup> optical data storage and image processing<sup>[10a]</sup> (for example by spectral hole burning),<sup>[9c]</sup> and enzyme mimicking<sup>[12b]</sup> are conceivable.

There has been a growing interest in the extension of the microporous molecular sieve synthesis and applications to mesoscopic dimensions. Typical areas for the application of mesoscopic zeolite-type structures are in separation (e.g., protein separation and selective adsorption of large organic molecules from waste waters) and catalysis (e.g., processing of tar sand and of the high distillates of crude oils to valuable low-boiling products). Another is in the supramolecular assembly of molecular arrays and polymers for electronic and optical applications.

Although there have been numerous attempts to carry over the crystallinity and the well-defined pore structure of zeolites to the mesoporous regime, the direct synthesis of three-dimensional mesoporous<sup>[13]</sup> materials containing cages and channels with access pores greater than 13 Å has until now been unsuccessful. Other routes to mesoporous solids such as forming pillars of layered compounds have been investigated.<sup>[14-16]</sup> Although mesoporosity was observed in some of the systems investigated, the pore size distribution was broader than in microporous zeolites.

The usual technique for preparing zeolites is the hydrothermal treatment of aluminosilicate gels or solutions containing metal (alkali or alkali earth) or organic ions (e.g., tetraalkylammonium ions) or molecules (e.g., amines). First progress towards enlarging the pore sizes in zeolite-type compounds was achieved by changing the composition of the gel from

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that of an aluminosilicate. This led to the discovery of the aluminophosphate VPI-5,<sup>(17)</sup> a one-dimensional channel structure with channel diameters of  $\approx 13 \text{ \AA}$ , and of the gallophosphate cloverite,<sup>(18)</sup> featuring a cavity with a diameter of about  $30 \text{ \AA}$  which is accessible, however, only through ~~the~~ apertures, *with effective kinetic diameters which are considerably less than  $13 \text{ \AA}$ .*

The ions and molecules present in the hydrothermally treated gel act as templates during its crystallization; that is, they direct the formation of a specific zeolite framework and are usually occluded in the voids of the crystallizing solids. Even today this template effect is not fully understood. One proposal is that the template molecules change the chemistry of the crystallizing gel. Organic templates, on the other hand, may also act merely as "void fillers", preventing the crystallization of thermodynamically more stable dense phases. One obvious way to zeolites with larger pores is the use of large molecular organic templates, which should give large voids. This approach was, of course, followed by many laboratories but over a long period has not led to a definite claim of a mesoporous structure.

Recently, researches of Mobil Oil Company<sup>(19, 20)</sup> used a new concept in the synthesis of porous material which at long last has led to the first synthesis of mesoporous structures. The templating agent is no longer a single, solvated, organic molecule or metal ion, but rather a self-assembled molecular array. This template leads to mesoporous zeolites with adjustable pore sizes between  $16$  and  $> 100 \text{ \AA}$ , covering well the mesoporous range of greatest interest. These compounds, named MCM-41 (MCM stands for Mobil's Composition of Matter), possess a hexagonal arrangement of parallel channels which can be directly visualized by a transmission electron microscope.<sup>(20)</sup> The arrangement of pores is very regular, and the pore size distribution measured by absorption is nearly as sharp as that of conventional zeolites.<sup>(19, 20)</sup> A structural model of an MCM-41 material is given in Figure 1.

C<sub>3</sub><sup>H<sub>7</sub></sup>

(( Fig. 1 ))

also

Kresge et al.<sup>(20a)</sup> and Beck et al.<sup>(20b)</sup> propose that a liquid crystal templating mechanism is operative in the synthesis of their mesoporous materials. Typically, the templates they use are quaternary ammonium ions  $C_nH_{2n+1}(CH_3)_3N^+$ , which are used as surfactants in detergents. These ions are known to form micelles in aqueous solutions (Fig. 2). In a picture similar to the recently proposed "can-and-cement" model of the crystallization of microporous zeolites,<sup>(21)</sup> these template molecules are assumed to be ordered in the aqueous gel; during crystallization, the silicate or aluminosilicate solution present between the template assemblies becomes the "walls" of the porous solid. Different types of order have been found in surfactant-water liquid crystals, including lamellar, hexagonal, and cubic phases.<sup>(22)</sup> Accordingly, MCM-41 materials, which have a hexagonal arrangement of mesoporous channels are templated by the hexagonal phase. Strong support for the liquid crystal template mechanism comes from the discovery of cubic and layered crystallization products<sup>(20, 23)</sup> that possibly are templated by the lamellar and cubic liquid crystal phases. According to the templating mechanism, the alkyl chain length  $n$  influences the pore size of the MCM-41 material. For example, for  $n = 12, 14$  or  $16$  the pore size is  $30 \text{ \AA}, 34 \text{ \AA},$  and  $38 \text{ \AA}$ , respectively.<sup>(19, 20)</sup> Another way to alter the pore size is the addition of "auxiliary" template molecules ("expanders") such as mesitylene.<sup>(19, 20)</sup> These substance can dissolve into the hydrophobic region of the

(( Fig. 2 ))

surfactant micelles, whereupon the micelle diameter and the pore size increases. This templating chemistry gives the opportunity to produce "tailor-made" mesoporous solids.

Investigations of the crystallization process of microporous zeolite-type compounds have shown that the "best" (i.e., the most strongly structure-directing) templates are rigid organic molecules stiffened by the presence of one or more ring systems. The potential diversity of micellar arrangements is large, since the order in the walls of the new mesoporous materials seems to be less strict than in conventional zeolites. Indeed, the atomic structure of the walls of the mesopores is of particular interest, both to aid understanding the synthesis mechanism and for use after synthesis as a structure-directing scaffolding for the assembly of molecular and atomic nanophases within the pores.<sup>[23]</sup> Tilted-angle electron and X-ray diffraction measurements of Mobil and at the University of California, Santa Barbara (UCSB) show no evidence of long-range ordering along the channel walls; only  $(hk0)$  reflections are observed for the hexagonal MCM-41 materials and no reflections at diffraction angles larger than about  $6^\circ$  for  $2\theta$  ( $\text{Cu}_K\alpha$  radiation) for pore sizes greater than  $30 \text{ \AA}$ . The best fit to the experimental X-ray diffraction data of MCM-41 is obtained with a continuous scattering model which assumes that the wall structure does not have long-range order. For the hexagonal mesoporous phase the results indicate that the channels are hexagonal (rather than cylindrical) and that the wall thickness is  $8 \pm 1.0 \text{ \AA}$ . The wall thickness appears to be relatively constant with increasing pore size to  $\approx 100 \text{ \AA}$ . The structural model shown in Figure 1 is based on these results.<sup>[24]</sup>

Solid state NMR results confirm the disorder in the framework. The hydroxyl group concentrations and  $^{29}\text{Si}$  NMR chemical shifts depend strongly on the procedure used to remove the template. After calcination at  $550^\circ\text{C}$  only one type of hydroxyl group is found at a concentration of approximately 1 for every 10 silicon atoms. These hydroxyl groups can be readily functionalized with  $(\text{CH}_3)_3\text{SiCl}$  (Mobil and UCSB) and by various other organometallics, including  $(\text{CH}_3)_2\text{GeCl}$ ,  $(\text{CH}_3)_2\text{Ga}$ ,  $(\text{CH}_3)_2\text{Zn}$ , and  $(\text{CH}_3)_2\text{Cd}$  (UCSB). The temperature stability of the pores is also remarkable. The "higher" angle reflections ( $2\theta > 1^\circ$ ), which the X-ray analysis confirms are a measure of pore geometry, vanish upon heating above  $800\text{--}900^\circ\text{C}$ ; however, the (100) scattering which defines the occurrence of pore periodicity can even be observed from samples heated to  $1200^\circ\text{C}$ . Small-angle and long-wavelength neutron diffraction studies at the National Institute of Science and Technology have confirmed the long-range ordering of the pores observed by the X-ray and electron diffraction studies, and along with solution NMR should be particularly useful in elucidating the mechanism of solution templating during synthesis.

Bein and Wu<sup>[25]</sup> from Purdue University have meanwhile reported the successful intrapore polymerization of aniline and thiophene derivatives in MCM-41 materials with an intrapore spacing of  $35 \text{ \AA}$ . Such encapsulated polymers are an important step towards the synthesis of oriented molecular wires (compare ref. [9d]).

There is little doubt that the new mesopore derivatives will make excellent supports with high surface area. Perhaps more importantly, they offer new horizons both in the synthesis of nanophase composites with the MCM-41 and cubic phase mesopores reported by Mobil and suggest exciting possibilities for the synthesis of other mesoporous materials of different compositions and geometries on account of the large number of variations of ordered molecular arrays that are

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available. In particular they provide a fascinating avenue to the chemistry of biomineralization and biogenesis, where nature has very effectively used ordered molecular arrays in templating inorganic phases. This, of course, has important consequences for the use of biomimetic synthetic procedures. In every sense a new solid state chemistry and materials science has been given to the scientific community by the Mobil researchers.

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Fig. 1. Schematic representation of the structure of a MCM-41 phase with an interplate distance of  $\approx 35 \text{ \AA}$ , amorphous wall structure, and hexagonal pores.

Fig. 2. Schematic representation of the exterior surface of a cylindrical micelle. The ends of the micelle cylinder are probably best visualized as hemispherical.



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