Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Materials

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The low-temperature formation of liquid-crystal-like arrays made up of molecular complexes formed between molecular inorganic species and amphiphilic organic molecules is a convenient approach for the synthesis of mesostructure materials. This paper examines how the molecular shapes of covalent organosilanes, quaternary ammonium surfactants, and mixed surfactants in various reaction conditions can be used to synthesize silica-based mesophase configurations, MCM-41 (2d hexagonal, $p6m$), MCM-48 (cubic $Ia3d$), MCM-50 (lamellar), SBA-1 (cubic $Pm3n$), SBA-2 (3d hexagonal $P6_3/mmc$), and SBA-3 (hexagonal $p6m$ from acidic synthesis media). 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. The effective surfactant ion pair packing parameter, $g = V/a_0l$, remains a useful molecular structure-directing index to characterize the geometry of the mesophase products, and phase transitions may be viewed as a variation of g in the liquid-crystal-like solid phase. Solvent and cosolvent structure direction can be effectively used by varying polarity, hydrophobic/hydrophilic properties and functionalizing the surfactant molecule, for example with hydroxy group or variable charge. Surfactants and synthesis conditions can be chosen and controlled to obtain predicted silica-based mesophase products. A room-temperature synthesis of the bicontinuous cubic phase, MCM-48, is presented. A low-temperature (100 °C) and low-pH (7−10) treatment approach that can be used to give MCM-41 with high-quality, large pores (up to 60 Å), and pore volumes as large as 1.6 cm^3/g is described.

Introduction

Considerable synthesis effort has been devoted to developing frameworks with pore diameters within the mesoporous range (2−50 nm) because of their possible use as catalysts, hosts for inclusion compounds and molecular sieves. Recently, scientists[1−5] at Mobil Oil Research and Development have synthesized a new family of mesoporous molecular sieves (M41S) with regular, well-defined channel systems by the crystallization of aluminosilicate or silicate gels in a concentrated solution of alkyltrimethylammonium ions. Many results in this research field have been reported, such as various synthesis and formation mechanisms for the M41S family (MCM-41, MCM-48, and MCM-50),[1−14] the syntheses of silica and alumina mesoporous materials with non-ionic polyethene oxide surfactants,[15,16] the synthesis of high aluminum MCM-41,[17−19] the synthesis of mesoporous materials by using a layered silicate (kanemite),[4,20−22] layered mesophase formation,[23] grafting metallocene complexes onto MCM-41,[24] template interaction and removal,[25] ion exchange and thermal stability of MCM-41,[26] the syntheses and catalysis of

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Ti-MCM-41,[27−29] V-MCM-41,[30] B-MCM-41,[31,32] Fe-MCM-41,[33] Mn-MCM-41, Mn-MCM-48,[34] V-MCM-48,[35] and Ti-MCM-48.[36] Some mesostructured transition element and other main-group element oxides have also been described.[6,7,37−42] A generalized synthesis method has been developed for a wide range of transition and main-group-element oxide mesostructured materials with cationic and anionic surfactants, using acidic and basic media (e.g., SBA-1, SBA-2 and SBA-3), low concentration of surfactants, and low reaction temperatures.[6,10,43] Previous research[1−5,10−13] has focused primarily on the synthesis and characterization of MCM-41 and MCM-48 containing alkyltrimethylammonium structure-directing agents. A systematic study on the structure directing effects of different quaternary ammonium surfactants has not been yet reported.

In general, molecular sieve and zeolite design is determined by the addition of a specific molecular species such as Et_3N and Me_4N^+ to the reaction mixture.[44] The exact role of the organic species and the mechanism by which they affect the formation of the product structure are only recently undergoing clarification.[45−47] In some cases, the organic species (so-called structure-directing agent or template) can be carefully chosen to synthesize designed zeolite structures[48] with inorganic condensation around a single organic molecule.

In contrast, biphasic mesostructures, such as MCM-48 and SBA-2, consist of spatially and chemically well-defined arrays of both inorganic species and organic molecules. The inorganic and organic arrays of these mesostructures meet at an interface surface. The interface curvature is energetically defined so as to optimize charge repulsion and van der Waals interactions. Phase transitions are associated with changes in the curvature of interface and may be understood phenomenologically as a competition between the elastic energy of bending the interfaces and energies resulting from the constraints of interfacial and charge separation.[49] Hence, size, charge, and shape of surfactants are important structure-determining parameters. These mesostructures can be generated through hydrogen-bonded, ionically or covalently bound inorganic/organic molecular units so that the formation of liquid-crystal-like biphase mesostructures should be subject to the usual structural constraints of liquid crystals.

The classical and contemporary *molecular* description of surfactant organization in amphiphilic liquid-crystal arrays is described in terms of the local effective surfactant packing parameter,[50,51] $g = V/a_0l$, where V is the total volume of the surfactant chains plus any cosolvent organic molecules between the chains, a_0 is the effective head group area at the micelle surface, and l is the kinetic surfactant tail length or the curvature elastic energy.[49] The interface surface bending energy can be written in terms of g, the actual surfactant packing parameter adopted by the aggregating chains in the phase.[52,53] The counterion in this classical model is not explicitly included.

In this paper, as a first approximation we explore the use of the molecular surfactant packing parameter to explain and predict product structure and phase transition. In classical micelle chemistry, as the g value is increased above critical values, mesophase transitions occur. The expected mesophase sequence as a function of the packing parameter is[52,54]

g	mesophase
$^1/_3$	cubic ($Pm3n$)
$^1/_2$	hexagonal (p6m)
$^1/_2$–$^2/_3$	cubic ($Ia3d$)
1	lamellar

Since $g = V/a_0l$, the value of g increases as: a_0 decreases; V increases; and l decreases. These transitions reflect a decrease in surface curvature from cubic

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($Pm3n$) through vesicular and lamellar. For surfactants to associate in a spherical structure, the surface area occupied by the surfactants polar head group should be large. If on the other hand the head groups are permitted to pack tightly, the aggregation number will increase, and rod or lamellar packing will be favored. The values of g (between $^1/_2$ and $^2/_3$) for the cubic ($Ia3d$) phase depend upon the volume fraction of surfactant chains.[52]

Among the wide variety of structures[54,55] that can be observed in surfactant or lipid containing lyotropic systems, hexagonal ($2d$, $p6m$) and lamellar phases are the two most common mesophases. Six lyotropic cubic phases, in which $Pm3n$ and $Ia3d$ are two typical mesophases, may be found in many surfactant and lipid systems (for a recent review, see ref 56). Several intermediate phases can be formed.[57,58] Similar systems follow the same succession of phases, but not all of the phases are always present. However, the formations of additional new lyotropic mesophases are also possible, as indicated by the fact that new cubic phases, which consist of micelles of type I (oil-in-water), appear to be present in some surfactant systems.[59−62] However, at this time no clear conclusions about the exact nature of the new phases have been obtained since the quality of the diffraction data is not adequate to determine their structures. Inorganic mesophases with good long-range ordering quality and better stability are helpful in characterizing new liquid-crystal-like structures.

New applications of mesoporous materials and the syntheses of new mesostructures materials require that we have a thorough understanding of the formation mechanism. Therefore, an investigation of structure directing effects of surfactants in mesoporous material syntheses is important from both the theoretical and practical points of view. In the present work we report the designed synthesis and postsynthesis hydrothermal treatment of silica-based mesoporous materials, the structure-directing effect of a series of surfactants in the formation of silica-based mesophases in both basic and strongly acidic synthesis condition, and the phase transition between different silica-based mesophases in hydrothermal conditions. In addition, the effects of mixed surfactants[43] and organic additives are discussed. The room-temperature synthesis of the bicontinuous cubic phase, MCM-48, is presented. A low-temperature and low-pH synthesis/treat approach that can be used to give MCM-41 with high quality (seven or more XRD peaks), large pores (up to 60 Å), and pore volume as large as 1.6 cm^3/g is described.

Experimental Section

Surfactants. The alkylammonium salts, $C_nH_{2n+1}(CH_3)_3NBr$ (n = 8, 10, 12, 14, 16, 18), are commercially available from Aldrich. $C_nH_{2n+1}(C_2H_5)_3NBr$ (n = 12, 14, 16, 18, 20, 22), $C_nH_{2n+1}(CH_3)_3NBr$ (n = 13, 15, 20, 22) and other one-chain one-charge head-group surfactants were synthesized and purified as described in ref 63. The hydroxy functionalized surfactants were synthesized as described in the literature.[64] The gemini surfactants $[C_nH_{2n+1}(CH_3)_2N-(CH_2)_s-N(CH_3)_2-C_mH_{2m+1}]Br_2$, designated as C_{n-s-m} ($n = m$ = 12, 14, 16, 18, 20, 22, s = 2−12) were synthesized using two methods (ref 65): (i) reaction of the α,ω-dibromoalkanes with alkyldimethylamine and (ii) reaction of alkanediyl-α,ω-bis(dimethylamine) with bromoalkylane. Divalent surfactants (C_{n-s-1}) were synthesized by reactions of the alkyldimethylamine with (3-bromopropyl)trimethylammonium bromide or corresponding bromoalkane with trimethylamine. All surfactants are bromides except where noted. Cetyltriethoxysilane was obtained from United Chemical Technologies.

Syntheses. Generally each of the silica mesophases (MCM-41, MCM-48, MCM-50, SBA-1, SBA-2, or SBA-3) was prepared as follows: first, quaternary ammonium surfactant was mixed with water and acid (e.g., HCl, HBr) or base (e.g., NaOH, tetramethylammonium hydroxide). To this solution tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), fumed silica (Cab-o-sil), or a silicate aqueous solution (e.g., sodium silicate, tetramethylammonium silicate) was added at room temperature and stirred for 30 min or longer. The mixture was then placed in an oven at 100 °C for a given time if a higher reaction temperature was required. The solid product was recovered by filtration on a Buchner funnel and dried in air at ambient temperature.

Postsynthesis Treatment. The dried sample from the basic synthesis system was mixed with 20−50 times its weight in water and the slurry was heated at 100 °C (or higher) for a given time.

Analyses. X-ray powder diffraction (XRD) patterns were taken on a Scintag PADX diffractometer equipped with a liquid nitrogen cooled germanium solid-state detector using Cu Kα radiation. The low-angle synchrotron X-ray diffraction pattern of the MCM-48 shown in Figure 8 was measured at Brookhaven National Laboratory. A Ge(111) incident beam monochromator and a Ge(220) analyzer were used to obtain a monochromatic wavelength of λ = 1.7048 Å.

High-resolution ^{29}Si MAS NMR spectra were recorded on a GE 300 spectrometer using ZrO_2 rotors. Measurement conditions were as follows: ^{29}Si resonance frequency, 59.705 MHz; pulse repetition, 240 s; pulse width, 7 μs; spinning speed, 5−6 kHz, standard, $Si(CH_3)_4$. The usual notation Q^x will be used for the Si sites, where x refers to the number of Si surrounding the central Si atom bridged by oxygen atoms. The nitrogen adsorption and desorption isotherm at 77 K were measured using a Micromeritics ASAP 2000 system. The data were analyzed by the BJH (Barrett−Joyner−Halenda) method using the Halsey equation for multilayer thickness. The pore size distribution curve came from the analysis of the adsorption branch of the isotherm.

Results and Discussion

1. Comparison of the Silica-Based Synthesis System with the Conventional Surfactant−Water Mixture.

In the conventional charged surfactant−water mixture, the micellar shape or packing of the surfactant is determined by a balance between three forces. One is the tendency of the alkyl chains to minimize their water contact and maximize their interorganic interactions; the second is the Coulombic interaction between the charged head groups; and, the third is the solvation energies. The packing parameter g provides a measure of the hydrophilic−hydrophobic balance, involving the first two of these interactions.

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In silica-based mesophase synthesis systems, the motions of surfactant molecules are limited to a certain degree. The strong interactions between silicate and surfactant (either ionic or covalent) and polymerization of silicate strongly influence the packing of the inorganic/organic array. To a first approximation, the effective packing parameter g can still be used to express the organic/inorganic ion pair packing, so that the synthesis of silica-based mesophases can be considered as the formation of lyotropic liquid crystals from a special surfactant system, in which inorganic species are attached to the surfactant. The synthesis system is thus similar to that of the conventional surfactant–water mixture, so that one can apply what is known of the surfactant–water and surfactant–additive–water mixtures to the silica-based synthesis system.

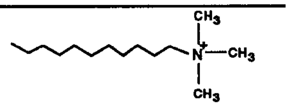
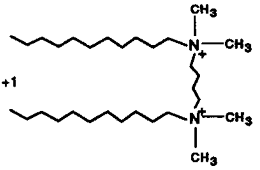
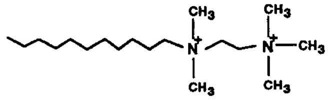
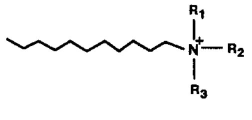
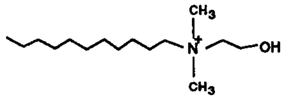
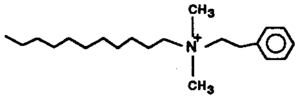
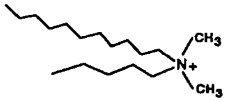
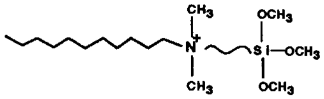
The final product phase is determined by surfactant molecule packing, which depends on the nature of the surfactant, the degree of polymerization of the silica framework, the interaction between the surfactant and the silica species, and other components of the reaction system. New mesophase behavior of the surfactant in this silica-based mixture system can be expected. This behavior will be helpful to further understand micelle and lyotropic liquid-crystal phases of the surfactant/molecular inorganic ion pairs.

For the systematic investigation of the formation of mesoporous materials, we selected a series of surfactants (see Table 1; with and without additive) which favor a range of g values when used as structure-directing agents to synthesize silica-based mesophases in different reaction conditions. The gemini surfactants are of particular interest since the effective head-group area can be systematically varied for a given organic tail length, e.g., from 1.05 nm^2 for $s = 3$ to 2.26 nm^2 for $s = 12$ for C_{12} tail.[66]

2. General Modification of *g* and Mesophase. The typical synthesis conditions and the results using TEOS as a silica source are listed in Table 2. The use of alkyltrimethylammonium ($C_nH_{2n+1}(CH_3)_3N^+$, $n = 10$, 12, 13, 14, 15, 16, 18) resulted in the formation of MCM-41. Under the conditions used here the odd number ($n = 13$, 15) surfactants do not show different structure-directing effects from the even number ($n = 14$, 16) surfactants.[67] Larger head-group surfactants (such as alkyltriethylammonium $C_nH_{2n+1}(C_2H_5)_3N^+$, $n = 12$, 14, 16, 18) favored SBA-1 in acidic media. Larger head-group surfactants are used in order to decrease the value of the surfactant packing parameter in order to generate maximum surface curvature.[50,52] With the variation of head groups of surfactants from H to C_2H_5, the products obtained in acid synthesis media (pH < 1) ranged from SBA-3 to SBA-1 (see Table 3). Bitailed surfactants gave lamellar phases in both acidic and basic media due to their larger hydrophobic volume, V, and their larger g value. The chiral surfactant, $C_{16}H_{33}N^+(CH_3)_2CH(CH_3)C_6H_5$, can be used to form MCM-41 and MCM-50 mesophases. The effect of the chirality of the surfactant on the chirality of the product structure has not yet been determined.

For the same kind of surfactant (e.g., CnTMA$^+$), the value of V/l does not alter significantly with chain length[68] since both V and l are roughly linearly dependent on the carbon number. The ratio V/l is close to 0.21 nm^2 for one alkyl chain and single head-group surfactants. However, when n is larger ($n \geq 20$), the hydrocarbon chain may coil a great deal so that l decreases,[69] while the volume of hydrocarbon chain does not change significantly. This results in an increase of g favoring the formation of low surface curvature mesophases. $C_nH_{2n+1}(CH_3)_3N^+$, $n = 20$, 22, surfactants thus lead to the formation of lamellar phases, while short-chain ($n \leq 18$) surfactants give MCM-41. Another example is that SBA-3 is obtained when $C_{20}H_{41}(C_2H_5)_3N^+$ is used as the surfactant in acidic medium, in contrast with the product being SBA-1 when $C_nH_{2n+1}(C_2H_5)_3N^+$ ($n \leq 18$) is used. The detailed synthesis results with C_{20}TMA$^+$ as a structure directing agent are listed in Table 4.

Table 1. Surfactants Used in this Research

Name	Example Structure
Alkyltrimethylammonium $C_nTMA = C_nH_{2n+1}N(CH_3)_3$ n=10, 12-16, 18, 20, 22	
Gemini ammonium C_{m-s-m} = $C_mH_{2m+1}N(CH_3)_2(CH_2)_sN(CH_3)_2C_mH_{2m+1}$ m = 12,14,16,18,20,22; s = 2-12	
Divalent surfactant C_{n-s-1} = $C_nH_{2n+1}N(CH_3)_2(CH_2)_sN(CH_3)_3$ n=12,14,16,18,20,22; s=2,3,6	
$C_nH_{2n+1}N(R_1)(R_2)(R_3)$ n = 16; R_1, R_2, R_3 = H, CH_3, C_2H_5, C_3H_7	
Hydroxy-functional ammonium $C_nH_{2n+1}N(CH_3)_2(CH_2)_mOH$ n=16; m=0, 1, 2, 3	
Benzalkonium $C_nH_{2n+1}N(CH_3)_2(CH_2)_mC_6H_5$ n=14,16,18,20; m=1, 2, 3	
Bichain ammonium $C_nH_{2n+1}N(CH_3)_2C_mH_{2m+1}$ n=12, 16, 18; m=2-6,12,16,18	
Organosilane $C_nH_{2n+1}N(CH_3)_2(CH_2)_3Si(OCH_3)_3$ n=14	

As n increases above 4, the substituted surfactants, $(C_{16}H_{33})(C_nH_{2n+1})N^+(CH_3)_2$, behave more and more like surfactants with two identical alkyl chains due to fact that the substituted group is too long and hydrophobic to remain fully exposed to the water hydrophilic region

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[66] Alami, E.; Beinert, G.; Marie, P.; Zana, R. *Langmuir* **1993**, *9*, 1465–1467.

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Table 2. Typical Synthesis Conditions and Results of Silica Mesophase Using TEOS as Silica Source

	Surfactant		Composition (mole, SiO_2 = 1.0)					product
no.	R	trait	R	HX (or MOH)	H_2O	additive	temp/time	phase
1	$C_{16-10-16}$	dimer	0.06	4.9 HCl	130		RT/1 h	SBA-3
2	$C_{16-12-16}$	dimer	0.05	0.62NaOH	115		100 °C/10 days	MCM-48
3	$C_{16}TMA^+$	normal	0.12	9.2 HCl	130		RT/1 h	SBA-3
4	$C16TMA^+$	normal	0.12	4.9 HBr	130		RT/1 h	SBA-3
5	$C_{16}H_{33}N(C_3H_7)_3{}^+$	big head group	0.12	4.9 HBr	130		RT/1 h	SBA-3
6	$C_{16}H_{33}N(C_2H_5)_3{}^+$	big head group	0.13	10.4 HCl	130		RT/1 h	SBA-1
7	$C_{16}H_{33}N(C_2H_5)_3{}^+$	with additive	0.13	10.4 HCl	130	0.61 *t*-AmOH	RT/1 h	SBA-3
8	$C_{20}TMA^+$	long chain	0.12	4.9 HCl	130		RT/1 h	lamellar
9	$(C_{12}H_{25})_2N(CH_3)_2{}^+$	bichain	0.12	6.2 HCl	150		RT/1 h	lamellar
10	$(C_{12}H_{25})_2N(CH_3)_2{}^+$	bichain	0.12	0.7 NaOH	150		100 °C/10 days	MCM-50
11	$C_{16}TMA^+$	normal	0.28	0.29 TMAOH	80		100 °C/16 h	MCM-41
12	$C_{16}TMA^+$	with additive	0.28	0.29 TMAOH	80	0.29 TMB	100 °C/6 h	MCM-50

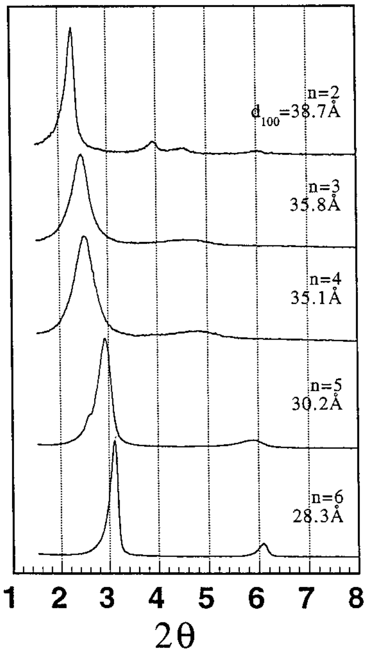


Figure 1. XRD patterns of silicate mesophases obtained by using $(C_{16}H_{33})(C_nH_{2n+1})N^+(CH_3)_2$ surfactants as structure-directing agents. Sample synthesis, reaction mixture molar composition: 0.1 surfactant:0.5 NaOH:1 TEOS:150 H_2O, at 100 °C for 1 week.

Table 3. Synthesis in Acidic Medium Using Surfactants with Different Head Group

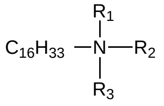
	R_1	R_2	R_3	product
 $C_{16}H_{33}-N(R_1)(R_2)(R_3)$	H	CH_3	CH_3	SBA-3
	CH_3	CH_3	CH_3	SBA-3
	CH_3	CH_3	C_2H_5	SBA-3
	CH_3	C_2H_5	C_2H_5	SBA-1
	C_2H_5	C_2H_5	C_2H_5	SBA-1

Table 4. Synthesis Results with $C_{20}H_{41}N(CH_3)_3{}^+$ as the Surfactant

	composition (mole, TEOS = 1.0)			temp time		product
no.	template	HX(or MOH)	H_2O	(°C)	time	phase
1	0.12	4.9 HCl	135	RT	0.5 h	lamellar
2	0.06	0.7 NaOH	140	RT	0.5 h	MCM-41
3	0.06	0.7 NaOH	140	100	0.5 h	MCM-50
4	0.06	1.4 NaOH	140	RT	0.5 h	MCM-50
5	hydrothermal treatment of sample no. 2			100	6 days	MCM-50

as part of the head group.[70] As expected, the synthesis products vary gradually from MCM-41 to MCM-50 and are accompanied by decreasing *d* spacings with increasing *n* (from 2 to 6). Their XRD patterns are shown in Figure 1.

3. Surfactant Precursor: Alkyloxysilane. The surfactant precursor, alkylethoxysilane, can hydrolyze into amphiphilic molecules under silica-based mesophase synthesis conditions.[71] These amphiphilic molecules can also organize with other silica species into a liquid crystal array. A lamellar phase is obtained from a reaction mixture with composition 0.18 $C_{16}H_{33}Si(OEt)_3$:1 TEOS:12.5 HCl:200 H_2O at room temperature for 1 h. Cetyltriethoxysilane can also condense into a lamellar solid without any other silica source in a concentrated solution in acidic medium. Both MCM-41 and MCM-48 can be synthesized by using *n*-tetradecyldimethy(3-trimethoxysilylpropyl)ammonium, C_{14}–Si, chloride as the covalently bonded surfactant–silica source. Surfactant C_{14}–Si is just C_{14}TMA in which one methyl group on the head group is replaced with $-Si(OCH_3)_3$. The synthesis result is as expected. C_{14}–Si and C_{14}TMA give similar synthesis results. The surfactant is presumably a part of the inorganic framework of the product in these cases. Some heteroatom (e.g., transition metal) silicate mesoporous materials can be made by using suitable heteroatom-containing surfactants.[35,36] It appears that the heteroatom is homogeneously distributed in the inorganic framework.

4. Hydroxy-Functionalized Surfactants. The hydroxyl group in the functional surfactant, $C_nH_{2n+1}N^+(CH_3)_2(CH_2)_mOH$, decreases the hydrophobicity of the head group so that the head group tends to remain in contact with water[72] (or silicate ion in solution), thus decreasing the affective cationic head-group area a_0. It therefore plays an important role in the entropic and enthalpic contributions of water organization to structure direction. The hydroxyl head-group surfactants favor formation of mesophases with low surface curvatures due to the smaller effective a_0. The product is a lamellar phase when $C_{16}H_{33}N^+(CH_3)_2(CH_2)_2OH$ is used, while a similar structured surfactant with a smaller head group, $C_{16}H_{33}N^+(CH_3)_2C_2H_5$, gave only a relatively high surface curvature mesophase, MCM-41. Table 5 compares some syntheses results. A hydroxyl group in

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Table 5. Typical Syntheses Using Hydroxy-Functional Surfactants

		composition (mole, TEOS = 1.0)				
no.	surfactant	R	HCl(or NaOH)	H_2O	temp/time	product phase
1	$C_{16}H_{33}N(CH_3)(C_2H_5)_2^+$	0.13	10. 4HCl	130	RT/2 h	SBA-1
2	$C_{16}H_{33}N(CH_3)(C_2H_4OH)_2^+$	0.13	10.4 HCl	130	RT/2 h	SBA-3
3	$C_{16}H_{33}N(CH_3)_2(C_2H_5)^+$	0.12	0.5 NaOH	62	100 °C/10 days	MCM-41
4	$C_{16}H_{33}N(CH_3)_2(CH_2)_2OH^+$	0.12	0.5 NaOH	62	100 °C/10 days	MCM-50
5	$C_{16}H_{33}N(CH_3)_2(CH_2)_3OH^+$	0.15	0.5 NaOH	150	100 °C/7 days	MCM-41

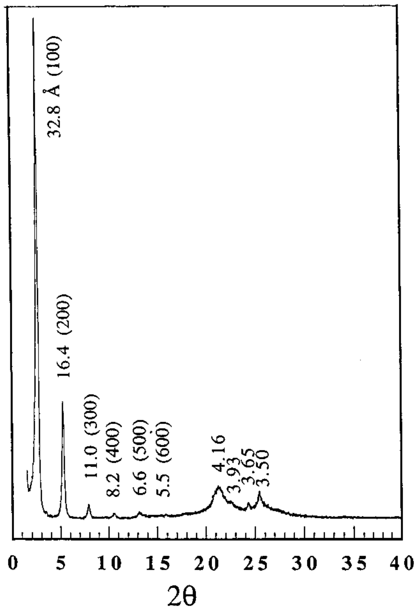

Figure 2. XRD pattern of lamellar silicate mesophase synthesized by using $C_{14}H_{29}CH(OH)CH_2N(CH_3)_3Br$ as structure-directing agent. Sample synthesis, reaction mixture molar composition: 0.3 $C_{14}H_{29}CH(OH)CH_2N(CH_3)_3Br$:0.4 NaOH:1 TEOS:100 H_2O, at 100 °C for 10 days.

Table 6. Typical Syntheses Using Gemini Surfactants[a]

Surfactant	A	B	C
$C_{16-2-16}$	lamellar	MCM-50	amorphous
$C_{16-3-16}$	SBA-3	MCM-50+MCM-41	MCM-50
$C_{16-4-16}$	SBA-3	MCM-41	MCM-50
$C_{16-6-16}$	SBA-3	MCM-41	MCM-41
$C_{16-7-16}$	SBA-3	MCM-41	MCM-41
$C_{16-8-16}$	SBA-3	MCM-41	MCM-41
$C_{16-10-16}$	SBA-3	MCM-41	MCM-41
$C_{16-12-16}$	SBA-3	MCM-48	MCM-48
($C_{16}TMA^+$	*SBA-3*	*MCM-41*	*MCM-50)*

[a] A: 0.06 surfactant:4.8 HCl:1 TEOS:130 H_2O, at RT for 1.5 h. B: 0.06 surfactant:0.65 NaOH:1 TEOS:150 H_2O, at RT for 1 day. C: 0.06 surfactant:0.65 NaOH:1 TEOS:150 H_2O, at 100 °C for 10 days.

the hydrocarbon chain of the surfactant, e.g., β-substituted, $C_{14}H_{29}CH(OH)CH_2N^+(CH_3)_3$, also has a small effective head-group surface area. A highly ordered lamellar silicate is obtained by using $C_{14}H_{29}CH(OH)CH_2N^+(CH_3)_3$. Its XRD pattern is shown in Figure 2. The low-angle diffraction arises from the characteristic lattice repeat, i.e., the long-range ordering of the lamellar mesophase, whereas the high-angle region is characteristic of the hydrocarbon chain packing within the layer.[73−75]

5. Gemini C_{m-s-m} and Divalent C_{n-s-1} Surfactants. "Gemini surfactant", C_{m-s-m}, is a name assigned to a family of synthetic amphiphiles possessing, in sequence, a long hydrophobic chain, an ionic group, a spacer, a second ionic group, and another hydrophobic tail.[66,76−78] The divalent quaternary ammonium surfactant, C_{n-s-1}, may be considered as an highly end member of gemini surfactant or a highly charged large head-group surfactant. Its structure-directing effect will be described below (synthesis of SBA-2). These surfactants are particularly interesting from a fundamental point of view: their structure can be considerably modified by acting on the length and nature both of the side chain and of the spacer group. The relative positions and distances of headgroups of conventional mono(quaternary ammonium) surfactants are determined primarily by electrostatic interactions and also by the packing requirements of disordered alkyl chains. Formally, the C_{m-s-m} surfactants may be considered as dimers (double-headed) of the two-chain C_mH_{2m+1}-$(CH_2)_{s/2}N^+(CH_3)_2$ surfactants. For bis(dimethylalkylammonium) surfactants, two quaternary ammonium species $C_mH_{2m+1}N^+(CH_3)_2$ are chemically linked at the level of the head group two by two through an adjustable polymethylene spacer (C_sH_{2s}). The presence of the spacer can strongly affect the distribution of distances between head groups, a narrow maximum at the distance corresponding to the extended length of the spacer and another maximum at the thermodynamic equilibrium distance (for detail see ref 79), i.e., the value of a_0. By this means we can change the V/a_0l of a surfactant by adjusting its spacer length.[78]

We used the surfactants in this family as structure-directing agents in order to synthesize a variety of silica-based mesophase products. The synthesis results and conditions are listed in Table 6. Their structure directing behavior is similar to that in surfactant−water binary system[65,66,77,78] and results in the structures expected for charge density matching. Small-*s* surfactants favor MCM-50, larger *s* surfactants favor MCM-41. $C_{16-12-16}$ gives MCM-48 at both room temperature and high temperature (100 °C), while $C_{12-12-12}$ gives MCM-41 at room temperature. Note that aqueous solutions of $C_{12-12-12}$ remain micellar over the entire range of composition and do not form lyotropic liquid crystal phases.[77] This circumstance demonstrates the importance of the inorganic species in the cooperative structure-directing mechanism for the concentration region in which the synthesis is carried out.

6. Mixed Surfactants Structure-Directing Effects. The effect of mixing unlike surfactants can be thought of as a simple average of two surfactant packing parameters. For example, a mixture of $C_{16-12-16}$ and

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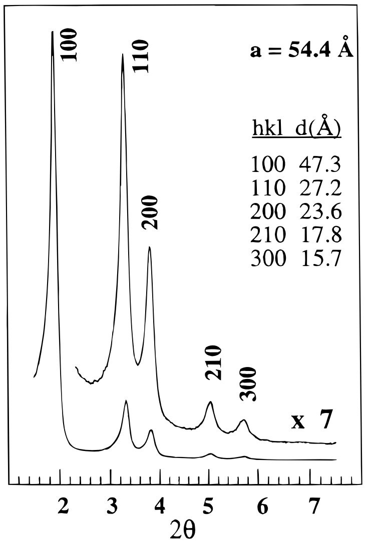

Figure 3. XRD pattern of high-quality MCM-41. The full width at half-maximum for the (100) peak is 0.17° of 2θ. Sample synthesis, reaction mixture molar composition: 0.025 C_{20-3-1}:0.036 C_{20}TMABr:0.5 NaOH:1 TEOS:150 H_2O, at 100 °C for 1 week. The sample was calcined at 500 °C.

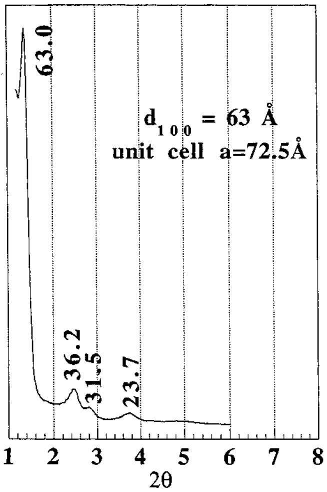

Figure 4. XRD pattern of large unit-cell MCM-41. Sample synthesis, reaction mixture molar composition: 0.025 C_{20-3-1}: 0.036 C_{20}TMABr:1.16 TMB:0.5 NaOH:1 TEOS:150 H_2O, at 100 °C for 10 days.

C_{16-3-1} is used in silicate mesophase synthesis. The products vary from MCM-48 to SBA-2 through MCM-41 as the fraction of C_{16-3-1} increases in the mixture.

The mixture of C_{n-3-1} and C_mTMA$^+$ can result in the formation of good-quality MCM-41. The MCM-41 easily gives five or more well-defined XRD peaks with reciprocal spacings, $1/d_{hk}$, ratios of 1, $\sqrt{3}$, 2, $\sqrt{7}$, 3, $\sqrt{12}$, $\sqrt{13}$, 4, $\sqrt{19}$, etc. The indexed XRD pattern of one example given in Figure 3. Another example is described below (hydrothermal treatment section, Figure 10). It is noteworthy that high-quality MCM-41 still can be obtained when $n = 22$, while single-surfactant C_mTMA$^+$ ($m \geq 20$) favors the lamellar phases and does not give MCM-41 at 100 °C. When a swelling agent (e.g., TMB) is introduced into this synthesis system, the product MCM-41 has a large unit cell and shows a good XRD pattern (four narrow peaks; Figure 4). This is one of the examples in this paper of large-pore (>45 Å) MCM-41 with a pure silicate framework. Our synthesis results indicate C_nTMA$^+$ is a good but not ideal structure-directing agent for the formation of MCM-41, even though C_nTMA$^+$ (e.g., C_{14}TMABr) can give a high-quality lyotropic liquid-crystal hexagonal phase with five or more sharp reflections.[80] C_nTMA$^+$ has only one charge per hydrophobic chain. More charges (from C_{n-3-1}, two charges per chain) in the surfactant head groups are apparently needed for the formation of high-quality MCM-41.

The high-quality MCM-41 is thermally stable, and the calcined sample still has at least five XRD peaks (Figure 3). As for MCM-41 obtained from C_nTMA$^+$ surfactant, small pore calcined material is more hydrothermally stable than a large pore one. For example, MCM-41 calcined (at 500 °C) from a C_{12}TMA$^+$ synthesis system gives a good XRD pattern after 3 h of heating in water at 100 °C, while the large-pore (~55 Å) material loses its structure under the same conditions. High-temperature calcination can increase the hydrothermal stability of these materials. The calcined (at 800 °C) large-pore (~55 Å) sample shows a clear MCM-41 XRD pattern (five or more peaks) after 2 h of heating in water at 100 °C.

7. SBA-3 and Acidic Reaction Media. Some surfactants gave different mesophases depending on whether a basic or acidic medium is used (Tables 4 and 6). At the acid and base pH extremes the mechanism of mesophase formation is completely different[6] (since negatively charged silicate ions are the counterion above the isoelectric point at pH ~ 2.0, while positively charged silica species are the co-counterion in acidic medium, below the isoelectric point). The differences in electrolyte concentration should be also considered with regards to their effects on mesophase formation. Clearly, the electrolyte concentration (>1 M) of low-pH media is higher than that in basic media (pH = 12). The decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent smaller electrical repulsion between the head groups in the micelle[69] cause closer packing of the surfactant molecules.

The synthesis results obtained using C_{20}TMA$^+$ as the structure directing agent below and above the isoelectric point are given in Table 4 as a typical example. C_{20}TMA$^+$ gave the lamellar phase in acidic synthesis medium. In basic media, the reaction mixture at a low ratio of OH^-/SO_2 forms MCM-41. A high ratio of OH^-/SO_2 gives MCM-50. The reason is the requirement of charge matching between the silicate and the surfactant micelle.[10]

So far, SBA-1 has been obtained only in acidic media. The globular surfactant micelle has the largest surface curvature of all lyotropic liquid crystals, and the micellar surface has the lowest charge density. The formation of the mesophase requires the charge matching of the inorganic species with that of the micelle. Thus, formation of mesophases with a globular micellar aggregate in basic medium is more difficult since the silicate framework charge density is higher (because of higher pH and relative low pK_a of silicic acid), while the silica framework has low charge density (zero in the product) in lower pH synthesis medium. Surfactants with large charged head groups, which can create higher

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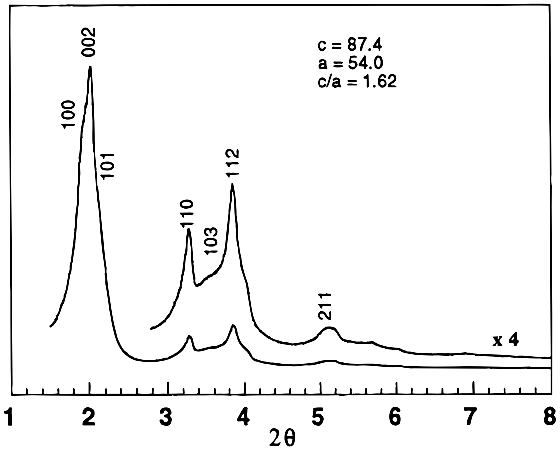

Figure 5. XRD pattern of SBA-2 (3d hexagonal, $P6_3/mmc$, phase). This material was synthesized by using C_{16-6-1} as structure-directing agent at 100 °C and calcined at 500 °C.

surface curvature and appreciable surface charge density, may be suitable for the successful synthesis of mesophases with globular micellar aggregates in basic medium.

8. SBA-2, a 3d Hexagonal Mesophase.[43] SBA-2 is a novel regular caged mesoporous silicate material. Its analogue has not been previously observed in a lyotropic liquid crystal system. SBA-2 is synthesized using divalent quaternary ammonium surfactants, C_{n-s-1} (e.g., C_{12-3-1}, C_{14-3-1}, C_{16-2-1}, C_{16-3-1}, C_{16-6-1}, C_{18-3-1}, C_{18-6-1}, C_{20-3-1}) in both basic and acidic media. Our experimental results show that SBA-2 has 3d spatial symmetry, space group $P6_3/mmc$ (No. 194), and is derived from a hexagonal close packing of globular surfactant/silicate arrays.[43] As expected for this geometry, the unit cell parameter c/a ratio is about 1.62. After calcination, the large-cage structured mesoporous silica framework remains. The structure-directing agent in SBA-2 can be removed by calcination at high temperature (500–600 °C). This material is thermally stable up to 800 °C. The XRD pattern of calcined SBA-2 at 500 °C is shown in Figure 5. Like MCM-41 and MCM-48, the cell of SBA-2 contracts during calcination. The calcined SBA-2 has a N_2 BET surface area of 500–700 $m^2\ g^{-1}$. The N_2 adsorption–desorption isotherms is type IV with a H2 hysteresis for even small pore SBA-2 (<25 Å, see Figure 6).

C_{n-s-1} surfactants have high charge densities and large head groups and therefore favor globular micellar aggregates.[60] For example, for $Pm\bar{3}n$ (~33–67 wt % surfactant), hexagonal and lamellar phases are observed for the $C_{12-3-1}Cl$–water system at room temperature.[60] In basic medium, SBA-2 can be obtained with varying unit cell and cage sizes by using different chain length surfactants over a wide synthesis range (from cell parameter $c = 77$ Å for C_{12-3-1} to $c = 108$ Å for C_{20-3-1}).

9. Addition of Organic Cosolvents. Organic cosolvents have been used to control the syntheses of mesoporous solids as well as lyotropic mesophases of surfactant–solvent binary systems. Organic cosolvents can solubilize in the surfactant phase depending on their nature. (1) Apolar additives associate with the hydrophobic part of the surfactant micelle. This penetration of the cosolvent molecule increases the hydrophobic volume and radii. When trimethylbenzene (TMB) is added as a swelling agent, large unit cell changes are observed. This approach is used in the large pore MCM-41 synthesis. (2) A suitable polar additive is able to enter the hydrophobic–hydrophilic "palisade" region of the micelle, with a relatively large increase in the volume of the hydrophobic core to form surfactant molecule aggregates with a lower curvature surface.

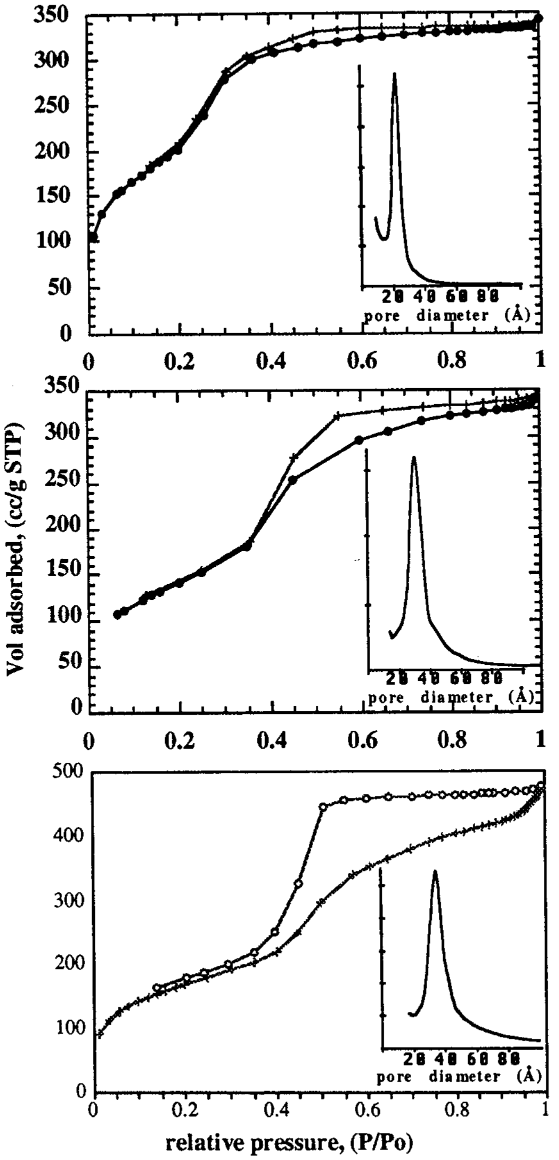

Figure 6. Nitrogen adsorption–desorption isotherm plots of SBA-2.

When organic compounds of low polarity are introduced into the synthesis system, the low surface curvature mesophase is the favored product (see Table 2, nos. 7 and 12). For example, $C_{16}TEA^+$ by itself forms SBA-1 (cubic) in acidic medium, however, the product is SBA-3 (hexagonal) if *t*-AmOH is added into the synthesis mixture). $C_{16}TMA^+$ favors MCM-41 over a wide range of reactant compositions. If TMB is added, the MCM-41 is replaced by the MCM-50. These results confirm that these more hydrophobic organic compounds codissolved with the surfactant hydrocarbon assemblies contribute most strongly to the hydrophobic chain volume, *V*.

In the case of SBA-2 syntheses from basic medium, C_{16-3-1} gives a SBA-2 with unit cell $a = 62$ Å, $c = 100$ Å when TMB/TEOS = 1.1; without TMB, a unit cell with $a = 54$ Å, $c = 87$ Å is found. However, when *t*-amyl

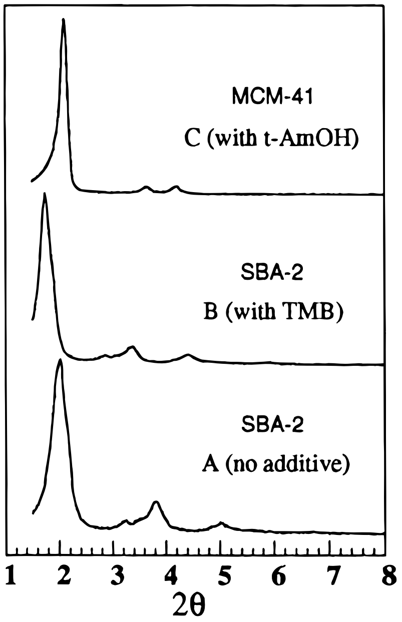

Figure 7. XRD patterns of products from C_{16-3-1} synthesis system with and without organic additives. (A) SBA-2 (cell a = 54.3 Å and c = 87.6 Å), without organic additive; (B) large-pore SBA-2 (cell a = 61.8 Å and c = 101.6 Å), with TMB (molar ratio TMB:C_{16-3-1} = 23); (C) MCM-41 (cell a = 48.4 Å), with t-amyl alcohol (molar ratio t-AmOH:C_{16-3-1} = 15).

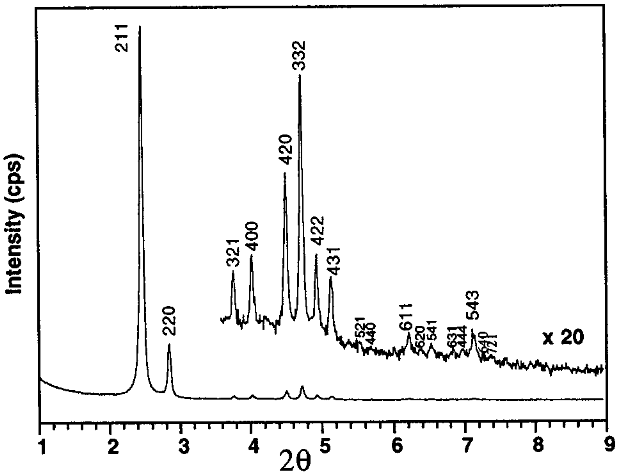

Figure 8. Synchrotron XRD pattern of as-made MCM-48. The sample was synthesized by using C_{16}TMACl as structure-directing agent at 100 °C. The unit cell a = 97 Å.

alcohol, a low-polarity additive, is added into the synthesis mixture, the SBA-2 product is replaced by MCM-41. Their XRD patterns are shown in Figure 7.

10. MCM-48, Cubic (*Ia*3*d*) Phase. MCM-48 is an analogue of a lyotropic liquid crystal, bicontinuous cubic (oil-in-water) *Ia*3*d* mesophase. The result upon indexing the diffraction peaks of MCM-48 (see Figure 8) shows a good correspondence to those predicted by the cubic *Ia*3*d* symmetry. A high molar ratio of surfactant/silica and a high concentration of surfactant were first believed to be the essential condition for forming MCM-48.[3] MCM-48 has been synthesized using $C_{14}TMA^+$ or $C_{16}TMA^+$ as the structure-directing agent in the presence of EtOH (which comes from the silica source TEOS) at 100 °C.[3,10] The direct synthesis of MCM-48 using other silica sources had not yet been reported. When $C_{16}TMA^+$ is used as structure-directing agent, we synthesized MCM-48 in similar reaction conditions by using SiO_2 (Cab-o-sil) in place of TEOS as the silica source in the presence of polar organic additives (such as $(CH_3)_2NCH_2CH_2OH$, $N(CH_2CH_2OH)_3$) but failed to synthesize MCM-48 using TMOS (tetramethyl orthosilicate) or sodium silicate as the silica source without organic additive. Polar organic additives are important in the formation of MCM-48 when using C_nTMA^+ as the structure-directing agent. For normal surfactant–water systems, it is widely believed that the role of the alcohol is to prevent the growth of the aggregates into infinite rods (hexagonal) or bilayers.[81]

$C_{16-12-16}$ favors the formation of MCM-48, even without organic additives using Cab-o-sil (SiO_2) or sodium silicate solution as the silica source. Its micellar structure is similar to the C_{16}TMABr–polar additive–water mixture in certain respects. The spacer ($C_{12}H_{24}$) of $C_{16-12-16}$ is long enough to penetrate the hydrophobic core of the micelle, but the spacer remains in the outer portion of micelle since it is bonded to the head groups.[79] Polar organic additives (such as EtOH, $(CH_3)_2NCH_2CH_2OH$, $N(CH_2CH_2OH)_3$) are solubilized by the micelle and are located in the palisade layer (the region between the head group and the hydrophobic core) because of their polarity and hydrogen bonding to water. TMOS does not give MCM-48 due to the high polarity and hydrophilicity of MeOH, and therefore does not penetrate the micelle surface. The systems that favor MCM-48 have similar palisade layers which contain an extra hydrocarbon chain or organic additive molecules that result in large volume fractions for the surfactant chains. A wide range of g values ($^1/_2$ to $^2/_3$) favors the *Ia*3*d* mesophase for large volume fraction of the hydrocarbon chain.[52]

The synthesis results using cetyldimethylbenzylammonium (CDBA) as a structure-directing agent support the above discussion. This surfactant also favors the formation of MCM-48 but is not a good structure-directing agent for the formation of MCM-41 at 100 °C. In the CDBA–NaOH–TEOS–H_2O synthesis system (at 100 °C), MCM-48 forms over a larger range. Good MCM-48 samples could be obtained at a low molar ratio of surfactant/TEOS (as low as 0.1) or low surfactant concentration (as low as 1.1 wt % in water). CDBA has a large head group and falls midway between that of triethylammonium and tripropylammonium. The latter two surfactant ions are not good structure-directing agents for the formation of MCM-41 and MCM-48 in basic synthesis medium. CDBA could be considered as a $C_{16}TMA^+$ surfactant with a solubilized benzene molecule anchored on the trimethylammonium head group. The benzene group, like the spacer $C_{12}H_{24}$ of $C_{16-12-16}$, can penetrate to a certain degree the hydrophobic core of the micelle, thus decreasing the head group size, and giving the cubic mesophase.

MCM-48 can be easily synthesized at room temperature by using gemini surfactants. Long-chain gemini surfactants favor the MCM-48 mesophase, even at extremely low ratios of surfactant/silica and low surfactant concentration. For example, a reactant mixture with molar composition 0.01 $C_{22-12-22}$:0.69 NaOH:1 TEOS:150 H_2O (concentration of $C_{22-12-22}$ is only 0.4 wt % in water) gave a MCM-48 sample at room temperature after aging for 1 day. Figure 9 shows the XRD

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(81) Madden, T. L.; Herzfeld, J. *J. Philos. Trans. R. Soc. London A* **1993**, *344*, 357.

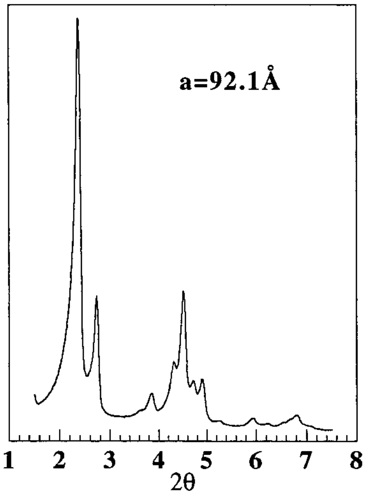

Figure 9. XRD pattern of room-temperature synthesis MCM-48 (unit cell *a* = 92 Å). $C_{22-12-22}$ was used as structure-directing agent.

pattern of room-temperature synthesis MCM-48 (the ratio of $C_{22-12-22}$:TEOS = 0.06 in the reaction mixture).

11. New Synthesis Approach for High-Quality Materials. This synthesis approach includes the synthesis of an as-made mesoporous silicate at room temperature and the postsynthesis hydrothermal treatment (at 100 °C) of this solid in water (pH = 7−10). The sample obtained is called a "treated sample". The treated sample has several excellent qualities.

In most cases, as-made silicate mesoporous materials are flexible if made at low synthesis temperatures and short synthesis times. The silicate frameworks consist of a large amount of silanols, which can further condense and rearrange in certain conditions.[9] We found that postsynthesis hydrothermal treatment could change the structure and properties of some M41S silicate mesoporous materials. The effect of postsynthesis hydrothermal treatment on different as-made silicate mesophases is dependent on the synthesis history of the sample and the surfactant used.

There are two ways to synthesize large-pore MCM-41 materials in the literature: using long chain surfactants and a swelling agent. These two methods have several drawbacks. The very long chain (>C_{22}) surfactant is not available, and its precursor is very expensive. In addition, the alkyltrimethylammonium surfactants with long chains (>C_{18}) are not good structure-directing agents for the formation of MCM-41. Moreover, the introduction of organic swelling agents (such as TMB) expands the pore size of aluminosilicate MCM-41 product but at the same time decreases the quality of the product. As noted above, TMB does not have a good swelling effect in terms of the structural quality for pure silicate MCM-41. Only one clear XRD peak is observed for pure silicate MCM-41 and larger pore (>50 Å) aluminosilicate MCM-41 obtained using TMB-containing synthesis conditions.[2,7] More recently, pore-size enlargement of MCM-41 (d_{100} from 40 to 70 Å) is observed[82] through hydrothermal treatment in the mother liquor via a second-step synthesis at 150 °C over a period of 10 days.

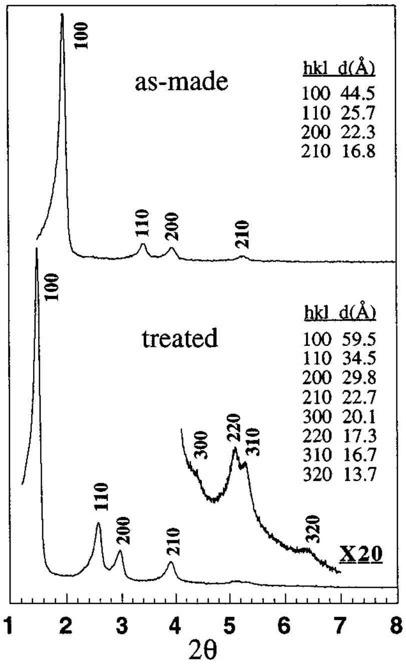

Figure 10. XRD patterns of enlarged MCM-41. The as-made sample was obtained from a reaction mixture with molar composition 0.11 C_{20-3-1}:0.12 C_{16}TMABr:0.5 NaOH:1 TEOS: 150 H_2O at room temperature for 1.5 h and then the solid product was hydrothermally treated in water (30 g of water/g sample) at 100 °C for 2 weeks to give the treated sample. The full width at half-maximum for the (100) peak of the treated sample is 0.13° of 2*θ*.

A milder and more convenient method, postsynthesis hydrothermal treatment, has been found in our laboratory. The mixture of C_{n-3-1} and C_{n-s-n} surfactants gives a good silicate hexagonal mesophase at room temperature. This solid product is then isolated by filtration, air dried, and put into water (pH = 7−10) for hydrothermal treatment. The unit cell of this mesophase is substantively enlarged by this postsynthesis hydrothermal treatment. For example, hydrothermally treated MCM-41 (good quality: eight clear XRD peaks, Figure 10) produced a lattice expansion of approximately 25−35%. The unit cell of these materials increases initially with time and then reaches a maximum as illustrated by the example shown in Figure 11. The enlarged pore-size sample has good thermal stability and stable walls (less cell shrinkage on calcination). The calcined samples accordingly have larger pore sizes, large surface areas, and big pore volumes. For example, the cell of as-made MCM-41 sample (synthesized at room temperature and using C_{22-3-1} and $C_{18}TMA^+$ as structure-directing agents) is $a = 54.5$ Å. After a two-time hydrothermal treatment (at 100 °C, 2 weeks each time) the cell increases to 79.6 Å. The treated sample is calcined at 500 °C to remove all surfactants. The calcined material has a cell of $a =$ 77.0 Å (shrinkage 3%) and gives eight XRD peaks (similar to that shown Figure 10). This material has a pore size of 60 Å, a pore volume of 1.6 cm^3/g and a surface area of 1086 m^2/g. Its N_2 adsorption−desorption isotherm and pore-size distribution curve are shown in Figure 12. Three well-distinguished regions of the adsorption isotherm are noticed: monolayer−multilayer adsorption, capillary condensation, and multilayer adsorption on the outer surface. In contrast to N_2 adsorption results[83,84] of MCM-41 with pore size less than 40 Å, a clear type H1 hysteresis loop in the adsorption−

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[82] Khushalani, D.; Kuperman, A.; Ozin, G. A.; Tanaka, K.; Garces, J.; Olken, M. M.; Coombs, N. *Adv. Mater.* **1995**, *7*, 842.

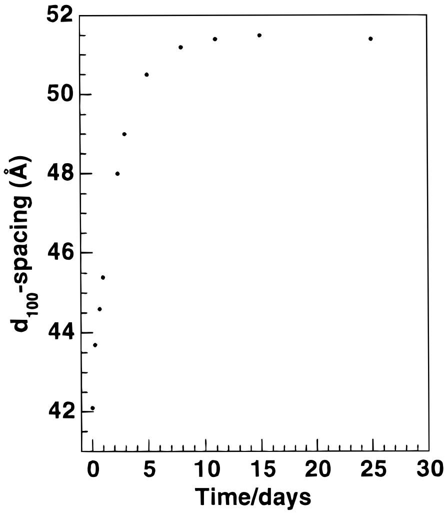

Figure 11. Relation between d_{100} of MCM-41 and postsynthesis treatment time at 100 °C. The original MCM-41 was synthesized from 0.027 C_{18-3-1}:0.017 $C_{16-7-16}$:0.5 NaOH:1 TEOS:150 H_2O, at room temperature for 2 h.

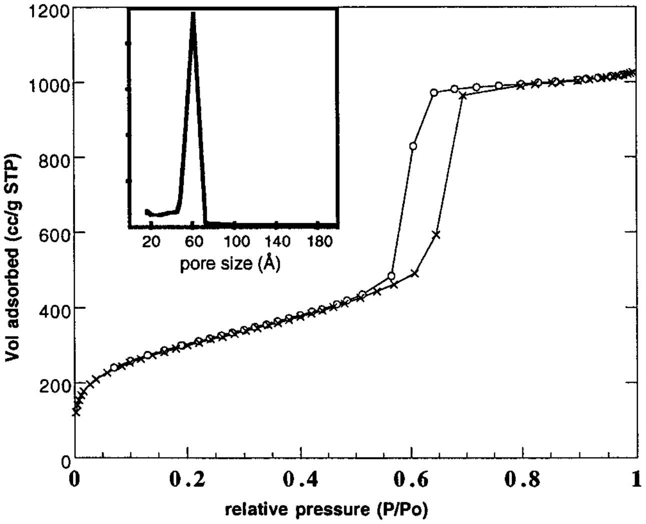

Figure 12. Nitrogen adsorption−desorption isotherm plots of the large-pore MCM-41. The inset is the pore size distribution curve from adsorption.

desorption isotherm is observed and the capillary condensation occurs at high relative pressure. These results confirm that the material has a large pore.[85]

No significant expansion of the unit cell is observed for MCM-41 and MCM-48 containing a single C_nTMA^+ structure directing agent under the same treatment conditions, but they are structurally more ordered after hydrothermal treatment. The XRD of MCM-48 treated hydrothermally show peaks that are narrower (Figure 13). In addition, long treatment times do not destroy the structure of the MCM-41. For example, the sample (MCM-41 containing $C_{12}TMA^+$) keeps the characteristic powder XRD peaks of the hexagonal phase after 200 days of hydrothermal treatment at 100 °C. Moreover, a sample containing neutral alkylamine[8] can also be improved. In comparison with the as-made sample, the treated sample gives narrower and clearer XRD peaks. This result also shows that MCM-41 materials containing surfactant are stable under mild hydrothermal conditions. Postsynthesis hydrothermal treatment also improves the thermal stability of the sample obtained at room temperature. The treated sample has a thermal stability similar to that of the sample synthesized at 100 °C and does not lose crystallinity upon calcination at 500 °C.

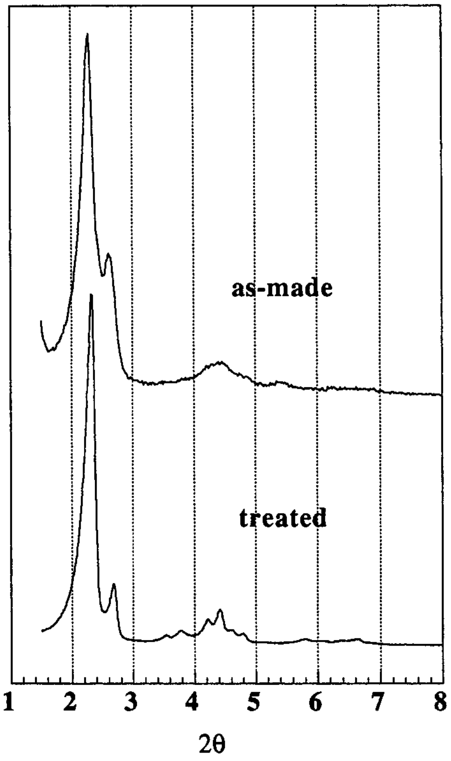

Figure 13. XRD pattern of treated sample MCM-48 (containing $C_{16}TMA^+$).

12. Phase Transitions. Several phase transitions are found during treatment of as-made samples under hydrothermal conditions in water (at 100 °C, pH = 7−10). If the structural function of quaternary ammonium surfactants in silicate mesophase formation can to a first approximation be related to that of pure surfactants in water, the effective surfactant ion pair packing parameter, $g = V/a_0l$, should be useful as a guide in predicting phase transitions.

(a) *Phase Transition from Lamellar to MCM-41.* The lamellar phase (d_{100} = 32 Å) synthesized using $C_{16}TMA^+$ transforms into MCM-41 through hydrothermal treatment (Figure 14). We can see clearly the gradual transition from the layer phase to hexagonal phase. The intermediate product is probably a intermediate phase[54] with elliptically shaped channels. Existence of the intermediate product is evidence that the transition occurred in the solid phase and not through dissolution to the liquid phase.

(b) *Phase Transition from MCM-41 to Lamellar.* C_{20}-TMA^+ leads to MCM-41 formation at low temperatures. This product treated hydrothermally (at 100 °C for 7 days) forms MCM-50. The XRD patterns are shown in Figure 15.

(c) *Phase Transition from MCM-41 to MCM-48.* A phase transition from MCM-41 (containing C_{n-12-n} surfactant, synthesized at room temperature) to MCM-

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[83] Schmidt, R.; Hansen, E. W.; Stocker, M.; Akporiaye, D.; Ellestad, O. H. *J. Am. Chem. Soc.* **1995**, *117*, 4049.

[84] Branton, P. J.; Hall, P. G.; Sing, K. S. W.; Reichert, H.; Schuth, F.; Unger, K. K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2965.

[85] Llewellyn, P. L.; Grillet, Y.; Schuth, F.; Reichert, H.; Unger, K. K. *Micropor. Mater.* **1994**, *3*, 345.

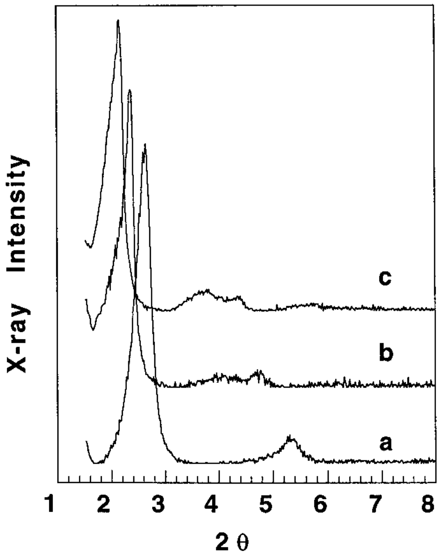

Figure 14. XRD patterns of observing mesophases in phase transitions (from MCM-50 to MCM-41). MCM-50 (lamellar mesophase) was treated hydrothermally at 100 °C for 0 (a), 1 (b), and 10 days (c), respectively. The lamellar mesophase was obtained from a mixture with composition of 0.27 C_{16}TMABr: 0.28 TMB:0.15 NaOH:0.14 TMAOH:1 SiO_2:70 H_2O at 100 °C for 8 h, filtrated, and washed with water.

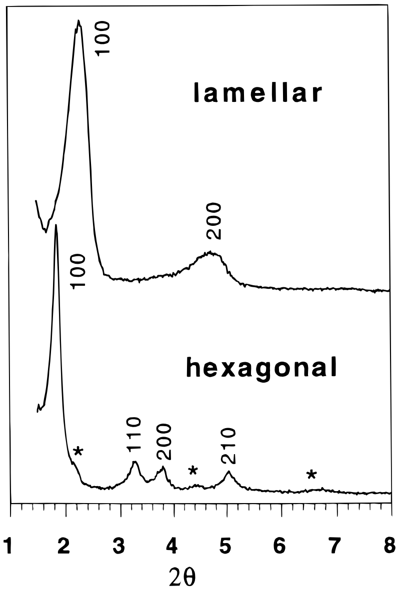

Figure 15. Phase transitions from hexagonal to lamellar (at 100 °C for 7 days). Peaks with * come from C_{20}TMABr crystal.

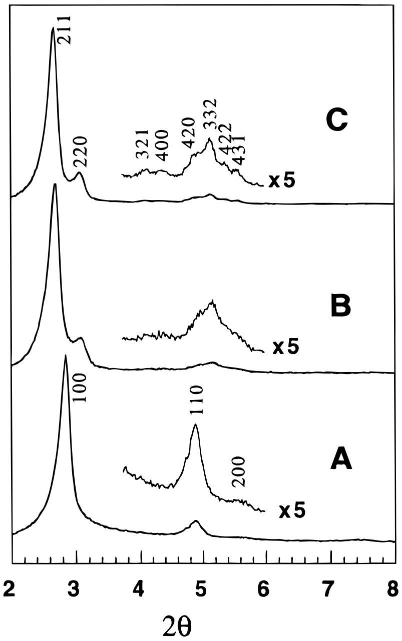

Figure 16. XRD patterns of phase transitions from MCM-41 to MCM-48 at 100 °C. The structure-directing agent is $C_{14-12-14}$. MCM-41 (A) was treated hydrothermally at 100 °C for 2 (B) and 5 weeks (C), respectively.

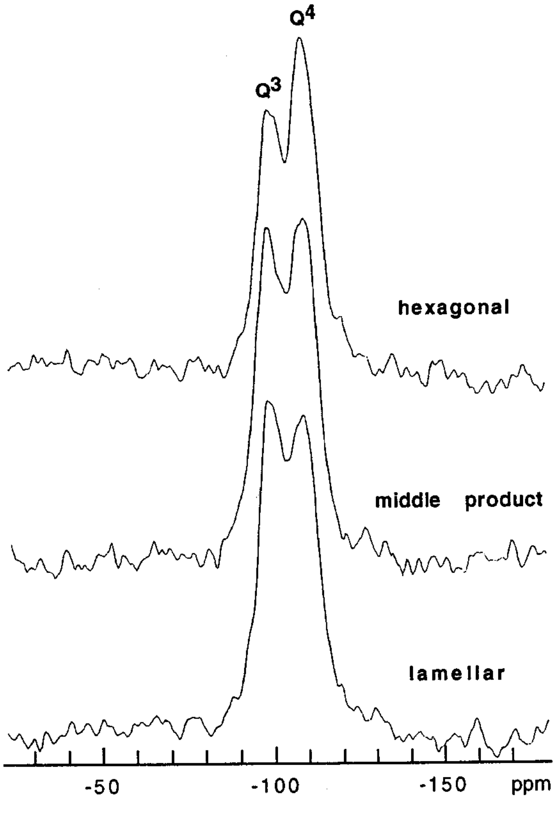

Figure 17. ^{29}Si MAS NMR spectra of the phase transitions from lamellar to hexagonal phase. Synthesis conditions are the same as for Figure 14.

48 also is observed under similar treatment conditions (Figure 16).

The results suggest that the mesostructure is formed at low temperatures or short reaction times, and further structural changes occur on thermal treatment. In most cases, we believe that the phase changes occur in the solid phase. While the liquid phase may play an important role, it is not necessarily through dissolution and new solid-phase formation because the media is nearly neutral (silicate has a very low solubility) and gradual transitions are observed (Figures 14, 16, and 17).

The effect of temperature on *g* is difficult to predict without a better understanding of the solvation and entropic thermodynamic forces at play. Counterion binding will also alter with temperature. In addition increasing the temperature accelerates the polymerization of the silicate framework but at sufficiently high temperatures rearrangement and dissolution of the silicate framework are enhanced. High-temperature intensifies the motion of the surfactant molecules and changes the effect of cosolvent organic species (e.g., EtOH). A more detailed discussion will appear in a future paper.[86] For some mixtures of reactants, differ-

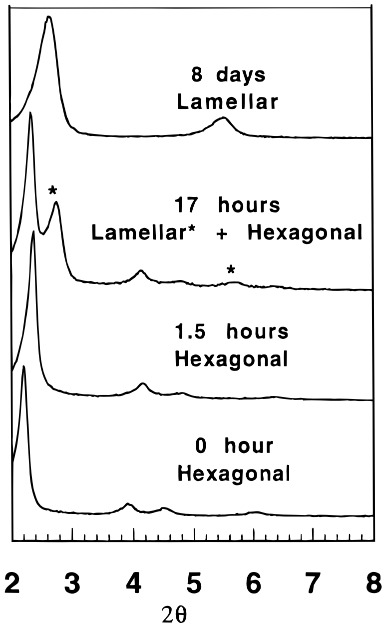

Figure 18. XRD patterns of mesophases synthesized at different temperature and time. The products were obtained from reaction mixture with molar composition of 0.6 NaOH: 0.12 C_{16}TMABr:1 TEOS:100 H_2O at room temperature for 2.5 h then at 100 °C for different reaction times.

ent synthesis temperatures gave different products. One example is listed in Table 4. Another effect of temperature on products is shown in Figure 18. C_{16}TMABr gives MCM-41 at room temperature in strong basic medium (for the reaction mixture composition, see Figure 18). This hexagonal phase disappears and a lamellar phase (d_{100} = 33 Å) is observed gradually at high temperature.

Another example of a high-to-low curvature phase transition is the transition from MCM-41 through MCM-48 to the lamellar phase. A reaction mixture with molar composition 0.031 C_{18-3-1}:0.206 $C_{14}TMA^+$:0.5 NaOH:1 TEOS:150 H_2O gives MCM-41 at room temperature. The product transforms into MCM-48, then into a lamellar phase when this mixture is heated at 100 °C. The XRD patterns of products from different reaction times are shown in Figure 19.

The effects of hydrothermal treatment on silicate mesophase solids are evident under mild conditions (100 °C). We believe that there are two main reasons for this: (i) the silicate framework condenses and undergoes reconstruction under hydrothermal conditions. This view is support by the results of ^{29}Si MAS NMR studies of the phase transition from lamellar to hexagonal (Figure 17). During condensation, the framework negative charge density decreases, therefore, the packing of the surfactant must change in order to maintain charge matching with the framework. In general, the phase transitions can be explained in terms of changes induced in the *g* value by reorganization of the surfactant molecules with temperature, condensation of the silicate phases, changes in the hydration behavior, and migration of organic additives.

Conclusions

Postsynthesis hydrothermal treatment is an excellent, relatively low temperature (100 °C) approach to obtain high-quality MCM-41 and MCM-48. The sample of MCM-41 obtained in this way is highly crystalline (4–8 narrow XRD peaks), has large pore sizes (up to 60 Å), big pore volumes (up to 1.6 cm^3/g), and large surface areas (>1000 m^2/g), and has a small (~3%) value change on calcination..

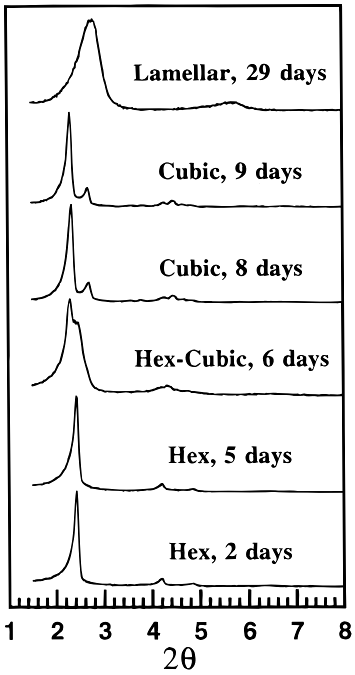

Figure 19. XRD patterns of products from C_{18-3-1}–C_{14}TMABr structure-directing agent system at 100 °C for different reaction times.

By appropriate matching of the surfactant, the silica source, and the reaction gel composition, the formation of a specific phase can be greatly facilitated, as we have shown for the synthesis of MCM-48 at room temperature using $C_{22-12-22}$ surfactant.

Organic species, such as EtOH, penetrate into the hydrophobic and palisade regions of surfactant arrays and thereby induce a structural rearrangement of the surfactant phase to reoptimize the interface charge density matching and the surfactant packing.[10]

A general pattern of synthesis behavior is observed using different surfactants with different *g* values under different reaction conditions. For acidic (pH < 0) syntheses media the phase sequence is as follows: **cubic ($Pm3n$, SBA-1), 3d hexagonal ($P6_3/mmc$, SBA-2) > 2d hexagonal (P6m, SBA-3) > lamellar.** For basic syntheses media the phase sequence changes to: **3d hexagonal ($P6_3$/mmc, SBA-2) > 2d hexagonal (p6m, MCM-41) > cubic (Ia3d, MCM-48) > lamellar (MCM-50).** The overall topology of the composite mesostructure is qualitatively described by the dimensionless effective surfactant packing parameter, $g = V/la_0$ as prescribed by the inorganic species or solid inorganic framework charge density. *g* may be used as an index of the structure directing effect. A majority of the known liquid-crystal morphologies have been observed for the mesosilicates and an unknown liquid crystal phase, $P6_3/mmc$, has been obtained in our laboratory.[43]

In predictable ways the inorganic framework and organic array affect and control one another in a cooperative fashion.[9,10] Suitable reaction conditions and

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(86) Landry, C.; Stucky, G. D., submitted.

starting materials can be chosen to control surfactant molecule packing in order to obtain the expected mesophase product. The designed syntheses in this paper can be extended to incorporate main group elements other than silicon or transition elements into the framework of mesoporous materials. As noted earlier,[6,10,71] the surfactant molecules can be associated with the inorganic species through ionic, covalent, or hydrogen-bonding interactions. Furthermore, we predict that by using the correct synthesis system and surfactant design, other known liquid-crystal cubic bicontinuous mesophases such as $Im3m$ and $Pn3m$[87,88] ($g > 1$) can be generated.

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