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TOWARDS THE RATIONAL DESIGN AND SYNTHESIS OF MICROPOROUS AND MESOPOROUS SILICA-CONTAINING MATERIALS

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ABSTRACT

The primary impetus for developing a mechanistic understanding of zeolite synthesis is the ultimate goal of the rational design and synthesis of novel zeolite pore architectures. To that end, the mechanisms by which the geometries of organic structure-directing agents are translated into the product pore architectures in the syntheses of high-silica and intermediate-silica containing zeolites are discussed. Two different mechanisms of structure direction and self-assembly via the formation of extended inorganic/organic composite structures or of purely-inorganic structures are proposed for the two different classes of materials, respectively. By considering issues such as hydrophobic hydration behavior of the structure-directing agent and the optimization of inorganic-organic van der Waals interactions, the successful design of structure-directing agents for the synthesis of new zeolite structures may be possible. Extension of the zeolite assembly process to the use of organic molecules that can form micelles can yield ordered mesoporous materials like MCM-41 and MCM-48. A unifying picture of the assembly processes occurring in the syntheses of micro- and mesoporous materials is presented.

INTRODUCTION

Zeolites and other crystalline, microporous solids have found great utility as catalysts and sorption materials. One of the reasons why this is so is because these crystalline oxides contain large internal surface areas accessible through uniformly sized pores of molecular dimensions. To date, the largest proven pore size is approximately 12-13 Å in the material called VPI-5.[1] The quest for larger pore, crystalline materials is ongoing.

Recently, workers at Mobil prepared ordered mesoporous materials.[2,3] These (alumino)silicate solids contain pores of uniform size in the range of ~15-100 Å. Thus, solids possessing mesopores with size uniformity comparable to that observed in crystalline, microporous materials can be prepared. Two types of mesoporous materials that can be synthesized are: (i) (alumino)silicates containing hexagonally arranged one-dimensional pores of tunable diameter from ~15 to 100 Å (denoted MCM-41) and (ii) (alumino)silicates possessing a three-dimensional pore system of size ~ 30 Å and revealing an X-ray diffraction pattern that can be indexed with cubic symmetry, space group : Ia3d (denoted MCM-

48).[2,3] These novel materials are prepared using organic surfactant molecules and a liquid crystal templating mechanism is proposed.[2,3] Additionally, Yanagisawa et al.[4] have synthesized mesoporous silicas from kanemite and organic surfactant molecules that also reveal a high degree of uniformity in the pore size distribution. The pore diameter can be tuned in this type of preparation as well.[4]

There is a long history of "templating" or structure-direction in the synthesis of crystalline, microporous materials. However, the organic-inorganic interactions are thought to occur between inorganic species and single organic molecules. With the mesoporous materials, the organic molecules may have the opportunity to first self-assemble into an aggregate of some type to function as a structure-directing agent. Thus, the question of whether isolated molecules or organic aggregates serve as structure-directing agents in the synthesis of mesoporous materials must be addressed, and it must be done so with caution.

At the request of Dr. Tatsumi, we write this article to: (i) discuss structure-direction in the synthesis of crystalline, microporous, silica-containing materials, (ii) describe structure-direction in the preparation of
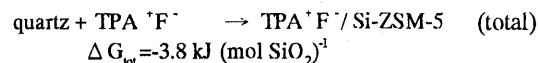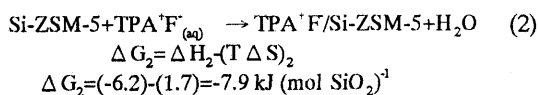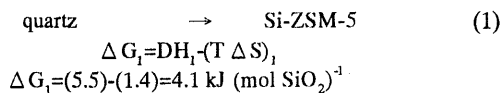
mesoporous materials and (*iii*) show the relationships between (*i*) and (*ii*). We will refer to the paper by Zones *et al.*[5] when discussing structure direction in microporous materials and it is recommended reading prior to proceeding further here.
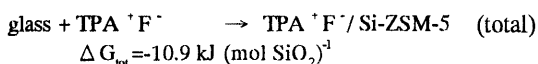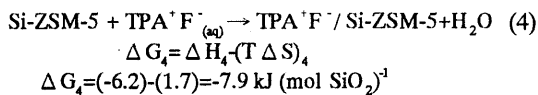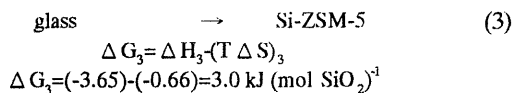
MICROPOROUS MATERIALS

Introduction. The routes by which crystalline zeolites are produced from an amorphous aluminosilicate or silicate gel are complex self-assembly processes that involve numerous simultaneous and interdependent equilibria and condensation steps. Consequently, zeolite crystallization is not well understood, except in that there does not appear to be a universal mechanism to describe all zeolite syntheses.[1] The addition of cationic or neutral organic molecules, e.g., alkylammonium ions, amines, or crown ethers, to zeolite synthesis gels can affect the rate at which a particular material is formed, or can make new structures or framework chemical compositions accessible. However, the exact role of the organic species and the mechanisms by which they affect the formation of the product structures remain to be elucidated.[1,6] In particular, the nature and extent of interactions between the organic and inorganic components of a zeolite synthesis gel are not well defined. Inorganic-organic interactions may provide the means through which the geometry of the organic molecule is translated into the zeolite pore architecture in instances of structure direction; it is possible that in the absence of such interactions, no crystalline product is formed or that the organic species serves simply as a space-filling agent with no geometric correspondence between the organic guest and the inorganic host. Knowledge of the mechanisms by which structure direction occurs is of critical importance to the goal of using of tailor-made organic moieties to synthesize new materials which incorporate particular structural features. In examining these issues here, two classes of materials, pure- or high-silica molecular sieves (Si/Al > 10) and intermediate-silica containing zeolites (~4 < Si/Al < 10) are considered. Because of the lack of organic molecule structure-direction in their syntheses, aluminum-rich zeolites are not discussed. The absence of structure-direction in this case is most likely because the highly charged and highly hydrophilic aluminosilicate gel is not compatible with the more hydrophobic organic species and/or that the volume-to-charge ratios of the organic molecules are too large to allow effective charge compensation of the aluminosilicate network.

Thermodynamics of Zeolite Synthesis. An understanding of the thermodynamic driving forces that are responsible for zeolite formation may provide some mechanistic insight into the assembly process. Recently, Helmkamp and Davis have provided an estimate of the termodynamic parameters for the tetrapropylammonium (TPA) fluoride-mediated synthesis of pure-silica ZSM-5 (Si-ZSM-5) from quartz and from amorphous silica (glass).[7] The synthesis of TPA^+F^-/Si-ZSM-5 from quartz can be considered as follows (T=298 K):

$$quartz \rightarrow Si\text{-}ZSM\text{-}5 \qquad (1)$$
$$\Delta G_1 = DH_1 - (T \Delta S)_1$$
$$\Delta G_1 = (5.5) - (1.4) = 4.1 \text{ kJ (mol SiO}_2)^{-1}$$

$$Si\text{-}ZSM\text{-}5 + TPA^+F^-_{(aq)} \rightarrow TPA^+F/Si\text{-}ZSM\text{-}5 + H_2O \qquad (2)$$
$$\Delta G_2 = \Delta H_2 - (T \Delta S)_2$$
$$\Delta G_2 = (-6.2) - (1.7) = -7.9 \text{ kJ (mol SiO}_2)^{-1}$$

$$quartz + TPA^+F^- \rightarrow TPA^+F^-/Si\text{-}ZSM\text{-}5 \qquad (total)$$
$$\Delta G_{tot} = -3.8 \text{ kJ (mol SiO}_2)^{-1}$$

Similarly, the thermodynamics of the synthesis of TPA^+F^-/Si-ZSM-5 from amorphous silica (glass) can be described as follows (T=298 K):

$$glass \rightarrow Si\text{-}ZSM\text{-}5 \qquad (3)$$
$$\Delta G_3 = \Delta H_3 - (T \Delta S)_3$$
$$\Delta G_3 = (-3.65) - (-0.66) = 3.0 \text{ kJ (mol SiO}_2)^{-1}$$

$$Si\text{-}ZSM\text{-}5 + TPA^+F^-_{(aq)} \rightarrow TPA^+F^-/Si\text{-}ZSM\text{-}5 + H_2O \qquad (4)$$
$$\Delta G_4 = \Delta H_4 - (T \Delta S)_4$$
$$\Delta G_4 = (-6.2) - (1.7) = -7.9 \text{ kJ (mol SiO}_2)^{-1}$$

$$glass + TPA^+F^- \rightarrow TPA^+F^-/Si\text{-}ZSM\text{-}5 \qquad (total)$$
$$\Delta G_{tot} = -10.9 \text{ kJ (mol SiO}_2)^{-1}$$

It is evident from the results for the synthesis of Si-ZSM-5 from quartz that although the transformation of the inorganic phase alone is not thermodynamically favorable, the presence of the organic structure-directing agent in the system renders the synthesis possible. The thermodynamic analysis underscores the importance of organic structure-directing agents in the synthesis of zeolites that would otherwise be inaccessible in the absence of these organic additives.

In reactions (2) and (4), the favorable enthalpic term ($\Delta H < 0$) is related to the van der Waals interactions between the occluded TPA molecules (or, more precisely, the TPA^+F^- ion pairs) and the framework of the Si-ZSM-5 host. This factor provides the primary thermodynamic driving force not only for the occlusion of the organic molecules into the void space of the inorganic material but also for the

overall synthesis of TPA⁺F⁻/Si-ZSM-5 from quartz or amorphous silica. There is a small, favorable contribution to the reaction energetics from the entropic term (T Δ S>0) in this process that likely reflects the entropically-favorable release of ordered water molecules from the hydrophobic hydration spheres of the TPA molecules as the organic species are occluded into the hydrophobic silicate material.

TPA/Si-ZSM-5 likely represents a nearly optimum case for inorganic-organic van der Waals interactions in zeolite synthesis. When the intermolecular interactions are less favorable and the enthalpic contribution to the driving force is thus less strong, it is possible that the entropic term determines whether the formation of inorganic-organic composite species and a crystalline product are thermodynamically possible. This analysis of the thermodynamic parameters involved in the synthesis of pure-silica zeolites provides a useful construct in which to assess the role of inorganic-organic intermolecular interactions and hydrophobic hydration of the organic species in structure direction and zeolite synthesis.

One must exercise caution when attempting to extend the thermodynamic analysis of zeolite syntheses involving F⁻ to those using OH⁻ as the mineralizing agent and/or the addition of heteroatoms such as aluminum. Pure-silica syntheses of ZSM-5 with TPA⁺F⁻ as the structure-directing agent result in the TPA⁺F⁻ ion pair being occluded in the ZSM-5 voids without the formations of silanol groups. When TPA⁺OH⁻ is used, only the TPA⁺ ion is occluded and is charge balanced by a Si-O⁻ defect. The addition of aluminum decreases the Si-O⁻ defect number density but also creates framework charge. Thus, in order to extend the aforementioned thermodynamic analysis to zeolite synthesis in general, coulombic interactions must be accounted for as well. At this time, it is not known how to accurately do this.

Structure Direction in the Synthesis of Pure-Silica and High-Silica Zeolites.

Pure-silica molecular sieves and zeolites that contain a high silica content are the simplest systems in which to assess organic structure-directing effects for two reasons. First, in these systems there is a limited number of synthetic variables: silica, water, organic species, and low concentrations of alkali metal hydroxides (small amounts of alkali metal ions may enhance the crystallization kinetics of some syntheses,[8] but high concentrations exhibit a strong structure-directing influence[7]). Second, the pure-silica product is hydrophobic and uncharged (except for non-surface $Si(OSi)_3(O^-)$ defect sites that balance the charge of a

cationic structure-directing agent),[9] and thus the predominant interactions between the organic molecules and the silicate species should be van der Waals forces.[10] Therefore, the influence of the geometry of the organic moiety on the shape and size of void spaces within the product structure should be apparent in a pure-silica or high-silica system. The relationships between size and shape of organic molecules and the zeolite void spaces that they form, i.e., the structure formed, is clearly demonstrated by Zones et al.[5] and Gies and Marler.[10]

ZSM-5 (MFI topology) is one of the most widely studied and commercially important zeolites. When pure-silica ZSM-5 (Si-ZSM-5) is synthesized using the tetrapropylammonium (TPA) cation as the organic structure-directing agent, the TPA molecules are located at the channel intersections with the propyl chains extending into both the linear and sinusoidal channels. The molecules are held tightly at these sites and can be removed only by calcination; they cannot diffuse into or out of the structure. Tight enclathration of the TPA molecules suggests that they must be incorporated into the silicate structure during the process of crystal growth. Direct evidence of van der Waals interactions between the organic structure-directing agent and inorganic species in the synthesis of pure-silica zeolites comes from the work of Burkett and Davis on the synthesis of pure-silica ZSM-5 (MFI) using the tetrapropylammonium cation (TPA).[11] A ¹H-²⁹Si cross polarization, magic angle spinning (CP MAS) NMR technique was employed by Burkett and Davis since Mentzen and coworkers have suggested that the H...Si interatomic distance necessary for efficient ¹H-²⁹Si CP is approximately that of a van der Waals contact (~3.3 Å.[12] Results from ¹H-²⁹Si CP MAS NMR spectra of freeze-dried samples obtained at intervals during the synthesis of ZSM-5 suggest that close contact between the TPA ions and the silicate species is established prior to the development of long-range, crystalline order (~4-5 unit cells, or ~100 Å). Evidence of structures on the length scale of 10-200 Å in this synthesis have also been observed by small-angle neutron scattering and small-angle X-ray scattering.[13,14] Specifically, the structures detected by NMR have weak, non-covalent, intermolecular interactions, i.e., van der Waals interactions, between the alkyl groups of TPA and the silicate species. This work suggests that structure-direction involves preorganization of silicate species by TPA prior to the formation of the long-range order of the crystalline zeolite structure. No analogous intermolecular ¹H-²⁹Si CP occurs when a non-structure-directing organic species, e.g., tetramethylammonium (TMA), is used in lieu of
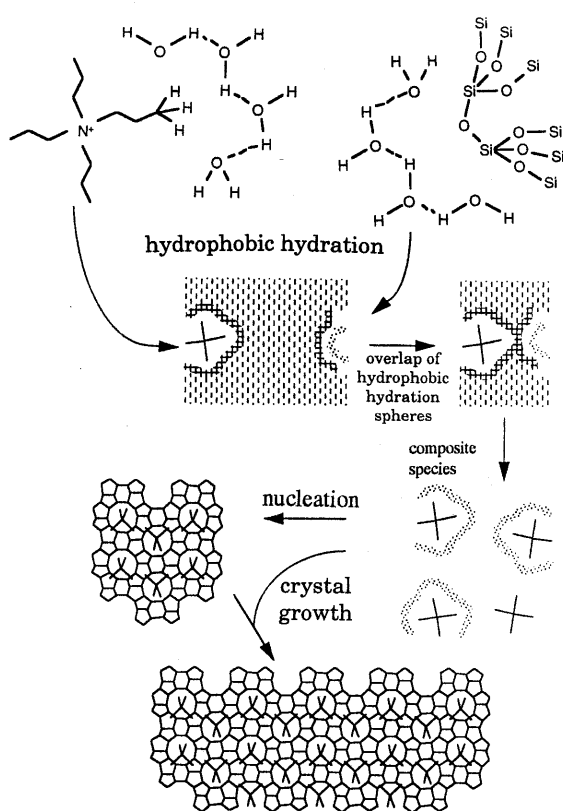
Figure 1. Proposed mechanism of structure direction in the TPA-mediated synthesis of Si-ZSM-5. Adapted from reference 15.
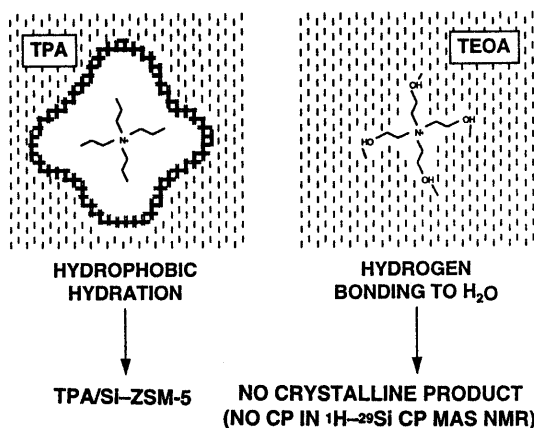

Figure 2. Schematic representation of TPA$^+$ and TEOA$^+$ in water.

TPA, suggesting that intermolecular interactions observed by the CP technique are relevant to structure direction. For the TPA-mediated synthesis of Si-ZSM-5 (see Figure 1), it was thus proposed that silicate is closely associated with the TPA molecules to form inorganic-organic composite species that are the key species in the nucleation and crystal growth processes for the self-assembly of Si-ZSM-5 (we now believe that we have trapped these species from a synthesis gel[15]).

The significance of hydrophobic hydration effects in the synthesis of pure-silica zeolites is suggested by the observation that tetraethanolammonium (TE OA), which is similar in size to TPA but does not form a hydrophobic hydration sphere in aqueous solution because it can participate in the hydrogen bonding network of water via the alcohol moieties (see Figure 2), does not serve as a structure-directing agent for the synthesis of Si-ZSM-5 or any other zeolite. No crystalline products were formed from synthesis gels containing TEOA, even at higher synthesis temperatures. Using mixtures of TEOA and TPA, Si-ZSM-5 was formed in 4 days at 175℃ only when a sufficient amount of TPA was present in the gel to completely fill the void space of the zeolite product (TPA/Si=1/24; gel composition 0.21 TPA_2O:0.29$TEOA_2O$:10 SiO_2:380 H_2O). However, no TEOA was detected by ^1H-^{13}C CP MAS NMR in the product formed under these conditions. When a lower TPA content was used (TPA/Si=1/96; gel composition 0.05 TPA_2O: 0.45 $TEOA_2O$: 10 SiO_2: 380 H_2O), no crystalline material was obtained under the same conditions of heating time and temperature. Similarly, no intermolecular ^1H-^{29}Si CP was observed in the TEOA-containing synthesis mixture after heating for 10 days at 110℃. The observation of intermolecular CP in the X-ray amorphous, heated synthesis mixture appears to correlate with the observation of a structure-direction effect; only when Si-ZSM-5 is eventually formed is efficient CP observed in the heated, X-ray amorphous precursor. Thus, when the organic molecule shows favorable interactions with the solvent, the solvent molecules can not be replaced by silicate species. Using the Zones et al. analogy,[5] the shell of the peanut can not be removed so the candy coating of the peanut can not be accomplished (see Fig. 5 of Ref. 5). Zones et al. show that organic molecules that are neither highly hydrophilic or hydrophobic are good structure-directing agents (Fig. 6 of Ref. 5). If the organic molecules are too highly solvated by water, then no interaction with silica occurs (TMA$^+$, ^1H-^{29}Si NMR experiments mentioned above). However, if the organic molecules are too hydrophobic, then they
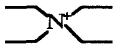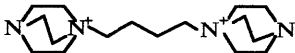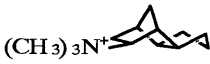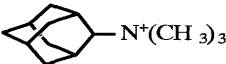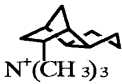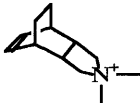
most likely aggregate in a random fashion and are therefore unable to direct the formation of well-ordered structures. Thus, the hydrophobic /hydro-philic properties of the organic molecule must be properly designed if one is to create new structure-directing agents.

The proposed mechanism for the synthesis of Si-ZSM-5 can likely be generalized to other examples of structure direction in the synthesis of high-silica and pure-silica zeolites. The primary impetus for developing a mechanistic understanding of zeolite synthesis is the ultimate goal of the rational design and synthesis of novel zeolite pore architectures. The true test of the validity of the proposed role of inorganic-organic interactions in zeolite synthesis (particularly for the synthesis of high-silica materials) lies in its applicability to the synthesis of new zeolites and molecular sieves. Although it may not be possible to control the precise atomic arrangements required to construct a particular structure, parameters such as the type of void space (one-dimensional channels, intersecting channels, isolated cages, or interconnect-ed cage networks), the size and shape of the void spaces and the intervening apertures, and the arrange-ment of the void spaces relative to each other within the crystal unit cell should be amenable to the influence of organic structure-directing agents. Many different topologies should be accessible to a pure-silica tetrahedral network because of the flexibility of the Si-O-Si bond[16] and because there is little energetic difference between the various porous silica phases and between these structures and dense phases, i.e., quartz (~10-12 kJ/mol).[17] The presence of aluminum in the tetrahedral network appears to favor certain structural features, such as intersecting channels and pores,[5] and small amounts of aluminum and/or other heteroatoms can apparently be tolerated in a synthesis gel that is influenced by organic structure-directing agents. However, even small amounts of a particular heteroatom can greatly affect the structure that is formed (see Table 1). One reason for this effect could be that Si-O-M (M=Al, B, Zn) angles have a more limited range of variation than Si-O-Si angles and that the optimum angles are smaller for the heteroatom angles than for the Si-O-Si angle. Additionally, low concentrations of alkali metal ions, particularly sodium, may facilitate zeolite synthesis, whereas high concentrations may mask or eliminate the relatively weak influence of the organic species.

Zones and co-workers have recently demonstrated the first example of zeolite synthesis by a priori design in the synthesis of SSZ-26.[5,18,19] With the goal of making a novel zeolite containing a multi-dimensional channel system with large-pore intersec-tions, a diquaternary ammonium propellane species

Table 1. Effect of aluminum, boron and zinc on the structure of molecular sieves obtained using organic structure-directing agents. (From reference 9.)

	SiO_2	SiO_2/Al_2O_3 <50	SiO_2/B_2O_3 <30	SiO_2/ZnO <100
	ZSM-12	Zeolite Beta	Zeolite Beta	VPI-8
	ZSM-12	Zeolite Beta	Zeolite Beta	VPI-8
	ZSM-12	Mordenite	Zeolite Beta	Layered Material
	SSZ-24	SSZ-25	SSZ-33	VPI-8
	SSZ-31	Mordenite	SSZ-33	VPI-8
	SSZ-31	SSZ-37	SSZ-33	—

was chosen based on geometric considerations. Conceptually, this compound is derived from a bicyclic, diquaternary ammonium species that has a linear axis and has been used in the syntheses of ZSM-12. Introduction of the fused cyclohexane ring generates a molecule that is too large to be contained within a one-dimensional channel. Thus, the diquaternary, bicyclic portion of the organic molecule may direct the formation of a channel structure while the third ring may disrupt the one-dimensional channel such that an intersection might be created (see Figure 3). The resulting high-silica zeolite, SSZ-26, is composed of intersecting ten-ring and twelve-ring channels (or, more correctly, an intergrowth of two related polymorphs, each composed of these intersecting channels), with one molecule of the organic structure-directing agent immobilized at each channel intersection, as anticipated.[20]
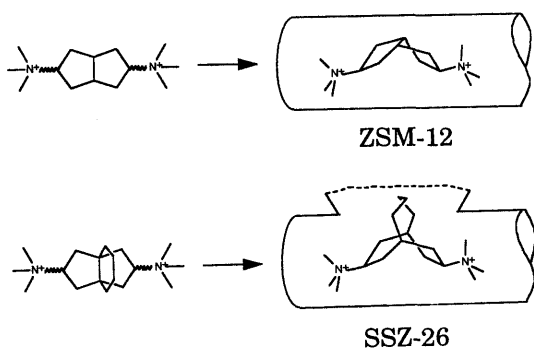

Figure 3. Representation of how a diquaternary ammonium propellane species might disrupt the formation of a linear channel structure in SSZ-26. Adapted from reference 18.

Structure Direction in the Synthesis of Intermediate-Silica Containing Zeolites. The syntheses of intermediate-silica containing zeolites are less amenable to structure direction by organic species than high-silica syntheses. Alkali metal ions are necessary to balance the negative charges introduced by framework aluminum, because even if organic cations are present, the zeolite typically cannot accommodate a sufficient number of organic cations in the void space to balance the framework charges. The high concentrations of alkali metal hydroxides that are thus usually used in these syntheses can strongly influence the inorganic gel chemistry and subsequent structure formation.[1,9] Organic structure-directing effects are weak relative

to these influences, perhaps in part because the interactions between organic molecules and the inorganic species are primarily electrostatic in nature. As a result, organic structure-directing effects appear in a much narrower range of synthesis conditions as the aluminum content is increased. Although aluminosilicate syntheses are a more complicated system in which to discern structure-directing effects, there are examples of structure direction in aluminosilicate zeolite syntheses.

The cubic polymorph of faujasite (FAU) is a naturally-occurring mineral that can also be synthesized at a variety of Si/Al ratios by numerous methods, both without and with organic additives (including 15-crown-5). The structure consists of one type of large supercage which is accessed through twelve-ring apertures. The FAU topology can be considered as stacked aluminosilicate sheet structures (faujasite sheets), each of which is composed of rings of six sodalite cages connected via hexagonal prisms, with an inversion center between adjoining sheets. If there is instead a mirror plane between adjoining faujasite sheets, the hexagonal polymorph of faujasite (EMT) is produced. The subtle difference in structure necessitates very specific synthesis conditions. Domains of EMT have been identified in intergrowths with FAU in several materials, but EMT has only been synthesized in its pure form from gels that contain 18-crown-6 as the structure-directing agent.[21-24] EMT contains equal numbers of two different elliptical supercages, and there is one complex of 18-crown-6 and a sodium ion (sodium is a component of the synthesis gel) in each of the larger and smaller supercages, as suggested by Raman spectroscopy,[24] static ^{13}C CP NMR,[24] and X-ray diffraction results.[25]

The cationic sodium/18-crown-6 complex is the structure-directing agent during crystallization, and both the sodium-binding ability and the shape of 18-crown-6 are apparently essential to this role.[24] However, the structure-directing effect is weak, and it can be masked by an increased concentration of sodium in the gel, which results in the crystallization of FAU. EMT is synthesized when the amount of 18-crown-6 present in the synthesis mixture is sufficient for single occupation of the product supercages, but reduction of the available 18-crown-6 concentration to one molecule per two supercages results in no formation of EMT.[24] This suggests that the presence of 18-crown-6 in both supercages is important for the synthesis of EMT. In the presence of mixtures of 15-crown-5 and 18-crown-6, intergrowths of varying amounts of FAU and EMT are synthesized,[22,26] with the relative amount of each polymorph present roughly proportional to the
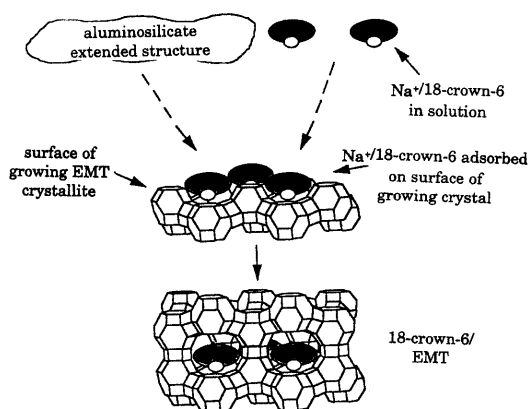
Figure 4. Proposed mechanism of structure direction in the18-crown-6-mediated synthesis of EMT. Growth occurs layer-by-layer.

amount of each crown ether used, suggesting that the synthesis is controlled by the organic species.

The close correspondence in size and shape between the sodium/18-crown-6 complex and the smaller supercage in EMT suggests a means through which 18-crown-6 may exhibit its structure-directing effect. The cationic sodium/18-crown-6 complexes are associated with the surface of the growing anionic, aluminosilicate crystallite via an electrostatic interaction. The essential interaction site is apparently the six-ring that becomes part of the smaller supercage after the next faujasite sheet is attached. This ring of six oxygen atoms in the framework of EMT and the ring of six oxygen atoms in 18-crown-6 are closely matched in size, and a sandwich-like complex of sodium may be formed at this site.[24, 25] A mechanism of synthesis (Figure 4) has been proposed that involves the assembly of sodium-templated, extended aluminosilicate structures, which may not necessarily resemble faujasite sheets. The specificity of this arrangement for a mirror plane between faujasite sheets (in EMT) rather than an inversion center (in FAU) is directed by the shape and size of the sodium/18-crown-6 complexes;[24] if the slightly smaller sodium/15-crown-5 complex is used, FAU is formed instead. The siting of the structure-directing agent molecules imposes geometric constraints on the placement of subsequent aluminosilicate units, and the geometry of the cationic organic species is the key to structure direction.

A second example of structure direction is the DABCO polymer-mediated synthesis of gmelinite

(GME). The organic species that are used as structure-directing agents in zeolite synthesis are usually small molecules that are accommodated within a single zeolite cage, channel intersection, or section of a one-dimensional channel that is smaller than one unit cell of the zeolite.[1] The use of organic polymers that contain regularly-spaced cationic tetraalkyl-ammonium groups presents the opportunity to influence not only the shape and size of the individual void spaces but also the relative arrangement of void spaces within the unit cell. To this end, Rollman and coworkers used alternating copolymers derived from 1,4-diazabicyclo[2.2.2]octane (DABCO) and dibromoalkanes ($Br(CH_2)_nBr$,n = 3,4,5,6,10) in the synthesis of the twelve-ring channel zeolite gmelinite (GME) from an aluminum-containing synthesis mixture that produces zeolite Y (FAU) and zeolite P (GIS) in the absence of polymer.[27,28] The polymer is occluded intact into the product, as confirmed by ^{13}C CP MAS NMR.[29] Using the monomeric N,N'-dimethylated derivative of DABCO, or using a polymer with a longer (decyl) or shorter (propyl) linkage between DABCO units, zeolite Y(cage structure) or zeolite P (channel structure) resulted.[27, 28]

The DABCO polymers influence several aspects of structure formation. First, a twelve-ring zeolite was synthesized because the diameter of the DABCO unit in the polymer is approximately 6.1 Å,[27,28] which is too large to be accommodated by a ten-ring unit. Second, a channel structure was produced despite the preference for cage structures in aluminum-rich syntheses. Third, the length of the repeat unit of the butyl polymer is approximately 8.7 Å,[27,28]which is nearly commensurate with the unit cell dimensions of the channel axis or a multiple thereof (~10 Å).[27-29] However, the feature that is unique to the use of a polymer as the structure-directing agent is that the gmelinite samples synthesized in the presence of the butyl polymer were not faulted.[27-29] In contrast, gmelinite that is synthesized by organic-free methods (or the mineral gmelinite) contains many stacking faults, and thus exhibits the adsorption properties of small-pore rather than large-pore (twelvering) zeolites.[27,30] Thus, the organic species not only controls the size and shape of the individual void spaces, but due to its polymeric nature it also influences the long-range arrangement of void spaces, producing a fault-free system. It is apparent that the polymer exhibits a distinct influence on structure formation.

Summary. In the investigations of the mechanisms of structure direction and self-assembly in the syntheses of Si-ZSM-5 and EMT and FAU, the common theme is the organization of extended

silicate or aluminosilicate structures, *i.e.*, on the length scale of 10-200 Å, by organic structure-directing agents as the essential process in zeolite nucleation and crystal growth. However, the nature of the extended structures and the means by which the organic species participates in their formation and the assembly into the final product are different for the two systems investigated. In the synthesis of Si-ZSM-5 in the presence of the tetrapropyl-ammonium (TPA), the formation of composite silicate-organic structures is determined initially by favorable overlap of the hydrophobic hydration spheres of the organic and silicate species. Subsequent optimization of intermolecular, inorganic-organic van der Waals interactions provides the essential structure-directing influence. By contrast, in the syntheses of EMT and FAU, the inorganic gel composition alone may determine the types of extended, aluminosilicate structures that are formed (in particular, each alkali metal ion favors the formation of certain structural types), while the organic species influence the orientation in which these structures assemble to create the long-range order within the crystalline zeolite. The formation of a sandwich-like complex via ion-dipole interactions between the sodium/18-crown-6 complex and the ring of six oxygen atoms in the smaller supercage of EMT is proposed as the key step in structure direction. (Very recently, Zones appears to have provided yet another example of this type of structure-direction in showing that the addition of dioxane to a zeolite P synthesis gel gives pure zeolite omega.[31]) In both cases, weak, non-covalent interactions between the organic and inorganic components that are easily masked by the influence of stronger structure-directing species, *e.g.*, high concentrations of alkali metal cations, provide the essential inter-molecular forces through which structure direction occurs.

The significance of extended structures in zeolite synthesis underscores the conceptual connection between the processes involved in zeolite self-assembly and the hierarchy of organization in self-assembled structures in biological systems.[32] Molecules spontaneously assemble into composite structures of increasing larger length scales. In both zeolite synthesis and biological systems, weak, non-covalent interactions, *e.g.*, van der Waals interactions and ion-dipole forces, play a significant role in the multipoint molecular recognition processes that occur at the different levels of organization. For example, hydro-phobic hydration and hydrophobic interactions provide important contributions to protein folding[33] and to the formation of lipid bilayer membranes; these organized structures provide the subunits for

larger architectures.

Judging from the example of the synthesis of SSZ-26, the prospects for the *a priori* design and synthesis of molecular sieves are optimistic.[34] One must start with an inorganic synthesis gel that is amenable to the influence of organic structure-directing agents, *e.g.*, a high-silica system in which the predominant non-covalent intermolecular inter-actions between the organic species and the inorganic framework are van der Waals interactions. However, one must also consider the limitations on which features one can control. Although it may not be realistic to attempt to control the absolute atomic arrangement within a new zeolite material, one may nevertheless be able to significantly influence the shape, size, and connectivity of the void spaces that are formed through the use of organic structure-directing agents with specifically-designed geome-tries. Thus, by considering issues such as hydrophobic hydration behavior and the optimization of inorganic-organic van der Waals interactions, the successful design of organic structure-directing agents and templates for the synthesis of new zeolite structures may be possible.

MESOPOROUS MATERIALS

Introduction. As discussed above, isolated molecules can function as structure directing agents in the synthesis of crystalline, microporous materials and there does appear to be conceptual connections between the zeolite self-assembly process and the organizational steps observed in biological systems. In biological structures, organic material larger than single molecules can function as templates. Thus, one might expect that organic molecular aggregates could serve as structure-directing agents in the preparation of porous inorganic materials.

Consider what happens when molecules of type $(CH_3)_3N(CH_2)_xCH_3$ are placed in water. If x is small, *e.g.*, x=0,1,2, the molecules remain isolated in solution. However, if x becomes large, *e.g.*, x=15 (hexadecyltrimethylammonium:C_{16}TMA), the mole-cules can spontaneously self-assemble into molecular aggregates, *i.e.*, micelles in which the hydrophobic hydrocarbon chains aggregate in the center and the polar groups are located at the surface in contact with the aqueous-phase. The critical micelle concen-tration is 0.03 wt% for C_{16}TMABr in water at room temperature.[35] In order to test whether molecular aggregation can effect the synthesis process, we heated a reaction mixture of composition 0.15 C_{16} TMA$_2$O · 1.0 SiO$_2$ · 50 H$_2$O at several temperatures above and below 150 ℃.[36] Above 150 ℃, micelles are not formed. Interestingly, at temperatures in

excess of 150 ℃, the zeolite ZSM-48 (pore size ~ 5-Å) is crystallized while temperatures below 150 ℃ yield MCM-41 (pore size ~ 30 Å). From ^{13}C CP MAS NMR spectroscopy, the C_{16}TMA remains intact in ZSM-48 and MCM-41. These data are consistent with the premise that isolated molecules structure-direct the formation of zeolites while the organic aggregation process leads to the preparation of MCM-41. More recently, workers at Mobil conducted more exhaustive experiments of this type.[37] By varying both x, $6 \leq x \leq 18$, and T, $100℃ \leq T \leq 200℃$, their results clearly support the premise that molecular aggregation (low T, high x) favors the formation of MCM-41 while conditions that most likely do not allow the formation of molecular aggregates (high T, low x) yield zeolites. At this point, we must make it absolutely clear that zeolites are crystalline inorganic materials while the inorganic portions of the mesoporous materials are not and more resemble amorphous solids in their local bonding.[38] Thus, it is not surprising that inorganic compositions known to yield amorphous solids also give organic/inorganic biphase arrays.[39,40] What would be of significance is the preparation of a biphase array with a crystalline inorganic portion.

High Temperature Assembly Processes.

As with zeolite syntheses, there appears to be numerous mechanisms for the assembly of organic/inorganic composites that can lead to ordered mesoporous materials. Attempts to define an all encompassing mechanism are therefore most likely futile. Thus, we will discuss several of the assembly processes that appear to exist.

The Mobil group originally proposed that MCM-41 could form by one of two mechanisms.[2,3] First, the C_{16}TMA ions could self-assemble into what is referred to as the H_1 phase (hexagonal arrangement of rod-like micelles in a binary aqueous-phase) after which silicate species penetrate into the aqueous inter-rod region and condense to form the final organic-inorganic composite material. Second, the silicate species influence the formation of the micelles and work in concert to form MCM-41. We investigated the synthesis of MCM-41 recording X-ray powder diffraction, thermogravimetric analyses and ^{29}Si NMR spectroscopic data on solid samples collected over the course of a MCM-41 preparation. Additionally, and most importantly, we followed the synthesis of MCM-41 by in situ ^{14}N NMR spectroscopy. The ^{14}N NMR spectroscopy can discern the presence of the H_1 phase.[41] At no time was the H_1 phase detected by in situ ^{14}N NMR spectroscopy.[41] Therefore, the pathway proposed by workers at Mobil that includes the formation of the H_1 phase must not

be correct and the organization leading to long-range order is due to synergistic effects between the organic and inorganic species.[41] Subsequent investigations using other techniques such as in situ SANS,[42] ^{2}H NMR spectroscopy[43], SANS and XRD[43] have confirmed our conclusions. This finding does appear to be a general feature that is applicable to all types of biphase array syntheses. However, other steps in the assembly process are method, i.e., composition, temperature, etc., dependent. Below, we first discuss assembly processes using high temperature and pH that more closely resemble conditions employed for zeolite synthesis.[1]

For high temperature syntheses of mesoporous materials via the original Mobil-type preparations, we proposed that MCM-41 can form by a mechanism schematically illustrated in Figure 5. Randomly-ordered rod-like organic micelles form initially (observed by in situ ^{14}N NMR at 95 ℃) and interact with silicate species via coulombic attractions between positively-charged surfactant molecules and negatively-charged silicate anions to form silicate coated micelles. These randomly-ordered composite species spontaneously pack into a hexagonal arrangement; one of the driving forces for the packing is condensation of the silicate species. While in the hexagonal array, further silicate condensation occurs (XRD patterns do not change but ^{29}Si NMR spectroscopy reveals an increase in the ratio of $Q^4/(Q^2+Q^3)$ silicon species). A single layer of silica around a rod-like micelle would consist of approximately four Si atoms per N (area of the surfactant head group is approximately $50 Å^2$).[44] This mechanism would suggest that MCM-41 possesses Si/N $\cong 4$ and shows a wall thickness of approximately 8 Å. MCM-41 has been prepared with Si/N=3.5-4.5[3,38] and a wall thickness of 8-10 Å.[3,38] Additionally, Beck et al.[3] have shown that the pore size of MCM-41 can be expanded above the value obtained from using only C_{16}TMA ions by introducing hydrophobic organic species, e.g., 1,3,5-trimethylbenzene, into the synthesis gel. Beck et al. claim that the addition of the hydrophobic organic molecules must be done early in the synthesis process and this result has been verified by Huo et al.[40] The mechanism for pore size enlargement is easy to rationalize with our synthesis mechanism. The rod-like micelles absorb the small organic species and increase their diameter and this ultimately increases the pore size of MCM-41. Swelling of C_{16}TMA micelles is well-documented.[45] The absorption and swelling of the micelles can occur any time prior to the silica encapsulation.

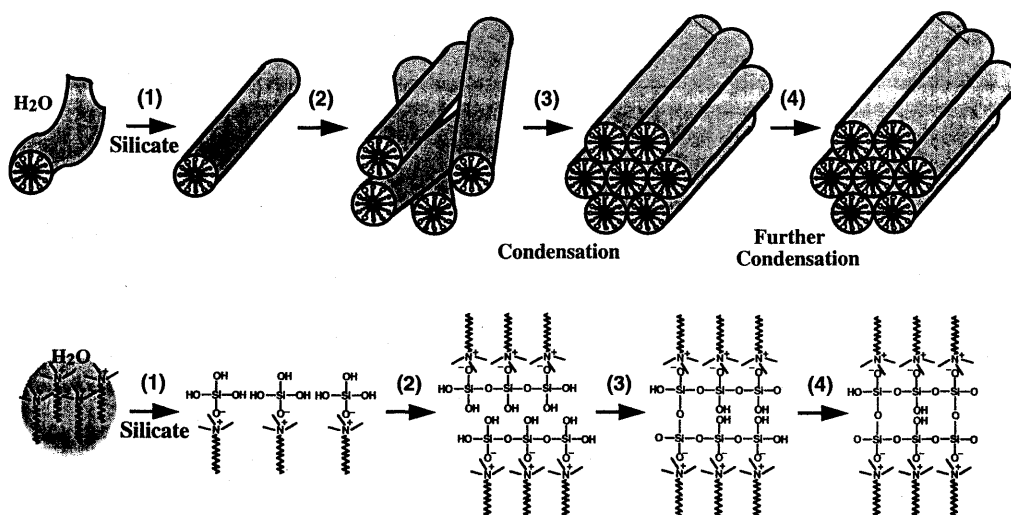Upon homogenizing the MCM-41 synthesis

Figure 5. Proposed high temperature synthesis of MCM-41. Adapted from reference 36.

mixture, a gel is formed. If this gel is exposed to ambient air for extended periods of time, XRD patterns reveal the presence of a lamellar phase (as water evaporates from the gel, the phase becomes more pronounced).[41] We do not believe that a lamellar phase actually exists as a precursor to MCM-41 as was suggested by Monnier et al.[46] but rather forms upon dehydration of the gel. Thus, we believe that only in situ techniques should be employed to probe the nature of the synthesis gel. Thus far, only two true in situ experiments have been performed; ^{14}N NMR[41] and SANS.[42] The in situ SANS experiments also do not reveal the presence of a lamellar phase prior to the formation of MCM-41.[42] All of the solids collected during the heating of the MCM-41 synthesis mixture reveal the presence of organic species irrespective of whether the XRD pattern shows the solid to be amorphous or MCM-41. Interestingly, all the samples have an organic content of 50 wt%, a water content of 10 wt% and nearly identical thermogravimetric analyses. The similarity in the TGA profiles suggests that the local arrangement of both organic and inorganic species within these solids is similar, although the long-range order varies with time.[41]

We have noticed that many syntheses give solids that show only one large peak in the XRD pattern. This is also true for some of the examples in the Mobil patents on the synthesis of MCM-41. The materials that reveal the (100), (110), (200) peaks show the hexagonal ordering of pores by transmission electron microscopy (TEM), while those that contain only a single XRD peak do not. The TEM images of materials having only a single XRD peak appear to contain randomly ordered cylinders. Surprisingly, these materials show high surface areas and fairly

uniformly sized pore distributions when compared to the solids containing hexagonally ordered pores. Thus, we speculate that these materials also form by silica encapsulation of rod-like micelles that now are not able to pack in an orderly fashion. The disorder could be related to the inhomogeneity of the synthesis medium.

It is interesting to note that the H_1 phase does not form with C_{16}TMA at concentrations of less than 26 wt% organic in a binary aqueous system. For the synthesis of MCM-41, a typical C_{16}TMA concentration is approximately 17 wt%. However, MCM-41 has been prepared from gels containing C_{16}TMA concentrations ranging from approximately 1 wt% to 29 wt%. With TEOS and a 29 wt% aqueous solution of C_{16}TMA at C_{16}TMA/Si ratios less than one, MCM-41 is formed. If the C_{16}TMA/Si ratio is raised to 1.1-1.4, a cubic phase is produced.[3,47] Further increases in this ratio yield a lamellar phase (ratio below 2) and the silicate octamer $(C_{16}TMA)_8 Si_8 O_{20}$ (ratio of 2). Thus, if the essence of our description of the synthesis mechanism for MCM-41 is correct, then we should be able to extend the analysis to describe how all of the aforementioned phases are formed.

We investigated the state of the C_{16}TMA species in synthesis gels prepared with TEOS and 29 wt% aqueous solution of C_{16}TMA by in situ ^{14}N NMR. C_{16}TMA/SiO_2 ratios between 1 and 2 yield the same ^{14}N NMR spectrum for gels at room temperature and at 95 °C; namely a single isotropic line that indicates the presence of micelles. Thus, in all cases we believe that the starting point for a mechanistic proposal must have the C_{16}TMA species assembled into micelles.

Figure 6 illustrates the phases that have been

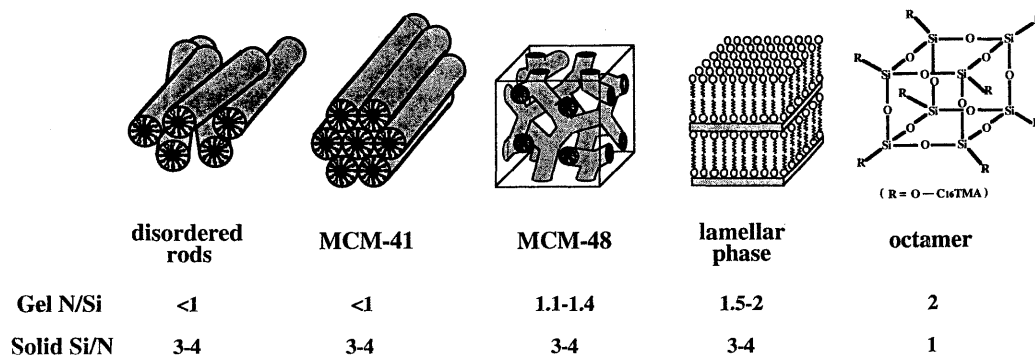|	disordered rods	MCM-41	MCM-48	lamellar phase	octamer
Gel N/Si	<1	<1	1.1-1.4	1.5-2	2
Solid Si/N	3-4	3-4	3-4	3-4	1

Figure 6. Phases formed from $C_{16}TMA/SiO_2/H_2O$. Adapted from reference 36.

synthesized using $C_{16}TMA/SiO_2/H_2O$. [2,3,35,47] The preparation of the cubic octamer with $C_{16}TMA$ /SiO_2/H_2O shows that at sufficiently high $C_{16}TMA$ /SiO_2 ratios, the surfactant plays no role in the formation of the final product. It is known that quaternary ammonium hydroxides, e.g., tetramethyl-ammonium hydroxide, form the cubic octamer at organic/$SiO_2 \geq 1$.[48] Thus, the $C_{16}TMA$ species act no differently than other quaternary ammonium ions at $C_{16}TMA/SiO_2 > 2$. We envision the formation of MCM-41, MCM-48 and the lamellar phase to all begin by having randomly-ordered micelles interact with silicate species via coulombic attractions to form organic-inorganic composite species that arrange into hexagonal, cubic or lamellar arrays for MCM-41, MCM-48 (Monnier et al.[46] propose that MCM-48 is composed of short rod-like organic aggregates that form two interpenetrating networks separated by a single silicate sheet) and the lamellar phase (organic-inorganic species could stack and then rearrange to form lamellar sheets of alternating organic and silicate domains), respectively. Since the N/Si ratio in MCM-41, MCM-48 and the lamellar product is <u>essentially the same</u>,[47] the role of the head-group area in determining the particular mesophase that is formed in a binary organic-aqueous phase system[49] may not be a critical factor in the formation of the organic-silica mesophases. Alternatively, a primary driving force for organic-inorganic mesophase formation could be the optimization of the surfactant-silicate interactions in a manner that allows the highest degree of silicate condensation. In all cases, the conversion of the silicate species into the final organic-inorganic composite occurs at yields approaching 90%.[41,47] However, the yields of $C_{16}TMA$ depend on the starting gel composition and are the highest at approximately 40% for MCM-41[41,47] and decline for MCM-48 and the lamellar phase.[47] These results underscore the fact that the formation of the final composite materials

are formed via kinetically-controlled processes.

The aforementioned interpretation of the possible synthesis mechanisms for mesoporous materials formation has been questioned.[40] Since $C_{12}TMACl$ does not form rodlike micelles at any concentration and $C_{16}TMA^+$ does not form rodlike micelles at low concentrations, e.g., 1 wt%, and both cases can yield MCM-41, the presence of rodlike micelles prior to adding the silicate phase does not appear to be a necessary condition for mesoporous materials preparation.[40] The key here is that silica and other species are clearly present in the synthesis mixture. It has been shown previously that the addition of silica, NaOH and NaBr each dramatically change the phase diagram of aqueous $C_{16}TMA^+$.[41] Thus, what is important is the state of the organic species at synthesis conditions, i.e., in situ! Thus, organic surfactants not capable of forming rodlike structures at conditions other than those of the biphase silicate assembly process may in fact do so when all components of the synthesis mixture are added and the system is heated.

Iton and co-workers performed in situ SANS measurements on the synthesis of MCM-41.[42] Solutions of $C_{16}TMABr$ showed no indication of the H_1 phase at 25 °C. The addition of sodium silicate caused the cylindrical micelles to form a close-packed array at 25 °C. However, when the gel was heated to 95 °C, the close-packed array disappeared. This result led Iton and co-workers to suggest that at elevated temperatures the gradual development (via silicate condensation reactions) of a silicate network around the micelles is not initiated from a close-packed state. Iton and co-workers clearly show that the addition of the silicate species can cause ordering at room temperature, i.e., a salt formation, and that this type of biphase array in which the silicate is not highly condensed can re-dissolve upon heating. The ordering of $C_{16}TMA^+$ micelles into biphase silicate

arrays by the addition of silica at room temperature has also been verified by Chmelka et al.[43] For this case, the micelles were spheres. Very recently, Edler and White have shown that if the hexagonal biphase array is formed at room temperature, over the course of several days at this temperature, the silicate species can condense to form MCM-41.[50]

Workers at Santa Barbara[40] propose that a mechanism of biphase silicate array formation involves isolated surfactant molecules that can ion pair with silicate species to then form the final composite structure. Thus, one interpretation involves isolated molecules while previous work would suggest micelles[37,41,42] (it is possible that spherical micelles can perform all the same functions as rodlike micelles with the additional feature that when the micelle-silicate species pack into an array, the organic species connect in a manner analogous to the rodlike micelles). At this point in time, there is no experimental data that can lead one to disregard either pathway.

It is easy to rationalize the formation of "salt-like" organic-inorganic array formations at near ambient temperatures as has been observed using silica and other metal oxides.[39,40,43,50] In Figure 7 we illustrate the proposed phase transitions that may occur in the preparation of mesoporous materials. Note that at low temperature when silica is not highly condensed, phase transitions can be reversible.[43] Additionally, one must be careful to distinguish between high and low temperature conditions since their behaviors do not have to be mutually compatible.

As mentioned previously, Yanagisawa et al.[4] have synthesized mesoporous silicas from kanemite and organic surfactant molecules. Here we distinguish the work of Yanagasawa et al. from that of Inagaki et al.[51,52] since we believe the latter investigations just formed MCM-41 using kanemite as the source of silica.[3] We have repeated the work of Yanagisawa et al. and proposed the following mechanism for the formation of mesoporous materials derived from kanemite at temperatures around 60-80°C (refer to Figure 8).[53]

The interlayer Na^+ cations in kanemite are exchanged by $C_{16}TMA^+$ cations that pillar the kanemite layers. Since kanemite has all Q^3 silicon, the $C_{16}TMA^+$-kanemite can be viewed almost like the organic-inorganic "salt" arrays observed when silica is added
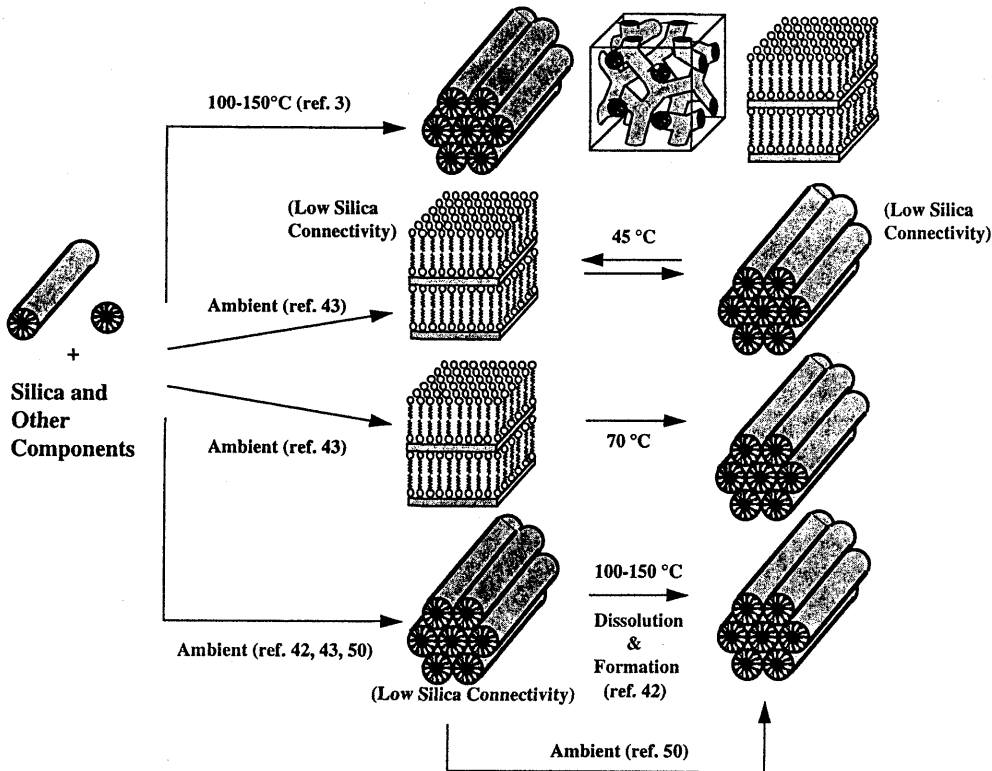

Figure 7. Summary of proposed phase transitions in the preparation of mesoporous materials.
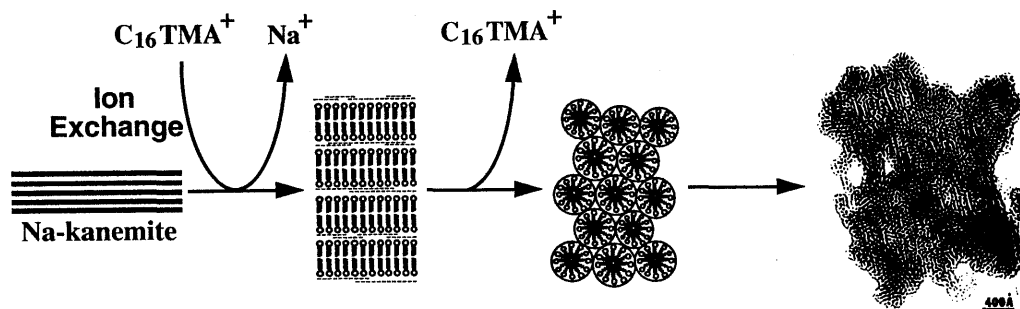
Figure 8. Proposed mechanism for the formation of mesoporous materials from kanemite. Adapted from reference 53.

to solutions of surfactants.[40,42,43,50] Next, the silicate species in the kanemite layers are reorganizing under the influence of the polar head group of exchanged surfactant cations. That is, the silicate single layers of kanemite are broken up and the silicate species are locally rearranged. Although the inorganic layers are initially ordered by the intercalated bilayers of the exchanged surfactant cations, the loss in structural integrity of the kanemite layers in combination with the ability of the surfactant molecules to change from a bilayered structure to a cylindrical micelle-like aggregate drives the reorganization of the organic-inorganic composite material. The silicate further rearranges to surround the forming cylindrical micelle-like aggregates, and condensation of silanol groups results in the formation of a three-dimensional inorganic network. During this process some of the $C_{16}TMA^+$ cations are displaced from the inorganic-organic composite phase. If the proposed mechanism is qualitatively correct, then it is apparent that the use of molecules that form micelle-like aggregates are required and single-layered silicates are most likely necessary because they would be the easiest of all layered silicates to allow for local destruction of their structure. Thus far, these types of reagents are the only ones that have allowed the formation of mesoporous materials with preparation methods of this type (molecules that do not form micelles and layered silicates that are not all Q^3 silicon do not form mesoporous materials).[53]

SYNTHESIS OF MICROPOROUS AND MESOPOROUS MATERIALS

A comparison of the routes by which zeolites and ordered mesoporous materials (high T and pH preparations) are produced shows that many of the mechanistic steps appear to be similar. Here we provide an overall mechanism for the organic mediated syntheses of ordered porous (upon removal of organic species) materials.

Addition of organic species into aqueous media can cause water to be organized in the vicinity of the organic. We believe that organic species that do not organize water will not function as structure-directing agents.[1,7,9] At high pH, hydroxyl ions catalyze the depolymerization of silica when the silicon source is non-monomeric, e.g., amorphous silica, fumed silica, etc. Soluble silicate species interact with the hydrated organic components via coulombic and van der Waals interactions and the quaternary ammonium ions assist in the condensation of the silicate species. Thus, the geometry of the organic species is translated into the inorganic component through multipositional molecular-level interactions (both coulombic and van der Waals; van der Waals interactions occur after silicate species condense to form hydrophobic regions). These organic-inorganic composite species then combine to form materials containing longer-range order. The driving forces for the assembly process include the favorable organic-inorganic inter-actions and the entropic gain by the release of ordered water around the organics when it is substituted by silicon species. With microporous materials, the inorganic portion can form crystalline structures. It is important to point out that the properties of the inorganic species are critical to the final structures that can be formed. For example, with tetraethylammonium hydroxide, zeolites ZSM-12, beta and VPI-8 are formed when the inorganic gel compositions are pure SiO_2, $SiO_2/Al_2O_3 \leq 50$ and $SiO_2/ZnO < 100$, respectively.[9] The addition of heteroatoms to silicates stiffens the T-O-T angle from Si-O-Si and shifts the optimum angle to a value lower than expected in pure silicates.[9] Thus, the heteroatom-containing frameworks will

most likely contain smaller T-O-T angles. When forming mesoporous materials this feature is not that critical since the inorganic portion is no longer crystalline. For the mesoporous materials, the number of cations requiring anionic silicate species for charge balancing is quite high. For example, with MCM-41 the product ratio of Si/N is approximately 3.5-4.5. This very low Si/N ratio is at least one reason why the MCM-41 (MCM-48) materials do not form crystalline inorganic walls; the fraction of silicon that charge compensates the organic species is too high to allow a crystalline oxide to form. With zeolites, typical Si/N ratios are 7 (worst case; zeolite beta) - 23 (ZSM-5).

The synthesis of zeolites and ordered mesoporous materials can be rationalized by a unified strategy of self-assembly involving structure-direction via numerous non-covalent interactions between organic and inorganic species that work in concert to create order on increasing length-scales throughout the synthetic process. Additionally, and unlike the mesoscopic phases formed in binary organic-water systems, the organic-inorganic composite materials formed at elevated temperatures are most likely produced by kinetically controlled processes. These are some of the same concepts that arise in biological assemblies, in both purely organic or organic-inorganic composites (biomineralization).

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