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The effect of alkan-1-ols addition on the structural ordering and morphology of mesoporous silicate MCM-41

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The effects of adding alkan-1-ols to surfactant–silicate gels during the synthesis of mesoporous silica MCM-41 are reported. Upon adding an optimal amount of medium carbon chain length alkan-1-ols ($C_mH_{2m+1}OH$, C_mOH; $m \geqslant 4$) to quaternary ammonium halides $C_nH_{2n+1}TMAX$ ($n = 10$–14, C_nTMAX, X = Br or Cl)–silicate systems, a marked improvement in the hexagonal order and the morphology of the synthesized MCM-41 materials was found. The optimal amount of added $C_mH_{2m+1}OH$ for the formation of well ordered hexagonal structure was found to decrease with increasing carbon chain length of the $C_nH_{2n+1}TMAX$ surfactant and $C_mH_{2m+1}OH$. However, when an excessive amount of alcohol is added, the mesostructure obtained from the longer carbon chain length $C_nH_{2n+1}TMAX$–silicate ($n \geqslant 12$) systems becomes lamellar. The addition of C_mOH ($m \geqslant 4$) offers a new synthetic approach to form lamellar-hexagonal liquid crystal intermediates necessary for synthesizing tubules–within–tubule (TWT) hierarchical structures whose morphology and size can be controlled by varying the water content and the $C_mH_{2m+1}OH$/surfactant ratio.

I Introduction

The engineering of mesoporosity in materials based on silica is emerging as a new and exciting research area of great scientific and technological importance.[1] The ability of porosity design, including their pore size and wall surface characteristics, is important toward imposing a framework for tailoring catalytic activities and opto-electronic properties of further embedded materials.[2] The accessible porosity can be utilized as the host for conducting or magnetic phases.[3–5] The microstructure of the composite is then dictated by the pore structure of the host. The electronic and magnetic properties of the composite materials can be tailored by altering the size, shape of the host and relative guest/host concentrations.

MCM-41 aluminosilicate is a new class of material that possesses uniform, adjustable pores in the range 1.5–10 nm. A rapid growing research interest related to the synthesis and characterization of MCM-41 mesoporous molecular sieves is evident within the research community.[6,7] Moreover, owing to the high surface area and high thermal stability characteristics of these mesoporous materials, a trend of their new applications as catalytic supports, molecular separation agents and nanocomposites is being realized.[8–15] The existence of periodic arrays of channel structures facilitates further fabrication of new materials, for example, by embedding electronic materials which together show interesting mesoscopic phenomena.[16,17] Synthetic techniques for controlling the size, periodic arrangement and the morphology of mesoporous materials are therefore in great demand.

Since mesoporous materials are commonly synthesized by the cooperative self-assembly of silicates and organic surfactants, the liquid crystal structure of the surfactant–silicate assembly is crucial in determining the mesostructure of the final products.[18–21] Factors influencing the structure and properties of the liquid crystal phase during synthesis include temperature and water content and concentration, type of counter ions and hydrophobicity of the surfactant and cosurfactants, *etc*. While the effects of some of these crucial factors have been explored intensively,[22–27] little research has been found to date on the effects of adding alcohols as cosurfactants during the synthesis of M41S materials.

Alcohols are known as effective cosurfactants in inducing many unique structures in surfactant solutions, such as cylindrical micelles, hexagonal phase, cubic phase and microemulsions.[28–30] For example, alcohols have been used in the preparation of mesoporous silica by Huo *et al.*[31] As a result, they were able to prepare uniform, millimeter-sized, mesoporous silica spheres from TBOS (tetrabutyl orthosilicate)–surfactant by the oil–water emulsion process under acidic conditions. Apparently, the presence of butanol, which formed during the hydrolysis of TBOS, promotes the formation of an emulsion. McGrath *et al.*[32] on the other hand used $C_{16}PyCl$–hexanol (Py = pyridinium) in brine, which forms a lyotropic L_3 phase template, to obtain nanoporous monolithic silicate the pore sizes of which can be tuned from 5 to 100 nm. In both cases, the addition of alcohols plays a role in promoting the formation of a large scale emulsion phase or a special liquid-crystal (L_3) phase of the ionic surfactant as a template. The effects of using alcohols as a structure modifier to lead to mesostructures in the nanometer range remain an interesting and challenging task. In a previous paper, we demonstrated that[33] by adding butanol to the $C_{10}TMAB$–silicate and $C_{12}PyCl$–silicate solutions, the formation of well ordered hexagonal structures of MCM-41 can be obtained. We report here a thorough study of the effect of alcohols on the synthesis of MCM-41.

For the surfactant–alcohol–water tertiary system, it is known[34–36] that medium carbon chain length alcohols, when used as cosurfactant, may penetrate into the palisade layer of the surfactant micelles and act as a ‘spacing agent’ to optimize the interaction between the OH group of the alcohol and the head group of the ionic surfactant. The addition of medium carbon chain length alcohols is also known to favour the formation of the micelles that have less local curvature (such as rod-like, disk-like micelles or lamellar phase).

The effect of alcohols on micelle structure can be understood qualitatively by the concept of a packing parameter model in the evolution of surfactant self-organization structure.[37,38] The surfactant organization depends on the effective volume (v_h), length (l_c) occupied by the hydrophobic group and effective surface area (a_0) of the hydrophilic groups of the surfactant.

The shape of the surfactant aggregate is then characterized by the packing parameter (g), such that:

$$g = v_h / l_c a_0 \quad (1)$$

When $0 \leqslant g < 1/3$, the surfactant aggregate is normally in the form of a spherical micelle, similarly, for $1/3 \leqslant g < 1/2$ a cylindrical micelle and for $1/2 \leqslant g < 1$ a flexible lamellar phase. Within the cylindrical micelle region, the larger the g value, the more favorable is formation of longer cylindrical micelles. For a given structure type, the three parameters a_0, v_h and l_c tend to balance each other such that the g value remains within the corresponding range. This approach has been used to explain the formation of various silica based mesophase configurations.[31,33]

While the incorporation of cosurfactants into surfactant aggregates is expected to increase the average volume per surfactant molecule, the average surface area may be slightly decreased due to the decrease in electrostatic repulsion of head group charges. Consequently, the packing parameter g would increase with the addition of cosurfactant, leading to an increase in micellar size and the formation of long rod-like micelles. It will be shown when alcohols are used as cosurfactants, that the structural order of the synthesized MCM-41 is improved.

In this work, we investigate the effects of adding alkan-1-ols to C_nTMAX ($n = 8$–14, X = Cl or Br)–silicate–water systems on the mesostructure and morphology of the MCM-41 materials. Related synthetic parameters such as the alkyl chain length of surfactants and the added alkan-1-ols, water content, alkanol/surfactant ratio and the types of counter ion and solvent were varied systematically to clarify their effects on the size and structural order of the resulting hexagonal mesopores.

Recently, there have been many efforts towards hierarchical self-organization in the sol–gel synthesis of aluminosilica.[39] Larger (lower curvature) structures can be constructed on top of the nanostructure. The rich structural and morphological transformations in alkaline silicate–surfactant liquid crystal phases are due to the delicate balance in head repulsion and tail attraction in the molecular self-organization of the system. As explained above, alcohols may affect the curvature in the organization in the nanometer scale whereas in the micrometer scale we have previously shown that the alkaline surfactant–silicate system can produce further hierarchical organization, such as the tubular form of MCM-41,[40] induced by phase transformations between lyotropic phases. Thus, one would expect that hierarchical structures can be controlled by using alcohols as a cosurfactant.

Here, we use mixtures of alkyltrimethylammonium halides and alcohols of various chain lengths as the organic template. We are interested in the fine adjustment of packing in the surfactant–silicate complex which affects the morphology of the products through curvature changes at the micrometer scale. The effects of adding alcohols with varied hydrophobicity on the formation of MCM-41 with the tubules-within-tubule (TWT) hierarchical structure[40] prepared from alcohol–C_nH_{2n+1}TMAX–silicate systems was examined.

II Experimental

Materials

The silica source, sodium silicate (27% SiO_2, 14% NaOH), was obtained from Aldrich or Merck. The quaternary ammonium surfactants, $C_nH_{2n+1}NMe_3X$ ($n = 8$–14, C_nTMAX, X = Cl or Br), were obtained from Aldrich, Acrôs or Tokyo Chemical Industry and were used without further purification. The alkan-1-ols (C_mOH) were purchased from Merck, Aldrich or Riede-de Haën. Sulfuric acid was obtained from Merck.

Synthetic procedure

The synthetic procedure used is based on the delayed-neutralization process reported previously.[33,40] A given amount of alkan-1-ol was dissolved into a C_nTMAX aqueous solution to form a clear solution and then sodium silicate was added. After stirring for *ca.* 10 min at room temperature (27 °C), a 1.20 M H_2SO_4 aqueous solution was added to the gel mixture dropwise to acidify the reaction system. Typically, the time required for complete acidification is *ca.* 0.5–1.0 h. The molar composition of the resultant gel is: 1.0 C_nTMAX: (2.10–1.30) SiO_2: (1.63–1.20) NaOH: (0.67–0.40) H_2SO_4: (0.6–2.0) C_mOH: (50–500) H_2O. The gel mixture formed was heated at 100 °C for 48–144 h in a static autoclave. The as-synthesized product was then calcined at 560 °C in air for 6 h to remove the organic template.

Characterization

X-ray powder diffraction (XRD) patterns of the synthesized samples were collected on a Scintag X1 diffractometer using Cu-Kα radiation ($\lambda = 0.154$ nm). N_2 adsorption–desorption isotherms were obtained at 77 K on a Micrometric ASAP 2010 apparatus. Transmission electron micrographs (TEM) were taken on a Hitachi H-7100 micrometer operated at 75–100 keV. Scanning electron microscopy (SEM) was performed on Hitachi S-2400 or S-800 operated at an accelerating voltage of 20 keV.

III Results and discussion

Structural ordering of hexagonal MCM-41

Effects of alkan-1-ol addition. To investigate the effect of adding alkan-1-ol on the hexagonal structure order of the MCM-41 materials, we first added alkan-1-ols with varied carbon chain length into a C_{12}TMAB–silicate solution during syntheses. The XRD patterns of the as-synthesized MCM-41 products obtained from various C_mOH/C_{12}TMAB ratios are shown in Fig. 1. The XRD pattern of the product synthesized in the absence of alcohol exhibits only a single broad peak near $2\theta = 2.5°$ indicating a poorly ordered mesostructure (Fig. 1A). As the alkan-1-ols (C_mOH; $m \geqslant 2$) were added, a highly ordered hexagonal structure of MCM-41 materials with at least four characteristic XRD peaks can be observed (Fig. 1B–G). It is noted that the optimal amount of added alkan-1-ol for the formation of a well ordered hexagonal structure decreases with increasing carbon chain length of the alkan-1-ols.[41–44] This behavior can be accounted for by the partition of alcohols and their influences on the surfactant packing. The partition coefficient, that is the molar ratio of the alkan-1-ol in the micellar palisade layer to that in the aqueous solution, has been found to increase exponentially with the increasing carbon chain length (m) of C_mOH.[45–47] The longer carbon chain length alkan-1-ols that have higher hydrophobicity are more favorable in penetrating into the micelles of C_{12}TMAB surfactant to form well elongated micelles. The cylindrical micelles in turn further interact with silicate oligomers to form well ordered hexagonal MCM-41 structure.

The formation of the mesostructure is most likely through a cooperative condensation of surfactants and silicates. From the thermodynamic point of view, the formation of mesostructure can roughly be divided into two steps, namely the formation of rod-like micelles and then the condensation of the hexagonal phase. Within the cylindrical micelle range, systems with higher g value will favor the formation of longer, rod-like micelles. The longer rod-like micelles also favor the formation of hexagonal phase because the entropy gained in randomization becomes less. The effects of alcohol addition on the formation of mesostructure observed in the present

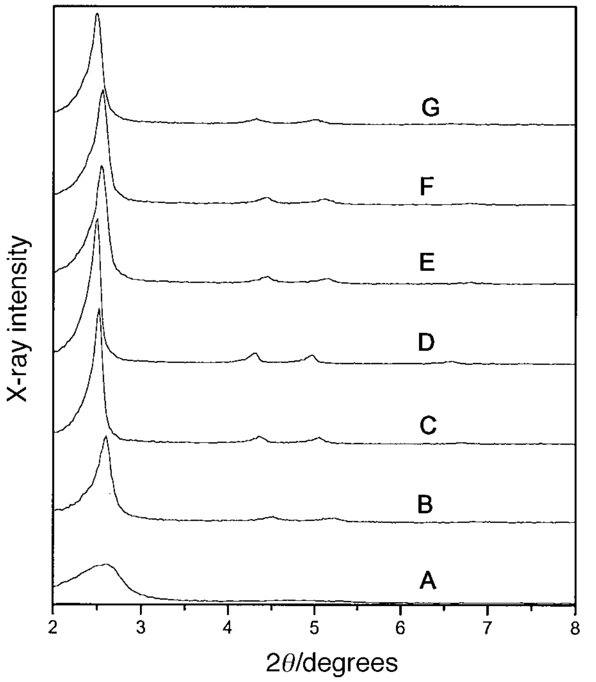

Fig. 1 XRD patterns of as-synthesized MCM-41 products prepared from C_{12}TMAB–C_mOH–silicate systems under various of C_mOH/C_{12}TMAB ratios. (A), without alkan-1-ol; (B), C_2OH/C_{12}TMAB = 5.77; (C), C_3OH/C_{12}TMAB = 1.77; (D), C_4OH/C_{12}TMAB = 0.40; (E), C_5OH/C_{12}TMAB = 0.20; (F), C_6OH/C_{12}TMAB = 0.10 and (G), C_8OH/C_{12}TMAB = 0.05.

investigation are therefore in line with the theoretical considerations. Our results indicate that the alcohol molecules effectively minimize the Coulombic repulsion between the head groups and the effective surface area a_0 is reduced to favor the formation of elongated cylindrical micelles and to produce a more ordered hexagonal phase.

Effects of carbon chain length and counter ion of the surfactant. Besides varying the chain length *m* of C_mOH cosurfactant in the C_{12}TMAB–C_mOH–silicate system, we also studied the effects of varying the carbon chain length of the surfactant by adding butanol to C_nTMAX–silicate ($n = 8$–14) systems. An examination of the C_4OH/surfactant ratio reveals that the optimal amount of the added C_4OH decreases with increasing surfactant carbon chain length.

The effect of surfactant counter ion was also investigated by replacing Br^- with Cl^-. It is observed that the chloride surfactants require more C_4OH cosurfactant to produce MCM-41 with well ordered structure compared to that prepared by bromide surfactant. This is due to the fact that the Cl^- counter ion has weaker adsorption strength and less electronic shielding with the cationic head group of the surfactant[48,49] (which results in a smaller *g* value). To increase the *g* value and hence to bring about the desired structural ordering of the MCM-41, the chloride surfactants system thus requires more alkan-1-ols to achieve an optimal *g* value balance.

Effects of adding polar organic solvents. While it is clear that the addition of medium carbon chain length alkan-1-ols favors the formation of hexagonal phase, we also investigated the effects of adding polar organic solvents such as acetone, methanol and acetonitrile to the C_{12}TMAB– and C_{14}TMAB–silicate aqueous system on the hexagonal structural ordering. The addition of polar organic cosolvents is clearly deleterious to the formation of structurally ordered MCM-41 materials as revealed by broadened XRD patterns. Presumably, these polar organic cosolvents are dissolved in the aqueous solution and hence decrease the hydrophobic driving force for micelle formation by interrupting the hydrogen bond network of water and thus inhibit the formation of well arranged hexagonal structure.[50,51] The addition of polar cosolvent tends to shift the packing balance towards the hydrophilic side and decreases the size of the micelles thus producing a less ordered hexagonal phase.

Effects of alkan-1-ol additives on the physical properties of MCM-41. To investigate the effects of adding alkan-1-ols on the physical properties of the calcined MCM-41 materials from the C_nTMAX–C_mOH–silicate system, we analyzed the XRD patterns and nitrogen adsorption–desorption isotherms of the MCM-41 materials with well ordered hexagonal structure. All samples possess high BET surface areas of *ca.* 1000 $m^2 g^{-1}$, as expected for ordered mesostructures. Table 1 shows that some of the important physical properties of the synthesized MCM-41, such as the *d*-spacing (d_{100}), pore size and wall thickness are not significantly affected by the addition of alkan-1-ols. C_mOH molecules are likely to stay within the palisade layers and, unlike hydrocarbon additives (*e.g.*, toluene or mesitylene), they essentially do not extend into the micellar core to have an appreciable effect on the pore size distribution of the resultant MCM-41. Moreover, as a result of the delayed neutralization process[33] in the synthesis, the wall thickness of the resultant MCM-41 (*ca.* 1.9 nm) was found to be larger than those obtained from conventional methods (*ca.* 0.8–1.0 nm). Accordingly, these materials exhibit good thermal and hydrothermal stability.

Effect of C_mOH/C_nTMAX ratio. According to the simplified packing parameter model, the presence of alkan-1-ols effectively increases the packing parameter (*g*) of the surfactant aggregate and promotes the formation of cylindrical micelles. It is expected that upon further increasing the alkan-1-ol content to the point where $g \geq 1/2$, the phase structure of the products should change to lamellar. Upon gradually increasing the C_6OH/C_{12}TMAB ratio in the C_{12}TMAB–C_6OH–silicate synthetic system, the mesostructure of the products varies accordingly in the order: poorly ordered mesostructure→well ordered hexagonal structure→less ordered hexagonal structure→lamellar structure (Fig. 2). Similar results were also found for the other

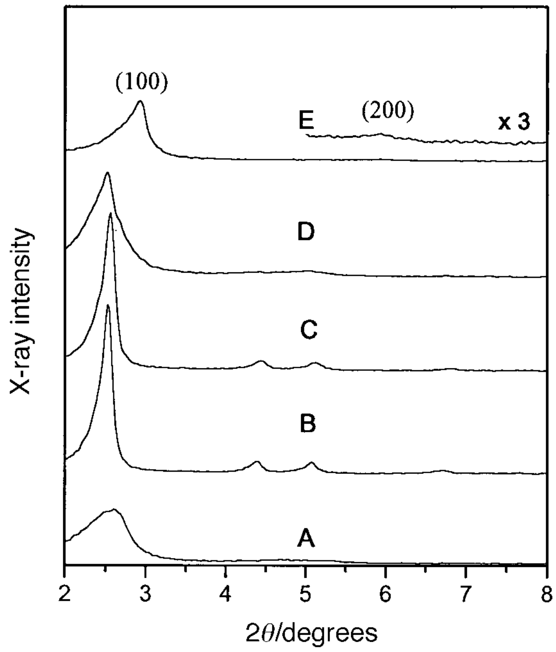

Fig. 2 XRD patterns of as-synthesized MCM-41 products prepared from C_{12}TMAB–C_6OH–silicate systems with varied $\eta = C_6OH/C_{12}TMAB$ ratios. (A), $\eta = 0$; (B), $\eta = 0.10$; (C), $\eta = 0.23$; (D), $\eta = 0.43$ and (E), $\eta = 0.77$.

Table 1 Effect of alkan-1-ol addition on pore size, *d*-spacing, unit cell parameter (a_0), wall thickness and the BET surface area of MCM-41 materials obtained from various C_nTMAX–C_mOH–silicate systems

Surfactant (C_nTMAX)	Alkan-1-ols (C_mOH)	*d*-Spacing, $d_{100}{}^a$/nm	$a_0{}^b$/nm	Pore size/nm	Wall thickness/nm	BET surface area/m^2 g^{-1}
C_{14}TMAB	None	3.68	4.25	2.38	1.87	1058
	C_2OH	3.70	4.27	2.40	1.87	1018
	C_4OH	3.75	4.33	2.42	1.91	1035
	C_5OH	3.75	4.33	2.40	1.93	1009
	C_6OH	3.74	4.32	2.40	1.92	1073
C_{14}TMACl	C_4OH	3.62	4.18	2.30	1.88	1038
	C_5OH	3.62	4.18	2.28	1.90	1049
	C_6OH	3.64	4.20	2.32	1.88	1006
C_{12}TMAB	None	3.40	3.93	2.03	1.90	1098
	C_2OH	3.30	3.81	1.95	1.86	1100
	C_4OH	3.39	3.91	2.08	1.83	1064
	C_5OH	3.36	3.88	2.00	1.88	1052
	C_6OH	3.38	3.90	2.02	1.88	1083
	C_8OH	3.40	3.93	2.06	1.87	1042
C_{12}TMACl	C_4OH	3.39	3.91	2.06	1.85	1079
	C_5OH	3.40	3.93	2.07	1.86	1095
	C_6OH	3.42	3.95	2.10	1.85	1078

^{a}Obtained from XRD. ^{b}Distance between two nearest pore centers; $a_0 = 2d_{100}/\sqrt{3}$.

C_nTMAX–C_mOH–silicate systems with $n \geqslant 12$ and $m \geqslant 4$. Alkan-1-ols with longer carbon chain length and counter ions with higher electronic shielding ability hence are more favorable in forming low curvatured (lamellar) mesostructures.

Synthesis of tubules-within-tubule (TWT) hierarchical structure MCM-41

Effect of C_mOH addition. Previously, we reported[40] that ordered mesoporous MCM-41 with TWT hierarchical structure can be successfully synthesized under highly alkaline conditions by forming a flexible, membrane-like intermediate phase which displays coexistence of lamellar and hexagonal mesostructure. MCM-41 with TWT hierarchical morphology can be prepared from suitably hydrophobic surfactant systems (for example C_{16}TMAX–aluminosilicate systems) and by careful control of the acidification rate. We also reported that, for the C_{14}TMAB and C_{12}TMAB surfactants which are less hydrophobic than C_{16}TMAB, the resultant MCM-41 products are mostly in broken tubular and microparticle morphology, as shown in Fig. 3A and C, respectively. However, by adding a given amount of C_mOH cosurfactant with $m \geqslant 4$, the hydrophobicity of the surfactant can be increased and hence favors the formation of a lamellar phase. Thus, it is envisaged that the addition of C_4OH cosurfactant to the less hydrophobic C_{14}TMAB or C_{12}TMAB surfactants should lead to the formation of hexagonal–lamellar intermediates, which are responsible for the formation of the TWT hierarchical structure.

The resultant products show distinct TWT hierarchical structures (Fig. 3B and D) and are obtained in high yields (*ca.* 80–95%). Their TWT hierarchical structures were also confirmed by TEM, which showed that the nanometer-sized parallel channels are arranged along the axes of the hollow, micron-sized tubules.

The TWT hierarchical structure can also be synthesized from other C_nTMAX–C_mOH–silicate systems ($n = 12$–14; X = Br or Cl; $m \geqslant 3$) by adding a given amount of C_mOH with suitable carbon chain length to such surfactant–silicate systems. However, it is important to note that the amount of C_mOH required to prepare TWT morphologies in high yields is always greater than that for just improving the hexagonal structure of MCM-41. When C_mOH with $m < 3$ was used as additive in the C_nTMAX–silicate system, the well ordered hexagonal MCM-41 products almost always had microparticle morphology.

Effect of water content. In an earlier report we have revealed that the surfactant/water ratio plays a significant role in the formation of the MCM-41 with TWT morphology. The formation of TWT morphology is restricted in a narrow range of surfactant/water ratio. Similarly, the water content is also crucial for the synthesis of TWT morphology for the present C_nTMAX–C_mOH–silicate system. At low water content, the resultant products are mostly in the form of microparticles. The morphology remains unchanged even when the C_mOH concentration is varied. For the surfactant–silicate system, we have proposed that mixed lamellar-hexagonal membrane intermediates, separated by water layers, are involved during the synthesis of TWT morphology. As a result of low water concentration, the membranes may be tightly aggregated and thus cannot possess adequate thermodynamics energy to bend or to curve themselves to form the TWT morphology.

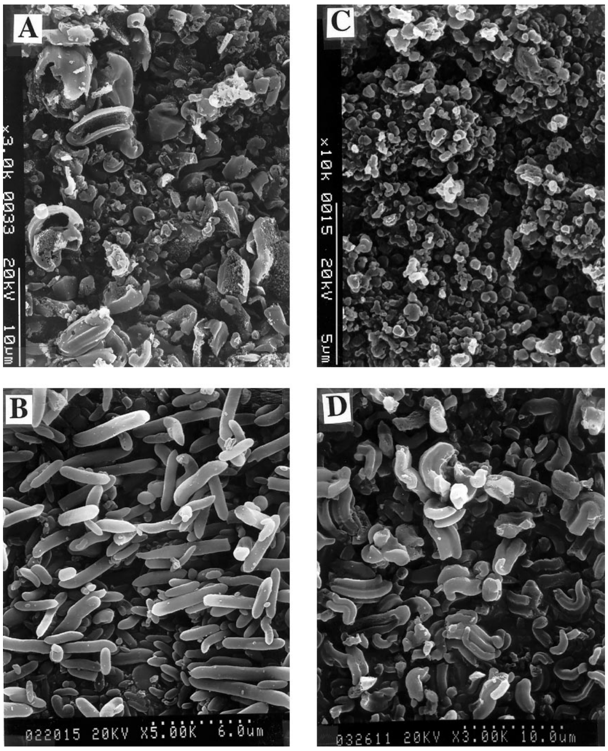

Fig. 3 SEM micrographs of the calcined MCM-41 materials prepared from (C_{14}TMAB,C_{12}TMAB)–C_4OH–silicate systems. (A), C_4OH/C_{14}TMAB = 0; (B), C_4OH/C_{14}TMAB = 0.60; (C), C_4OH/C_{12}TMAB = 0 and (D), C_4OH/C_{12}TMAB = 0.85.

The yield of the TWT morphology, however, gradually decreases upon further increase of the water content. It is suggested that the excess water tends to prohibit the formation of lamellar–hexagonal membrane intermediates required for the formation of TWT structure.

Effect of C_mOH/C_nTMAX ratio. As described above, an excess water content tends to impede the formation of MCM-41 with TWT morphology. This situation can be improved by introducing additional C_mOH cosurfactant. Upon increasing the $C_4OH/C_{14}TMAB$ ratio, the yield of the TWT structure also increased. A similar trend was also observed for the $C_{12}TMAB$–C_4OH–silicate system. Therefore, besides the importance of water content, the addition of C_mOH also plays a crucial role in not only the overall product yield but also in adjusting the micrometer-scale tubular diameter of the TWT structure.

IV Conclusions

We have demonstrated that careful addition of alkan-1-ols during the synthesis of MCM-41 is an excellent method for synthesizing and adjusting both the mesostructure and morphology of mesoporous silicates from cationic surfactant (C_nTMAX)–silicate systems. In particular, the hierarchical TWT morphology can be easily prepared by correct adjustment of the relative compositions of C_mOH, water and surfactant. The role of alkan-1-ol additives can be understood as either cosolvent or cosurfactant depending on the overall hydrophobicity of the C_nTMAX–C_mOH–silicate system under consideration. The variations of the morphologies and the mesostructures can be interpreted in terms of either cosolvent or cosurfactant effects through adjustment in the packing behavior of the surfactant–alkan-1-ol–silicate systems. The results presented here may contribute towards enriching the understanding of the aggregation behavior in cosurfactant–surfactant–water ternary systems. Given the richness of phase behavior in ternary cosurfactant–surfactant–aqueous systems, it could open up a new method of synthesizing other interesting hierarchical MCM-41 materials through various intermediate phases. This comprehensive study should also invoke the capability in fine-tuning the structural ordering and morphology of mesoporous materials. Such a capability would be useful in future applications of MCM-41 materials in producing catalytic supports or embedded nanomaterials.

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