

Using the Organic-Inorganic Interface to Define Pore and Macroscale Structure

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Introduction

One of the most fascinating underlying aspects of the biogenesis of materials is the space/time definition of structure¹, function, and morphology at multiple length scales from complex mixtures of reactants and accessible processes. Paradoxically, spatial and kinetic incompatibilities during assembly result in instabilities that make it easy to temporally modify product composition, assembly, and macroscale form. In the same manner, in the synthesis of ordered mesoporous materials, competing spatial sequences in the solvent media as well as the reactants are useful in defining domain separation and ultimately pore structure and morphology in mesoporous phases. In practice this means hydrophobic/hydrophilic, polar/nonpolar, and organic/inorganic interfaces, but it should be emphasized that the differences in property (e.g. hydrophobicity or polarity) need not be large to generate highly structured composite phases with well-defined periodic domain definition.² Competing interactions and assembly processes generally have different entropic and kinetic handles that can be used to orchestrate hierarchical structure and functionality in the composite product. Entropic control of the system processes can be implemented, for example, by the solvent media used in the reaction or by temperature. When weak assembly forces are used, the structural evolution can be directed by external fields or the co-assembly of a competing process.

All this synthesis freedom presents unprecedented opportunities in mesopore structure design but also some formidable synthetic challenges in reproducibly creating processible materials with designed pore and macroscale morphology. The following discussion focuses on two approaches to achieving this goal: (1) the use of competing interactions, which includes the thermodynamics and kinetics of the assembly processes in the microphases and their interfaces; and (2) the use of designed competing spatial regions in the molecular species that have inherent chemical incompatibilities to direct structural organization. The latter can be used both for structure templating and for creating long-range order.

Competing Interactions: The Silica-Organic Interface

The mesostructured materials of interest to this Conference have spatially distinct inorganic and organic regions which at the very least have dimensionally well-defined cross sections, which result in uniform pore sizes. In order for this to be achieved, there must be some collective organization of the organic and inorganic components, and an integral part of that process lies at

the interface between the spatially distinct organic and inorganic regions. The extent to which the organic and inorganic domains have properties and structure that are characteristic of the corresponding bulk phases, and more importantly their processing into different shapes and forms, depends on the strength of the interface inorganic-organic (IO) interactions relative to entropic and the self-assembly energetics

The Silica-Organic Interface

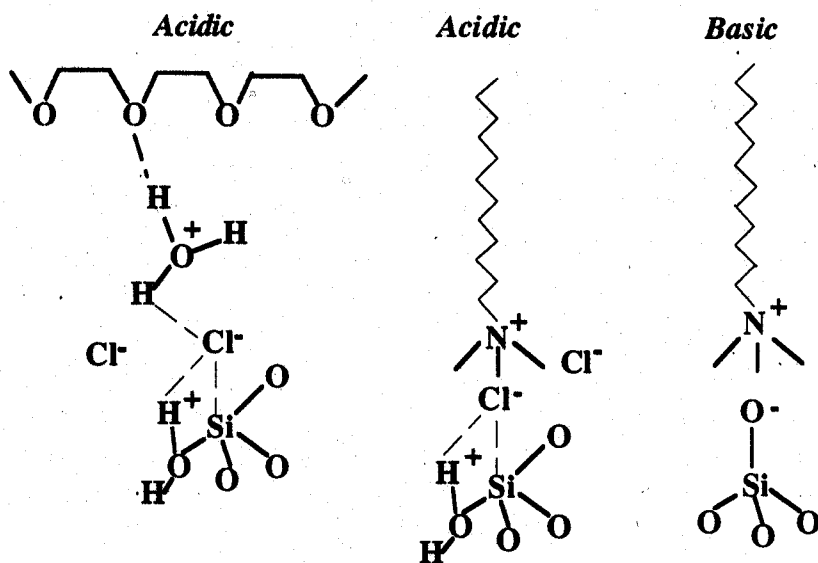


Figure 1

within the organic and inorganic domains. The chemist's challenge is to balance the organic-inorganic and organic-organic interactions, solvation, and inorganic-inorganic interactions at two or more interfaces in such a way as to control structure and form on the desired multiple length scales.

One example of how this can be done is the kinetic limitation of silica polymerization under basic conditions by using low temperatures and careful pH control. Low temperatures are also favorable to organic assembly: optimum organic organization can be more readily achieved with molecular organic/inorganic species at relatively low temperatures. This combination has been used to show that in the absence of inorganic polymerization, these mesophases have liquid crystalline properties similar to those of conventional aqueous lyotropic liquid crystal systems.^{3,4} In order to maintain these liquid crystal-like properties and optimize long-range composite ordering during polymerization of the inorganic species, the inorganic and organic domains must be able to reorganize on the same kinetic time scale into mutually compatible configurations.

The use of weak interface interactions such as those shown in Figure 1 (Acidic) permits one to use the competing kinetics and rate of silica polymerization (through changes in pH, biphasic mixing, hydrophobicity of the silicon alkoxide precursors, etc.) and composite assembly to define different shapes and form on longer length scales, such as fibers^{5,6}, spheres^{7,8}, films^{9,10,11,12,13,14,15,16}, and other designed morphologies.¹⁷ This approach has been reviewed in some detail recently¹⁸, but in view of the increasing application of acid silica synthesis chemistry^{19,20} for topological structure control as well as the creation of both new mesostructured

phases and ultra-large mesopore structures, a few comments which hopefully reflect a more recent perspective seem appropriate.

Strong Interface Interactions

At one end of the scale, the use of strong covalent^{21,22,23} organometallic or direct ionic organic-inorganic interactions^{24,3,4}, (Figure 1, Basic) in surfactant-mesopore synthesis works well to generate molecular inorganic-organic units that form their own liquid crystal arrays independent of the organization that one would get from the organic component alone. The structural phase is defined by the liquid crystal behavior associated with the molecular inorganic/organic species and the assembly of mesophases with different structural symmetry can be carried out starting with these species.

A good deal of the controversy concerning the mechanism of the assembly of mesoporous silica structures, and for that matter pure silica molecular sieve structures in basic aqueous media with anionic silica species has arisen because of disagreements on the role of charges and Coulombic interactions. Classical liquid crystal scientists treat amphiphiles, such as the quaternary ammonium surfactants, as being neutral species with the head group charge completely shielded by the anions surrounding it in solution or in a liquid crystal array. The driving force for the assembly and the structural organization that takes place is totally attributed to van der Waals interactions involving the organic tail and the shape/size of the organic groups that are present.

Inorganic chemists, brought up on the relatively good modelling and predictions that can be made using simple Coulombic interactions for ionic lattices, including ones like tetramethyl ammonium chloride in which the cations and anions are also well screened by their first coordination spheres, know that the only way the energetics of such a array can be fit is through the use of Ewald summations and Madelung potentials that take into account long-range Coulombic interactions. Furthermore it is well established that the strong short-range Coulombic forces, attractive and repulsive, generate a highly organized, crystalline lattice. The thought that adding an organic tail to one of the four tetrahedral positions of an ammonium ion in an ammonium salt somehow completely eliminates the role of Coulombic forces in the assembly of and order of the two-dimensional array of charges that results seems at best provincial. Attempts to relate "cloud formation" during the synthesis of mesoporous structures in basic media to the critical micelle concentrations (cmc)²⁵ may be misleading in that phase separation may depend as much or more on the Coulombic lattice energy component associated with the charged head group as on the van der Waals forces. Solubility products of salts have a Coulombic lattice energy component. In support of this perspective, the association of cationic surfactant micelles and their cmc₁ and cmc₂ values are very sensitive to the anion that is present.²⁰ Both Coulombic and van der Waals components are important, and neither should be neglected as is frequently the case. It should also be noted that during the past six years of research in the area of mesoporous silica materials, in aqueous media the most highly organized and structurally well-defined materials are formed only by introducing a significant amount of charge into the assembly process, either in basic media with

anionic silica species as is done in the synthesis of the M41S family^{26,27} and FSM-16²⁸ or in acid media using cationic silica species as we have done for the synthesis of the UCSB and SBA family of mesoporous phases.

Weak Interface Interactions

At the other extreme from the strong interaction scenario in basic media, if the organic-inorganic interface interaction is relatively weak (e.g., hydrogen bonding as in the acidic intermediate case shown in Figure 1), the initial organization of the organic phase may only be slightly modified, but still capable of directing the silica assembly at long length scales. In this way amphiphilic or non-ionic surfactants and polymers can be used to interface through hydrogen bonding between an organized organic array (e.g., oil-in-water emulsion) and charged inorganic species so that the identity and structure-directing ability and dynamics of the organic organization are more fully utilized in the creation of processed macrostructures with ordered mesoporous arrays such as oriented thin films, fibers, or other designed morphological shapes.

The synthesis of hexagonal and cubic mesoporous silica phases at $\text{pH} < 2$ (~ the aqueous isoelectric point of silica)^{19,20} was an important demonstration that cationic silica species could be used to create periodic porous silica phases that were stable to calcination; and, that hydrogen bonding interactions between inorganic species and the organic structure-directing agents could be used to create 3-d periodic mesoporous silica structures. This chemistry has led to highly organized mesoporous silica structures with large pore sizes ($> 300 \text{ \AA}$)²⁹ and numerous new phases including those with $\text{P6}_3/\text{mmc}$ ^{21,30,31}, $\text{Pm}3\text{m}$ ^{16,31}, $\text{Im}3\text{m}$ ³¹ and $\text{Pm}3\text{n}$ ^{19,20} symmetries.

In addition, almost all the advances that have been made in controlling the macrostructure of ordered silica mesostructured materials use acid media syntheses with cationic pH values below the silica aqueous isoelectric point¹⁹ or acid catalysis in a more non-aqueous media.¹⁵ The latter case may simply reflect a shift of the isoelectric point for forming the cationic silica species in a non-aqueous environment. The different entropic and interaction energies in the nanoscale organic, inorganic, and interface regions during the assembly result in structure frustration with incompatible local packing constraints that forbid an optimal geometry where the free energy is everywhere minimized. During synthesis and processing, before there is extensive silica polymerization, the inorganic/organic structures may readily undergo structural changes or transformations³² to relieve stress through rotational displacements of the surfaces (disclination defects) (Figure 3).^{33,34} The use of weak hydrogen-bonding interactions at the silica/organic interface enhances precursor fluidity and synthesis processing by hydrodynamics, shear fluid flow, cosolvents, emulsions, two-phase oil/water interfaces, or by the application of external fields.³⁵ Thus, the acid synthesis route conveniently provides control over the topological construction process of mesoporous materials at both the molecular and macroscale levels.

The successful application of the silica anion chemistry that is the basis for MCM-41^{26,27} or FSM-16²⁸ syntheses^{3,4} for morphogenesis purposes has only been realized in a few instances.^{36,37,38,39} The direct Coulombic interaction of the cationic surfactant with the anionic

silica species gives a salt-like character to the interface that limits easy processing into the smooth continuous surfaces that are accessible with the acid synthesis approach. The consequences of this are also reflected in other properties, including composition. As-synthesized MCM-41^{26,27} does not have the same composition as that of the corresponding hexagonal phase made using the same surfactant under acid synthesis conditions, which has one halide ion/surfactant molecule in the mesostructured product, has generally thinner walls, smaller surface area, and surfactant species that require acid wash (ion exchange) for their removal as opposed to a simple water/ethanol wash for the acid synthesized mesostructured material.^{19,20} The acid-synthesized hexagonal honeycomb phase, SBA-3, is not the same as the base-synthesized MCM-41^{26,27} or FSM-16²⁸ mesoporous materials although they appear to have the same crystallographic symmetry.

Interface Charge Density, Spatially Competing Sequences and Domain Definition **Organic/Inorganic Framework Charge Matching**

Composite materials, including nanostructured biomaterials, have by definition spatially distinct domains. The relative sizes and patterning of these domains can be determined by using templates with spatially competing hydrophobic and hydrophilic sequences and by charge-matching the organic phase charge density with that of the framework as well as through space/time control of the kinetics of the assembly. Interface charge matching of amphiphilic (ionic and non-ionic) surfactants with the inorganic species and domains (Figure 1) not only is an important controlling factor in the assembly of mesoporous materials, but also, as noted above, is a primary reason for the differences in composition and surfactant removal of base-synthesized, compared to silica acid-synthesized, mesostructures.

Along with the use of competing hydrophobic-hydrophilic or polar-nonpolar molecular sequences, charge matching during synthesis is a powerful tool in the creation of porous materials on all length scales. Until recently there were only two zeolite cage structures, faujasite and hexagonal faujasite, that had intersecting twelve-ring micropores. This use of charge-matching, multi-process assembly using organic templates that have spatially competing hydrophobic/hydrophilic regions has resulted in three new large-micropore zeolite structures.⁴⁰ One of these falls in the mesostructure classification with a cage that is 20 Å in two mutually perpendicular directions. Transition-metal-based zeolite analogs of analcime, chabazite, gismondine, sodalite, faujasite, and rho are examples of some of the zeolite structure types that have been synthesized and characterized by *single-crystal* X-ray diffraction. The concentration of transition metal atoms in the framework can be controlled by varying the charge and geometry of the organic templates. Mn, Zn, Co, Mg, and Al phosphates can be used, confirming the applicability of the approach to different inorganic compositions. In this synthesis, divalent and trivalent ions are both introduced and the siting of the transition metal atoms within the cage is determined by their proximity to the charge on the organic cation. When the hydrophobic sequences of the organic molecule are small, the symmetry of the cage is determined by the symmetry of the organic species. Thus the symmetry of the inorganic framework *and* selective

metal-atom siting in the inorganic framework are determined by *templating*, not just 'structure direction'.^{41,42,43}

This is a new generalized synthesis method which has been applied for the first time to zeolite-type structures in which the majority of metal atom sites are occupied by transition metal atoms. It should also apply to other non-oxide compositions and structures. The methodology has already made it possible to synthesize as single crystals not only zeolite analogs that have never been synthesized in any composition or in a non-aluminosilicate system (merlinoite, phillipsite, and thomsonite), but also zeolite-like structures that were theoretically predicted but never found as minerals or previously synthesized.

Spatially Competing Sequences and Domain Definition

From a molecular perspective the structural function of surfactants in mesophase formation can to a first approximation be related to that of classical surfactants in water or other solvents with parallel roles for organic additives.²¹ The effective surfactant ion pair packing parameter, $g = V/a_0l$, as proscribed by the inorganic species or solid inorganic framework charge density remains a useful molecular index to predict the geometry of the mesophase products, and phase transitions may be viewed as a variation of g in the liquid crystal-like solid phase. A majority of the known liquid crystal morphologies have been observed in our laboratory for the mesosilicates, including previously unknown liquid crystal phase structures. A schematic showing the phases that have been identified is given in Figure 2. The phases shown in italics in Figure 2 are highly ordered, periodic structures made using non-ionic block copolymers.

The combination of molecular design of surfactant molecules and the metastable organization that results from the collective interactions of the organic/inorganic assembly has led to numerous new mesoporous structural phases, including a 3-d hexagonal cage structure³⁰, several new cubic cage structures ($Pm3n$ ^{20,19}, $Im3m$ ³¹ and $Pm3m$ ^{16,31}), and at least one orthorhombic channel mesoporous structure.⁴⁴ The structures of several other new phases are

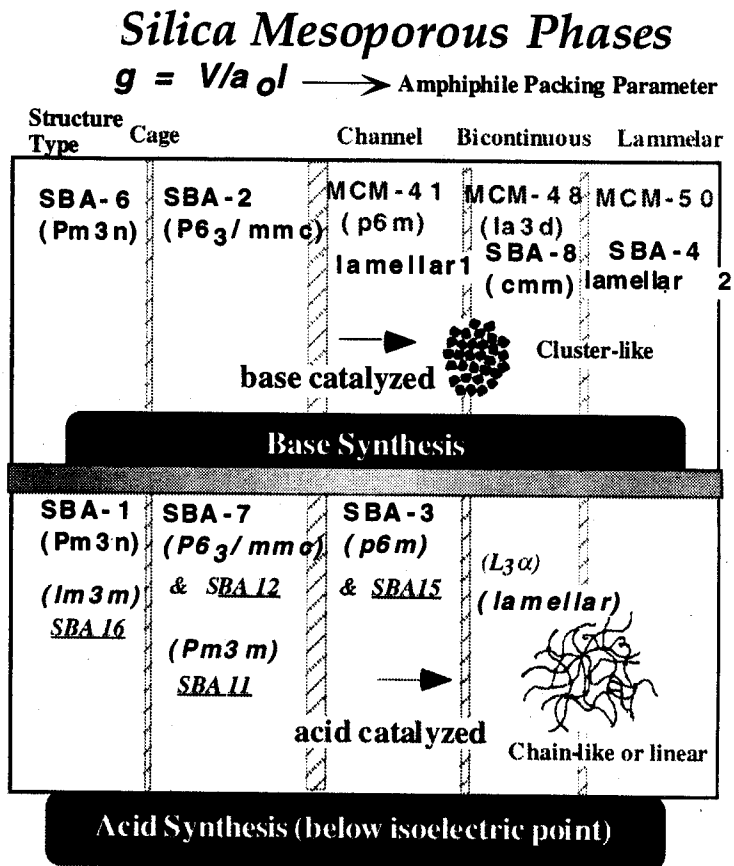


Figure 2

currently being investigated in our laboratory.

The role of solvent, including water and organic solvents or cosolvents, is particularly important.^{30,21} Organic co-solvent species, such as EtOH, penetrate into the hydrophobic region of surfactant arrays, and thereby induce a structural rearrangement of the surfactant phase to re-optimize the interface charge-density matching and the surfactant packing. Solvent and co-solvent structure direction can be very effectively used by varying polarity and hydrophobic/hydrophilic properties and by functionalizing the surfactant molecule, for example with hydroxy group or variable charge.

The ultimate periodic symmetry for composite assembly in which the inorganic phase is disordered on a short-range scale is determined by organic molecular packing requirements (and charge matching with the inorganic interface) for both the strong (S+I-) and weak (S+X-I+) or (S⁰H+)(X-I+) organic-inorganic interface interactions. This means for example that composite phases that have similar space group and lattice symmetries can be made with the acid and base synthesis procedures (Figure 1) even though the compositions, diffraction intensities, and other properties are different.

Phase transformations are easily accessible and very useful in mesoporous synthesis^{3,21} and will not-be discussed here. However, in relation to the differences in properties of acid-versus base-organized silica assemblies, a general pattern of phase transformation behavior is often observed using different surfactants with different g values under different reaction conditions. For acidic (pH < 0) synthesis media the phase sequence is: cubic (Pm3n, SBA-1), 3-d hexagonal (P6₃/mmc, SBA-2) > 2-d hexagonal (p6m, SBA-3) > lamellar. For basic syntheses media the phase sequence changes to: 3-d hexagonal (P6₃/mmc, SBA-2) > 2-d hexagonal (p6m, MCM-41) > cubic (Ia3d, MCM-48) > lamellar (MCM-50).

Spatially Competing Sequences and Domain Definition with Block Copolymers

The organization that takes place in the assembly of amphiphilic surfactants, ionic or neutral arises because of chemical incompatibilities and differences in the chemical potentials of the different species that are present. By attaching a hydrophilic head group to an organic tail a homogeneous composite material can be formed, since the charge or polarity of the organic head group is compatible with the charged silica species present in solution. However, the organic parts of the assembly will still organize and define the hydrophobic domains separate from the hydrophilic head group region.

The differences in polarity or hydrophobicity does not need to be large for organization to take place. An alkylene oxide block copolymer which is segmented by regions that differ only by a single carbon atom as in the EO_xPO_yEO_x block copolymers (EO = ethylene oxide, PO = propylene oxide) will wish to segregate the EO segments from the PO segments simply because of the differing degrees of solvation by water molecules. However the segregation is limited due to the polymer connectivity. A resulting compromise for a collection of these polymers is the formation of periodic microstructures which organize to minimize the interface area between unlike chemical

species.

The potential usefulness of these polymer phases is manifold. Length scales of a resulting mesostructured silica phase will be comparable to the size of the block copolymer molecules, typically tens of nanometers. The microstructure is directly coupled to the geometry and chemical and physical properties of the molecules within the polymer segments so that it can be modified in a variety of ways. The domain interfaces are also readily adjusted by modifying the polymer segment incompatibility. The consequences are that even for these non-ionic systems, a large variety of 3-d ordered phases are accessible.

Work is progressing rapidly in this area in several laboratories, with several groups investigating the formation of hybrid materials using polymeric surfactants. Pinnavaia and co-workers^{45,46} first used nonionic surfactants to synthesize worm-like disordered mesoporous silica and alumina in neutral media assembled by hydrogen-bonding interactions.^{45,46,47} Attard *et al.*⁴⁸ have synthesized hexagonal mesoporous silica phases using concentrated (~50 wt.%) C₁₂EO₈ solutions and suggested that the formation of mesoporous silica under these conditions occurs by a "real" liquid crystal template route. Göltner and Antonietti have recently followed up on this approach using concentrated non-ionic surfactant and polymer arrays^{49,50} and have shown that if amphiphilic block copolymers are used, the block copolymer properties enhance the ductility and elasticity of the resulting composite so that it can be molded into monolithic blocks.⁴⁹

Templin *et al.*⁵¹ have used high concentrations of poly(isoprene-*b*-ethyleneoxide) di-block copolymers (PI-*b*-PEO) to make lamellar and hexagonal aluminosilicate-polymer mesostructures that are highly ordered on length scales to ~40 nm. The syntheses were carried out in an acidic and non-aqueous solution (a mixture of CHCl₃ and tetrahydrofuran). The thermal stability of these materials and removal of the organic phase to create mesoporous structures has not yet been described.

In our laboratory, a family of mesoporous (20 ~ 300 Å) silica structures have been synthesized by the use of commercially available nonionic alkyl polyethylene oxide oligomeric surfactants and polyoxyalkylene block copolymers in acid media.^{29,31} The pore structures are highly ordered, and the phases identified in this family include cubic Im $\bar{3}$ m, cubic Pm $\bar{3}$ m (or others), 3-d hexagonal (P6₃/mmc), 2-d hexagonal (p6mm), continuous sponge L₃ phase, and lamellar (L _{α}) periodic symmetries. The hexagonal, p6mm, SBA-15 mesoporous structures have BET surface areas of 690 ~ 1040 m²/g, pore sizes of 46 ~ 300 Å, silica wall thicknesses of 31 ~ 64 Å, and pore volumes as large as 2.5 cm³/g. Four or more diffraction peaks are observed even for periodicities over 200 Å. Rather remarkably, the calcined ordered mesoporous silica are thermally stable in boiling water for at least 48 hours. Several phases have been made into fibers, oriented thin films, and other morphologies with excellent pore fidelity, and their applications in several areas are currently under investigation. The assembly of the inorganic and organic periodic composite materials appears to take place by a hydrogen bonding (S⁰H⁺)(X-I⁺) pathway and the kinetics of this assembly have been determined.

Summary

The intent of this brief overview is to present a selected review of some of the current research in the area of mesoporous materials. Not included are porous materials in the range of 50 nm to several microns which also have been described recently and are currently being studied. There is now a continuum of nearly monodispersed porosities that can be created for almost any mean pore size for a variety of compositions and structural phases through the mesoscale regime. The evolution of the development of these materials and their applications will be an exciting part of the future.

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