Molecular or Supramolecular Templating: Defining the Role of Surfactant Chemistry in the Formation of Microporous and Mesoporous Molecular Sieves

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We have explored the ability of alkyltrimethylammonium surfactants of the type $C_nH_{2n+1}(CH_3)_3NBr$ to serve as structure directing agents, or templates, for the formation of microporous or mesoporous molecular sieve frameworks. At equivalent gel compositions and reaction conditions, it was observed that the alkyl chain length of the surfactant molecule dictated the nature of the silicate product obtained. Over the entire range of synthesis temperatures examined (100–200 °C), the shortest alkyl chain length surfactant ($n = 6$), produced amorphous or microporous zeolitic materials, such as ZSM-5. The zeolite contained the intact surfactant cation consistent with a commonly observed molecular templating effect. At 100 °C, as the surfactant chain length was increased ($n = 8, 10, 12, 14,$ and 16), the formation of mesoporous molecular sieves (MCM-41) was observed. In these cases, a combination of surfactant chain length and reaction conditions favor surfactant aggregation (micelles), and hence, the formation and utilization of supramolecular templates. At synthesis temperatures of 200 °C, zeolitic and dense-phase products were obtained for even the higher alkyl chain lengths, suggesting that these supramolecular aggregates were disrupted and molecular structural direction dominated. ^{13}C CP/MAS data of MCM-41 and zeolitic materials prepared with identical surfactants indicates that the role of the organic directing agent is different in the formation of these two classes of materials. MCM-41 materials have NMR spectra that suggest a micellar array of surfactant and the zeolite materials exhibit spectra that are indicative of a more rigid, isolated environment for the surfactant. The data are consistent with a hypothesis that single surfactant molecules serve to direct the formation of microporous materials whereas mesoporous molecular sieves, such as MCM-41, are formed by surfactant aggregates. These results reinforce the LCT (liquid-crystal templating) mechanism proposed for the formation of the mesoporous MCM-41 materials and further add to our understanding of the formation of inorganic porous materials.

Introduction

The design of complex organic structures is guided by an arsenal of rational synthetic pathways. One may construct, in a stepwise manner, a structure of desired dimensions and functionality by choice of appropriate building units and reaction conditions. In sharp contrast, a challenge facing the molecular sieve chemist is the rational design of complex *inorganic* frameworks such as those observed in zeolitic materials. For these oxide frameworks, the formation usually take place via an extraordinarily complex array of reactions in media where the reactants (organic and/or inorganic species) and conditions can be continuously changing and various equilibria are established. Thus, understanding of synthetic pathways for these inorganic materials is usually limited to an analysis of the final structure and a rationalization of how structural components may have led to its synthesis.

Zeolite and molecular sieve scientists have speculated concerning the mechanisms reponsible for building complex inorganic frameworks. It has been postulated, for example, that small oxide clusters containing double-four, -five, or -six rings of alternating silicon and oxygen atoms may serve as secondary building units (SBU) of large silicate frameworks. Furthermore, other species such as three- and four-membered silicate rings have also been postulated.[1-6] Despite spectroscopic evidence for such species in heterogeneous gels producing zeolites, there is little information on how, or even if, such units assemble to form the final structures. In fact, there has been speculation that these SBU may not be stable at the elevated temperatures and high alkalinity levels that are typically required for zeolite formation.[7-10]

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Another broadly studied area concerning the formation of molecular sieve materials concerns the concepts of structural directing agents or templates. Templating has been defined, in a general sense, as a process in which an organic species functions as a central structure about which oxide moieties organize into a crystalline lattice.[1,11,12] With the benefit of further insight into the mechanisms of formation of molecular sieves which has been gained in the past several years, Davis has elaborated on the above definition to include the role of the organic molecules as (1) space-filling species, (2) structural directing agents, or (3) templates.[1] In the simplest case of space filling, the organic merely serves to occupy a void about which the oxide crystallizes. Therefore, the same organic can be used to synthesize a variety of structures or vice versa. Structural direction requires that a specific framework is formed from a unique organic compound. However, this does not imply that the resulting oxide structure mimics identically the form of the organic molecule. True "templating" requires, in addition to the structural directing component, that there is an intimate relationship between the oxide lattice and organic form such that the synthesized lattice contains the organic "locked" into position. Thus the lattice reflects the identical geometry of the organic molecule.[1]

Given the above, it is likely that a broader understanding of the crystallization mechanisms of zeolitic and molecular sieve materials can be obtained by a detailed examination of the tendencies of organic molecules to direct the formation of a particular structure. An understanding of how organic molecules interact with each other and with the inorganic frameworks that they template would increase our ability to design rational routes to molecular sieve materials.

Toward this end, we have recently described[13,14] the synthesis of a new family of silicate/aluminosilicate mesoporous molecular sieves designated as M41S. We have proposed a mechanism for their formation (liquid–crystal templating, LCT), in which supramolecular assemblies of alkyltrimethylammonium surfactants serve as one component of the operative template for the formation of these materials.[14] The discovery of these new materials leads to an extension of the structure directing, or templating concepts. In the formation of these mesoporous materials a combination of supramolecular cationic surfactant aggregates and anionic silicate species comprise the functional templating agents. Others have recently elaborated on this mechanism.[15,16] The ability to tailor these surfactant assemblies so that

they may be used to design novel molecular sieve materials is a preliminary step in progressing the rational synthesis of inorganic frameworks.

Herein we begin to probe the differences between synthetic pathways leading to the formation of zeolites and those leading to the formation of mesoporous M41S type materials. We explore the boundaries of reaction conditions and surfactant chain length which favor formation of microporous zeolites or mesoporous M41S materials.

Experimental Section

Materials. The silica source was sodium silicate, N brand, 29 wt % silica obtained from P. Q. Corp. The quaternary ammonium surfactant compounds [$C_nH_{2n+1}(CH_3)_3NBr$ for n = 6, 8, 10, 12, 14, and 16] were obtained from Kodak and American Tokyo Kasei. Sulfuric acid (96.1%) was obtained from J. T. Baker Chemical Co. All chemicals were used as received.

Instrumentation. X-ray powder diffraction was obtained on a Scintag XDS 2000 diffractometer using Cu Kα radiation of wavelength 1.541 78 Å, a step size of 0.05° 2θ, a counting time per step of 5 s, and an energy-dispersive detector. Peak positions and peak amplitudes were obtained using a deconvolution algorithm supplied by Scintag.

^{13}C CP/MAS NMR spectra were obtained on a Bruker MSL-400 spectrometer at 100.6 MHz using a contact time of 1.5 ms, 6.0 μs pulses, a 2.5 s recycle delay, and a spinning rate of 3.5 kHz. ^{13}C solution NMR data were obtained on a Bruker AM-250 spectrometer at 62.9 MHz using 20 wt % solution in D_2O, gated decoupling, and a 30 s delay.

Synthesis. For this study we chose a simple reactant gel composed of surfactant halide, sodium silicate, and water. To make a direct comparison between surfactants, each reaction was carried out at an equivalent surfactant:silica mole ratio (0.5), surfactant concentration (11 wt %), and pH (10). Each experiment was carried out according to the following procedure:

Water, surfactant halide, sodium silicate (37.4 g), and 10 wt % sulfuric acid (11.2 g) were combined, in order, with stirring. The reactant weights of the water and the individual surfactant halides for each experiment are shown in Table 1.

In all cases except for the C_{16} system, the water–surfactant mixture was a clear solution, at room temperature, prior to the addition of the silicate source. For the C_{16} system, the mixture required a slight elevation of temperature (~35–40 °C) for the surfactant to be completely dissolved. The silicate–surfactant mixtures were allowed to stir for approximately 30 min and then the pH was adjusted to 10 by the addition of small amounts of 50 wt % sulfuric acid (Table 1). The resultant gels were then crystallized for 6 days under static, autogenous conditions in polypropylene bottles (100 °C) or stainless steel Parr bombs (at 150 or 200 °C). After cooling to room temperature, the solid products were recovered by filtration on a Buechner funnel, washed thoroughly with distilled water, and air dried. The products were then calcined at 540 °C for 1 h in flowing nitrogen, followed by 6 h in flowing

Table 1. Preparation of Reaction Mixtures

surfactant cation $C_nH_{(2n+1)}(CH_3)_3N^+$ n	grams of water[a]	grams of surfactant[b]	grams of 50% H_2SO_4[c]
6	160	20.6	2.5
8	167	23.2	2.7
10	175	25.8	2.3
12	183	23.0	2.1
14	190	29.9	3.0
16	199	33.5	1.9

[a] Water was adjusted to make each surfactant 11 wt % of total mixture. [b] Each surfactant quantity represents 0.092 mol of surfactant; surfactant:silica mole ratio = 0.5. [c] Amount of 50 wt % acid added to adjust to pH = 10.

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A
100°C

B
150°C

C
200°C
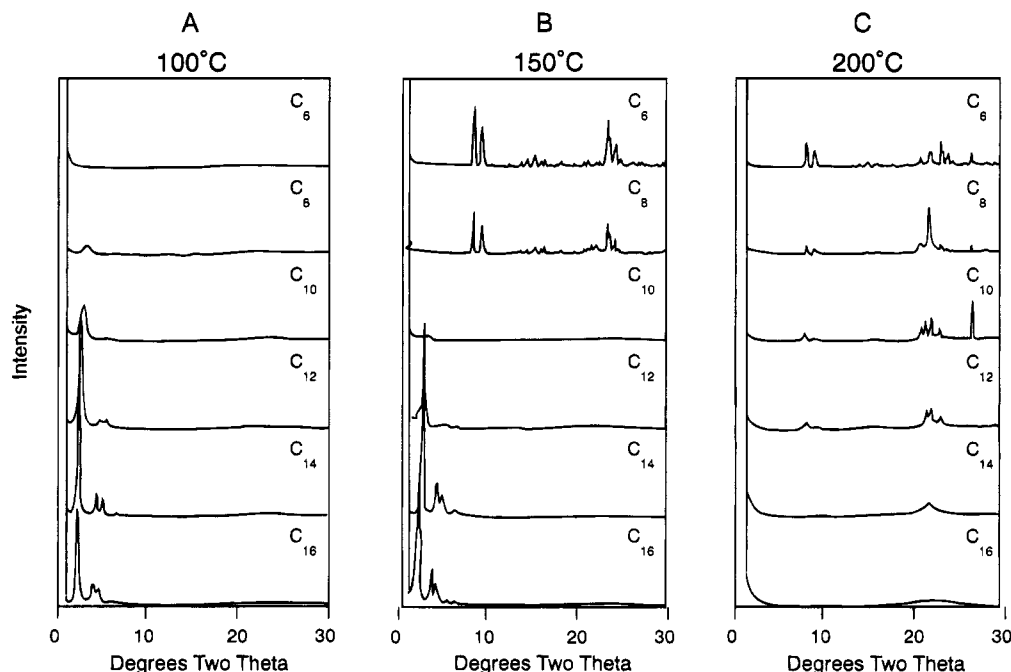
Figure 1. X-ray powder diffraction patterns of calcined products formed using surfactant having alkyl chain lengths of $n = 6$, 8, 10, 12, 14, and 16 at (A) 100 °C, (B) 150 °C, and (C) 200 °C.

Table 2. Elemental Analyses of Preparations at Various Temperatures

surfactant cation $C_nH_{2n+1}(CH_3)_3N^+$		wt %				C/N molar ratio	N/Si molar ratio	pro-duct[a]
n	temp, °C	C	N	Si	Ash			
6	100	7.52	0.76	36.8	82.0	11.5	0.04	A
	150	6.90	0.74	41.1	87.1	10.9	0.04	Z
	200	4.39	0.67	43.7	92.1	7.6	0.03	Z
8	100	16.1	1.48	33.1	68.3	12.7	0.09	M
	150	6.26	0.62	41.2	89.4	11.8	0.03	Z
	200	1.39	<0.5	45.3	98.3		<0.02	Z
10	100	25.5	2.17	25.9	53.2	13.7	0.17	M
	150	18.0	1.59	30.6	65.8	13.2	0.10	M
	200	2.93	<0.5	45.0	95.8		<0.02	Z
12	100	28.1	1.97	25.6	52.2	16.6	0.15	M
	150	20.6	1.40	30.7	67.5	17.1	0.09	M
	200	4.05	<0.5	42.5	94.1		<0.02	Z
14	100	30.5	1.84	23.9	49.5	19.3	0.15	M
	150	24.6	1.27	26.9	60.4	22.6	0.10	M
	200	29.4	1.60	27.4	64.5	21.4	0.12	A
16	100	45.6	2.49	12.7	26.3	21.4	0.39	M
	150	34.4	1.89	20.3	47.0	21.2	0.19	M
	200	33.5	1.53	25.3	56.7	25.5	0.12	A

[a] Determined by XRD: A (amorphous), M (MCM-41 type), and Z (zeolitic).

air. The X-ray powder diffraction patterns of the calcined products are shown in Figure 1a (100 °C), 1b (150 °C), and 1c (200 °C). The chemical analyses of the as-synthesized products are shown in Table 2.

Results and Discussion

At the lowest synthesis temperature (100 °C), the C_6 surfactant preparation produced amorphous material with no evidence of the formation of either zeolites or microporous material. As the surfactant chain length increased, MCM-41 materials were formed and no zeolitic products were observed. The C_8 and C_{10} surfactant compositions produced MCM-41 type materials but with less well-defined X-ray powder diffraction

patterns. Well-defined MCM-41 exhibiting three or four X-ray diffraction peaks, which could be indexed on a hexagonal lattice, was synthesized from C_{12}, C_{14}, and C_{16} surfactant containing mixtures.

At 150 °C, both the C_6 and the C_8 surfactant preparations produced well-crystallized zeolitic ZSM-5 type products. The use of surfactants to template microporous materials such as zeolites has been previously described.[17] Ill-defined MCM-41 type materials having one or two low-angle X-ray powder diffraction peaks were produced from both the C_{10} and C_{12} preparations. The C_{14} and C_{16} surfactant derived products were well crystallized MCM-41 materials displaying discrete hexagonal X-ray diffraction patterns.

At 200 °C, the formation of zeolitic materials, ZSM-5 for the C_6 surfactant and mixtures of ZSM-5, ZSM-48, and dense phases for the C_8-C_{14} surfactants, was evident except for the C_{16} product which was amorphous. For the synthetic conditions used there was no evidence of MCM-41 materials for any of the various surfactant chain lengths at 200 °C.

Formation of ZSM-48 and/or ZSM-5 from very similar synthesis gels is often observed, particularly in highly siliceous gel media.[18] The materials both have structures containing the ferrierite sheet that occurs in ZSM-5, ZSM-11, ZSM-48, ZSM-22, and ZSM-35 (synthetic ferrierite). The structures of ZSM-48, ZSM-5, and ZSM-11 are closely related. The channel systems of ferrierite (ZSM-35), ZSM-5, and ZSM-48 do not preclude the inclusion of a long-chain quaternary amine as has previously been reported.[17b,c,18]

As noted above, some of our zeolite preparations (as shown by the X-ray diffraction patterns) contain ZSM-

(17) See for example: (a) Jacob, N. E.; Joshi, P. N.; Shaikh, A. A.; Shiralkar, V. P. *Zeolites* **1993**, *13*, 430–434. (b) Beck, J. S.; Schlenker, J. L., U.S. Patent 5,213,786, May 25, 1993. (c) Davis, M. E. Presentation at 1994 MRS Meeting, Boston, MA, April 1994; and MRS Symposium Series, *Better Ceramics Through Chemistry VI*, in press.

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48 as one of the materials crystallized, for example, ZSM-48 crystallized in the C_8 containing preparation at 200 °C. For these reasons we do not make great distinctions in Table 2 as to the zeolites formed (besides those for the C_6 surfactant which are highly crystalline ZSM-5) because they are often observed to be mixtures of ZSM-5 and/or ZSM-48, along with some dense phases. In this regard, Table 2 merely lists the acronym Z when referring to the synthesis product, referring to the formation of a mixture containing zeolitic products.

The elemental analyses of the synthetic products (Table 2) also are reflective of the material produced. MCM-41 type materials retained relatively high levels of surfactant as indicative by the lower ash weight percentage. Typically the N/Si molar ratios were >0.10 for these mesoporous materials, whereas those forming the zeolitic products has ratios <0.05. The amorphous materials had ratios somewhat between these two values. The C/N molar ratios of all the products suggest that the surfactant molecule remained intact regardless of the product obtained. Although these values were not too precise, the C/N ratios started about 10 derived from the C_6 system (compared to an expected value of 9) and increased to about 22 for the C_{16} system (expected value of 19).

Note that a wide range of crystallinities exists for the synthesized MCM-41 materials. This suggests that the micellar type arrangement proposed as template may or may not be well formed at the time when the silica polymerizes to form the MCM-41 structure. The poor level of crystallinity observed for the materials with C_8 and C_{10} surfactants is consistent with the idea that at these chain lengths, solution energetics are only marginally favorable for micellar/silicate interactions to occur. At the slightly longer C_{12} chain length conditions are optimal to form well crystallized MCM-41.

The lower quantities of organic in the C_8, C_{10}, and C_{12} zeolitic materials in the 200 °C preparations, compared to that found for the C_6 zeolites, may be understood since the zeolites prepared at these conditions are not of high crystallinity (as may be inferred from the diffraction patterns compared to the C_6 materials which are clearly identified as ZSM-5) and contain mixtures of ZSM-5, ZSM-48, and dense phases. Indeed, the C_8 and C_{10} samples contain some dense phase materials (quartz-type diffraction lines between 20 and 25° 2θ which cannot contain template. ZSM-48 which contains a single linear channel system is expected to contain less organic than the two-dimensional ZSM-5 system.

The ^{13}C NMR spectra of pure $C_{12}H_{25}(CH_3)_3N^+$ in solution, as crystalline solid, and of materials synthesized with it at 100, 150, and 200 °C are presented in Figure 2. The data in Figure 2 confirm that the $C_{12}H_{25}$-$(CH_3)_3N^+$ remains intact during the formation of the MCM-41 or the zeolite. These NMR data support the role of the surfactant as structure directing agent in the synthesis of mesoporous MCM-41 and microporous zeolitic materials.

Comparison of the solution- and solid-state NMR spectra (Figure 2A,B) for $C_{12}H_{25}(CH_3)_3N^+$ reflects the differences in the mobilities and local environments of the carbon atoms in each of these species. The much broader resonances observed for the surfactant in the crystalline solid relative to solution are indicative of the
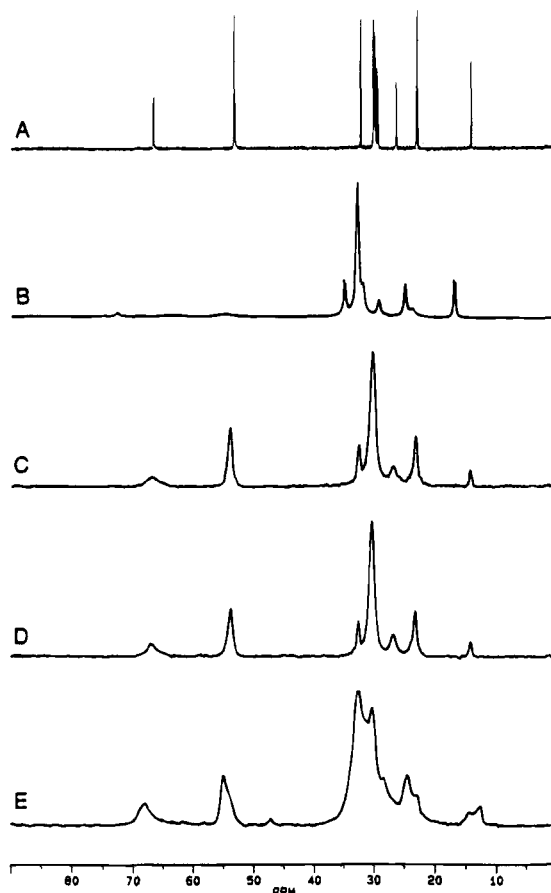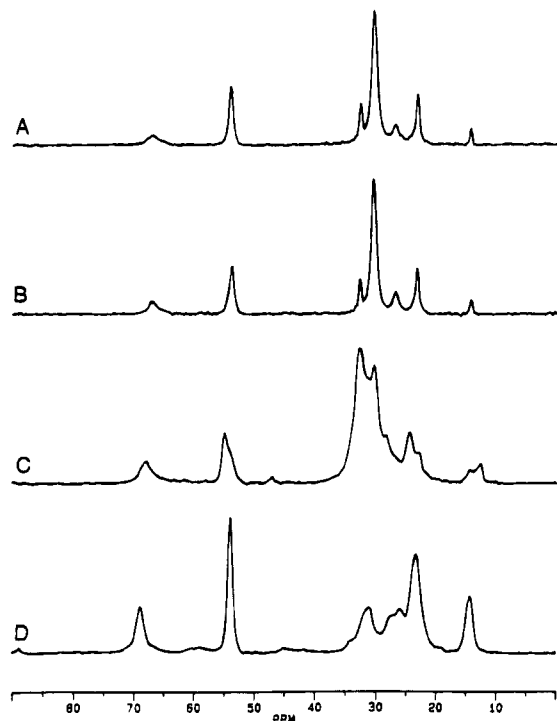

Figure 2. ^{13}C NMR spectra of $C_{12}H_{25}(CH_3)_3N^+$ in (A) solution, (B) crystalline solid, (C) in synthesized MCM-41 at 100 °C, (D) in MCM-41 at 150 °C, and (E) in zeolite at 200 °C.

higher packing density in the solid and the greater mobility in solution. Also the slight differences in chemical shifts observed in the solid versus solution indicate differences in the local carbon environments and demonstrate how sensitive the shifts are to slight changes in these environments.

Comparison of the solution and solid state NMR spectra for $C_{12}H_{25}(CH_3)_3N^+$ with the spectra of the MCM-41 materials synthesized (Figure 2A,B versus Figure 2C,D) with this surfactant cation show relatively sharp resonances for the cations in MCM-41 with shifts that are similar to those observed for the surfactant cation in solution. Thus, the NMR chemical shift data indicate that the organic cation is in a more fluid like micellar environment, similar to the surfactant in solution, in the MCM-41 materials. The presence of a micellar array in the MCM-41 is further substantiated by differences in the cross-polarization behavior of the solid organic cation and of the cation in MCM-41. That is, the mobility of the hydrocarbon ends in the MCM-41 case are reflected in the decrease in spectral intensity for the methyl groups at 12 ppm. Yet, since the polar ends of the surfactant in MCM-41 can be cross polarized demonstrates that the surfactant is not simply present as a solution species.

Comparison of the NMR spectra of the zeolitic material and the MCM-41 materials (Figure 2E versus 2C,D) synthesized with the $C_{12}H_{25}(CH_3)_3N^+$ surfactant show broader peaks for the zeolite case. Although the resonances are broader, the individual chemical shifts are similar to the solution species. The similar chemical

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Figure 3. ^{13}C NMR spectra of MCM-41 material synthesized by $C_{12}H_{25}(CH_3)_3N^+$ (A) at 100 °C, (B) at 150 °C, (C) zeolite material synthesized at 200 °C, and (D) zeolite material synthesized by $C_6H_{25}(CH_3)_3N^+$ at 150 °C.

Figure 4. Proposed mechanistic pathways for the formation of (A) microporous materials and (B) mesoporous materials.

shifts indicate that the surfactant molecules are not densely packed together as in the crystalline solid but are indeed isolated from each other within the zeolitic void space. The spectral broadening is more likely due to the effect of the size and shape of the channel walls of the zeolite on the surfactant occluded within the channels. This effect is also observed for zeolite synthesized with other surfactants. For example, shown in Figure 3 are the ^{13}C CP/MAS spectra of the MCM-41 and zeolite materials synthesized with $C_{12}H_{25}(CH_3)_3N^+$ and the spectrum of a zeolite synthesized with C_6H_{25}-$(CH_3)_3N^+$. Comparison of the spectra of the two zeolites with the two MCM-41 materials are consistent with the surfactant being in a more rigid and confined environment in the zeolite.

The above results reinforce the hypothesis that M41S materials are formed through a mechanism in which aggregates of cationic surfactant molecules in combination with anionic silicate species form a supramolecular structure, whereas microporous materials formed by molecular organic species. Aggregation of surfactants to form liquid-crystal species with smaller alkyl chain length quaternaries such as C_6 and C_8, under most conditions, is generally an energetically unfavorable event.[19,20] The solubilities of these short chain quaternaries are quite high (>50 wt % in water is easily achieved), and aggregated structures are not necessary to minimize hydrophobic interactions. Thus, it may be expected that these quaternaries present in the reaction mixture at equivalent concentration to their longer chain counterparts do not easily form the supramolecular aggregated structure implicated in the formation of MCM-41.
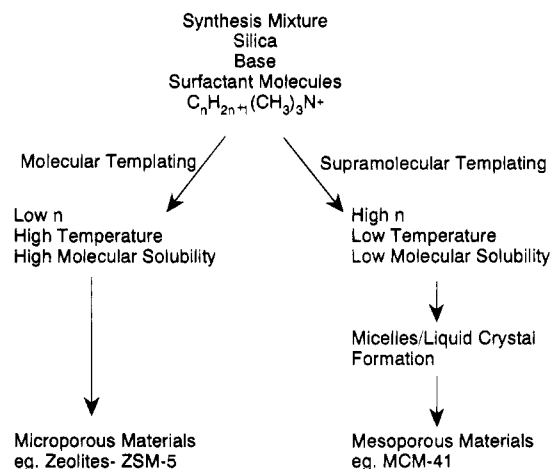
The short-chain surfactant molecule appears to function more like a single-chain, pore-filling agent related to even smaller alkyl chain length quaternaries such as tetramethylammonium, tetraethylammonium, etc. The resultant product is microporous. On the other hand, micellar and liquid-crystal structure formation would be favorable for the larger alkyl chain length surfactants, resulting in mesoporous products. These proposed synthesis pathways are illustrated in Figure 4.

The effect of temperature on the surfactant preparations that form M41S materials also supports this supramolecular aggregation mechanism. As indicated above, MCM-41 products were obtained at 100 °C, and crystallinity (as determined by XRD) improved with increasing surfactant chain length. At the higher temperature (150 °C) only the C_{14} and C_{16} systems form well-defined hexagonal structures within this set of conditions. These data are consistent with a boundary of phase stability for particular surfactant phases within particular chemical composition and temperature regimes, a concept well documented in solution chemistry of surfactants.[19,20]

Finally at 200 °C, MCM-41 type products are not observed suggesting that even for these longer alkyl chain length surfactant systems, micellar formation is not favorable or has been disrupted.

Interestingly, under the synthesis conditions used, the products were either zeolites or M41S type materials. No cocrystallization products were observed. This suggests that the mechanism for the formation of M41S materials may not implicate the same intermediates or follow the same pathways proposed for formation of zeolites.

The idea that a supramolecular assembly of molecules can serve as a templating agent contrasts considerably with the zeolite chemist's extensive experience with classical templating phenomena. As stated above, only in rare instances has a particular organic molecule been used to produce a specific zeolite whose internal cavities conform rigorously to the molecular shape. For example, the molecular fit of a $C_{18}H_{36}N^+$ triquaternary amine (tri-quat) in the structure of the Mobil zeolite ZSM-18 is, perhaps, the most elegant example of organic templating.[21,22] Examples of templating in a broader sense include the synthesis of SSZ-24 with an adamantamine derivative[23] and the synthesis of hexagonal

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faujasite with an 18-crown-6 template.[24-27] Other materials have been prepared in which there is at least some steric relationship between an organic and an inorganic framework. Thus, in traditional zeolite synthesis, there has been little opportunity to "tailor" make a desired inorganic species by designing a particular template. This occurs, in part, because the fully crystalline lattices, associated with traditional zeolitic materials are subject to a limited array of bond angles and structural subunits dictated by synthetic conditions and framework composition.

Greater flexibility in tailoring M41S materials may be integrally linked to the wide range of flexibility in bond angles accorded a material which does not possess the fully crystalline framework of a traditional zeolite. In this case, one may introduce directed perturbations in the system, such as changing the surfactant chain length or adding solubilizates, to realize a profoundeffect in the final silicate products.[14] Thus, there is great opportunity to study the interactions between the aggregates of surfactant molecules which form the M41S templates and the inorganic matrices which form around them. An understanding of these interactions becomes particularly important when one realizes that the identical surfactants used in the synthesis of M41S may also be used to form zeolitic materials.

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