Energetically Favored Formation of MCM-48 from Cationic–Neutral Surfactant Mixtures

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The cubic mesoporous silica molecular sieves MCM-48 have been obtained as an energetically favorable mesophase via a synthesis route using the surfactant mixtures between alkyltrimethylammonium bromides and polyoxyethylene alkyl ethers, with sodium silicate as the silica source. The MCM-48 mesophase was stable under the synthesis conditions for longer than a month, preventing a subsequent transformation to lamellar phases. Metal sources and salts could be added to the synthesis mixture during this period to incorporate metallic elements within the siliceous framework and to increase hydrothermal stability. The product yield amounted to 4.2 mol of SiO₂ per surfactant, which was 5 times that of the previously reported synthesis procedure using hexadecyltrimethylammonium bromide and tetraethyl orthosilicate. The present synthesis results demonstrate that the use of mixed surfactants is emerging as a new useful strategy for the synthesis of mesoporous molecular sieves.

1. Introduction

The mesoporous silica reported as MCM-48 by Kresge et al.1,2 is one of the most interesting materials among many mesoporous silica molecular sieves found recently.1–6 The structure of the MCM-48 materials may be described by the gyroid surface discovered by Schoen,7 and the Q^{20}rod structure belonging to the cubic Ia₃d space group.1,9,10 The enantiomeric pair of independently interpenetrating three-dimensional networks of the mesoporous channels described in this way are believed to be much more resistant to pore blockage while being used as adsorbents and catalyst supports than the one-dimensional channels of a more widely known hexagonal mesoporous silica, MCM-41.11–15 The MCM-48 channels are constructed with atomically disordered silica walls about 1 nm thick. Despite the atomic disorder, the MCM-48 materials can be synthesized in the form of single crystals.11,16 Yet these superior properties of MCM-48 were not fully exploited. Although the discovery of the MCM-48 materials was reported simultaneously with the hexagonal MCM-41 by Kresge et al. in 1992,1,2 research reports until now on applications of these materials have been severely biased to MCM-41.16–19 The bias may be attributed largely to the fact that the synthesis of MCM-48 required very specific synthesis conditions.

Various synthesis routes to MCM-48 were developed in order to overcome the synthetic shortcomings.11–15,20–23 These synthesis results show that the crystallinity of the MCM-48 products went through an optimum as a function of time. The MCM-48 products were obtained as an intermediate between the transformation from a hexagonal or disordered surfactant–silica mesophase to a more stable lamellar mesophase. The kinetically controlled synthesis is believed to have been a major cause for many of the problems in the MCM-48 synthesis and application. It is therefore highly desirable to find a synthesis procedure obtaining MCM-48 as an energetically favored mesophase.

Recently, Xu et al.14 have reported that the transformation of the MCM-48 mesophase to lamellar can be quenched by adjusting the pH of the reaction mixture. The pH control is a very useful method for quenching the mesophase transformation from a reaction kinetic point of view. In that case, however, the MCM-48 mesophase becomes contaminated by the hexagonal and disordered surfactant–silica mesophases which form after the pH adjustment from the silica sources remaining in the reaction mixture.

Here, we present a synthesis route which obtains high-quality MCM-48 samples as an energetically favored mesophase. The present method uses a mixture between cationic surfactants and neutral surfactants. Except for the use of the surfactant mixture, the MCM-48 synthesis procedure is similar to that of MCM-41 which was reported by Ryoo and Kim24 using a pH adjustment. This synthesis method has the advantage of achieving a remarkably high product yield of 4.2 mol of SiO₂ per surfactant, as compared with the production of only 0.8 SiO₂/surfactants11 using hexadecyltrimethylammonium bromide (HTMABr) as a single surfactant. More importantly, its long-term product stability provides us opportunities to perform various experiments under synthesis reaction conditions, such as the addition of salts for the improvement of its hydrothermal stability and the addition of metal sources for framework incorporation.

2. Experimental Section

The silica source used in the present synthesis experiments was an aqueous solution of sodium tetrasilicate (11.3 wt % Na₂Si₄O₁₁ and 88.6 wt % H₂O), which was prepared with colloidal silica Ludox HS40 (39.5 wt % SiO₂, 0.4 wt % Na₂O, and 60.1 wt % H₂O, Du Pont), distilled water, and NaOH.24 The surfactant mixture was prepared by dissolving a cationic surfactant (vide infra) and a neutral surfactant (or amphiphilic neutral species) simultaneously with heating in distilled water. The surfactant solution was cooled to room temperature. The silica source at room temperature and the surfactant solution were quickly poured into a large polypropylene bottle. The bottle was capped and shaken rapidly and vigorously. The gel mixture
thus obtained was heated for the formation of the surfactant—
silica mesophases under static conditions at 373 K. The
mesophases were formed afloat at an early stage of heating.
When this happened, the bottle containing the reaction mixture
was sometimes agitated in order to induce precipitation on the
bottom. Precipitated products from the reaction mixture were
then filtered, washed with distilled water, and dried in an oven
at 393 K. The products were calcined in air at 823 K, after
most of the surfactants were removed by washing with a HCl—
ethanol mixture.25,26 The product yield was determined from
sample mass recovered after the calcination. X-ray powder
diffraction (XRD) patterns were recorded at room temperature
using a Rigaku MiniFlex instrument operating with a Cu Kα
X-ray source.

The synthesis and characterization experiments were repeated
many times, changing the surfactants, the surfactant mixing ratio,
and the hydrothermal reaction time at 373 K. In some experi-
ments, the reaction mixtures were cooled to room temperature
after a certain reaction period at 373 K and subsequently added
with acetic acid to adjust the pH to 10.24 The reaction mixtures
were heated to 373 K again. The pH adjustment and subsequent
heating sometimes was repeated twice, depending on the
aim of the synthesis experiments.

The cationic surfactants used in the synthesis experiments
were n-alkyltrimethylammonium bromides (ATMABr), where
the carbon numbers in the alkyl groups were varied over C12—
C18. The ATMABr surfactants were received from Aldrich and
used without further purification. Various neutral surfactants
and other amphiphilic molecules were used in combination with
one of the cationic surfactants. The neutral surfactants included
polyoxyethylene alkyl (and aryl) ethers represented by the
formula CnH2n+1O[C2H4O]mH [CnEO]m for brevity, where n
ranges from 12 to 18 and m from 3 to 10. These surfactants
were donated by Hansong Chemicals.27 Triton X-100 [CH2C-
(CH3)2CH2C(CH3)2CH4O(C2H4O)9] received from Daejung
was also used as a neutral surfactant.

3. Results

Figure 1 shows the XRD patterns of the surfactant—silica
mesophases obtained from the starting mixtures of 5.0 SiO2/
1.25 Na2O/fns C12(EO)m/(1 − fns) HTMABr/400 H2O, where a
fraction of the neutral surfactant fns was varied from 0.05 to
0.25. To obtain the mesophases, the starting mixtures were heated
at 373 K for the reaction times given in Figure 1. The pH of
the reaction mixtures was not adjusted during the reaction
periods. The XRD patterns were collected from these synthe-
sized surfactant—silicate mesophases without calcination. The
results show that the structure of the mesophase was very
sensitive to both fns and the hydrothermal reaction time.
The structure corresponded to the hexagonal mesophase, MCM-41,
when fns was given as 0.05. As fns increased to 0.18, the
mesophase formed within 4 days of the reaction period became
identical to the cubic Ia3d mesophase, i.e., MCM-48. Further
increases in the reaction time under this condition resulted in
the structural transformation to a lamellar mesophase. When fns
was increased to above 0.25, the product was lamellar
regardless of reaction times after 1 day.

Figure 2 shows the XRD patterns for the surfactant—silica
mesophases recovered at various steps of the synthesis with 5.0
SiO2/1.25 Na2O/0.85 HTMABr/0.15 C12(EO)4/400 H2O. Figure
2a was obtained after 2 days of the initial reaction period. Figure
2b was obtained after the pH of the reaction mixture was
subsequently adjusted to 10. The pH adjustment required 0.6
mol of acetic acid per total Na present in the reaction mixture.

Note that the XRD pattern in Figure 2b was much lower in
intensity than that of the result shown in Figure 2a. This
difference resulted from the contamination with an amorphous
silica—surfactant mass that precipitated due to the pH change.
The incorporation of the amorphous silica increased the product.
yield from 2.5 mol of SiO₂ per total surfactant to 3.8. Figure 2c was obtained after the reaction mixture containing the amorphous precipitate was heated for 2 more days under the reaction condition. This XRD pattern is characteristic of a high-quality MCM-48 material. The product yield was 3.8 SiO₂/surfactant, which was much more than the 2.5 mol of SiO₂ recovered before the pH adjustment. Evidently, the additional amount of the MCM-48 product was obtained as a result of the reaction after the pH adjustment. The additional reaction led to an increase in the pH from 10 to 11. These results indicate that the structural transformation from MCM-48 to lamellar was prevented by adjusting the pH of the reaction mixture to 10 after 2 days of the initial reaction period. The effect of the pH adjustment was not simply kinetic quenching of the product transformation from MCM-48 to lamellar, but it made the formation of the cubic mesophase more favorable.

The product yield and XRD patterns of the product were monitored during the reaction period from 4 to 30 days following the pH adjustment. However, no significant changes were detected during the reaction period. The XRD pattern obtained after 30 days is shown in Figure 2d. The MCM-48 mesophase exhibited the long-term stability under the reaction condition following the pH adjustment, confirming that the structural transformation shown in Figure 1b could be prevented by the pH adjustment. As described above, the pH of the reaction mixture increased from 10 to about 11, consequent to the additional product formation. About 0.1 mol of acetic acid per Na were required in order to lower this pH to 10 again. Upon subsequent heating for 2 days at 373 K, the product yield increased to 4.2 mol of SiO₂/surfactant. The XRD pattern of the product shown in Figure 2e was still of high quality MCM-48.

4. Discussion

Mixed surfactants exhibit complex phase behaviors in aqueous solutions. In many cases, two different surfactants are completely miscible and form liquid-crystalline micellar mesophases cooperatively. The structure of the micelle packing in the liquid-crystalline mesophases may be determined by various effects, such as their head-to-tail packing parameters, electrostatic interaction, and hydrogen bonding between the headgroups of the two different kinds of surfactant molecules. The phase behavior becomes more complicated when silica sources are present to form surfactant–silica mesostructures in the aqueous solution. The present synthesis system consists of sodium silicate, hexadecyltrimethylammonium bromide (HTMABr), and the C₁₂(EO)₄ surfactant dissolved in basic solution. The silicate anions in the solution are strongly attracted by electrostatic attraction surrounding the headgroups of the HTMABr surfactant micelles. The effects of the C₁₂(EO)₄ surfactant may be singled out by keeping all other experimental parameters constant, except for the increase in the C₁₂(EO)₄/HTMABr molar ratio.

Our results in Figure 1 show that the structure of the silica–surfactant mesostructures in this case changes continuously from hexagonal to lamellar. The Ia₃d cubic mesophase appears in the middle of the transition. These changes are consistent with the general tendency of the H → Q → L phase transitions observed with decreasing the surface curvature around the surfactant micelles, where H, Q, and L refer to the hexagonal, cubic Ia₃d, and lamellar mesophases, respectively. These results may be explained by the concentration of the silicate anions on the surface of the surfactant micelles. The neutral surfactant has no strong interaction with the silicate anions, and consequently its incorporation to the micelles will lead to a dilution of the silicate at the surface. The low surface concentration and subsequent polymerization may well lead to a significant contraction of the micellar surface, resulting in a phase transition from H to L. It is therefore likely for other cubic mesophases such as Im₃m and Pn₃m to appear in the middle of the H → L transition. We have made a great deal of effort for the isolation of the cubic mesophases, changing the neutral-to-cationic surfactant ratio, the surfactant-to-silica ratio, and the pH of the reaction mixture, but still we failed. Probably, only the Ia₃d mesophase is stable enough for isolation under our present synthesis conditions at 373 K.

Compared to the strong influence, the effects of the neutral surfactant should decrease if the synthesis is performed under strong acidic conditions via a S⁺X⁻/I⁻-type ionic mechanism, where S⁺ stands for a surfactant, I⁺ for an inorganic silica species, and X⁻ for a counteranion of S⁺. In this case, the silica species is positively charged due to the adsorption of H⁺. The synthesis occurs through the formation of electrically triple-layered micelles. The influence of the silicate condensation is very weak in this case compared with the synthesis in basic solutions taking place through a S⁺I⁻–type ionic mechanism. We have performed synthesis experiments with 5.0 SiO₂/HCl/Na₂CO₃/C₁₂H₂₅NH₂/(1 – fNa) HTMABr/1000 H₂O, changing fNa up to 0.5. However, we have always obtained hexagonal materials in agreement with our speculations.

XRD patterns in Figure 1b show that the cubic Ia₃d mesophase is not a thermodynamically favorable end product unless the pH is adjusted to around 10, even if the mixed surfactant is used. The cubic mesophase is formed rapidly within 24 h before the pH adjustment. However, its XRD pattern indicates poor structural order compared with results reported in other works. Similar results to Figures 1 and 2 can be obtained using other surfactants or amphiphilic species such as dodecylamine (DA), C₁₂H₂₅NH₂, other C₆H(EO)₄m, and Triton X-100 instead of LE4. For example, a highly ordered MCM-48 product can be obtained from a mixture of 5.0 SiO₂/1.25 Na₂O/0.89 HTMABr/0.11 Triton X-100/400 H₂O. The optimum condition for this
MCM-48 sample obtained from 5.0 SiO$_2$/1.25 Na$_2$O/0.15 C$_{12}$ (EO)$_4$/0.85 HTMABr/400 H$_2$O. Inset: The corresponding pore size distribution curve obtained from the adsorption by Barrett–Joyner–Halenda method.

**Figure 3.** Nitrogen adsorption–desorption isotherms at 77 K for MCM-48 sample obtained from 5.0 SiO$_2$/1.25 Na$_2$O/0.15 C$_{12}$ (EO)$_4$/0.85 HTMABr/400 H$_2$O. Inset: The corresponding pore size distribution curve obtained from the adsorption by Barrett–Joyner–Halenda method.

**Table 1:** Surfactant–Silica Mesostructures Obtained from Mixtures between HTMABr and Neutral Surfactants$^a$

<table>
<thead>
<tr>
<th>surfactant</th>
<th>$f_m$</th>
<th>mesophase</th>
<th>surfactant</th>
<th>$f_m$</th>
<th>mesophase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{12}$ (EO)$_4$</td>
<td>0.05</td>
<td>H</td>
<td>DA</td>
<td>0.11</td>
<td>H</td>
</tr>
<tr>
<td>0.11</td>
<td>C</td>
<td>0.20</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.18</td>
<td>C</td>
<td>0.25</td>
<td>L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$<em>{12}$ (EO)$</em>{10}$</td>
<td>0.11</td>
<td>H</td>
<td>TX-100</td>
<td>0.05</td>
<td>H</td>
</tr>
<tr>
<td>0.20</td>
<td>C</td>
<td>0.11</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>L</td>
<td>0.20</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Hydrothermal synthesis was performed at 373 K for 2 days using starting mixtures with the molar composition of 5.0 SiO$_2$/1.25 Na$_2$O/400 H$_2$O. Inset: The corresponding pore size distribution curve obtained from the adsorption by Barrett–Joyner–Halenda method.

**Table 2:** Typical Synthesis Conditions for MCM-48 Materials Giving Various Lattice Parameters

<table>
<thead>
<tr>
<th>cationic surfactant</th>
<th>neutral surfactant$^b$</th>
<th>$f_m$</th>
<th>$d_{211}$ spacing (nm)$^c$</th>
<th>lattice parameter (nm)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{12}$TMABr</td>
<td>C$_{12}$ (EO)$_4$</td>
<td>0.25</td>
<td>3.79</td>
<td>9.28</td>
</tr>
<tr>
<td>C$_{12}$TMABr</td>
<td>C$_{12}$ (EO)$_3$</td>
<td>0.20</td>
<td>3.99</td>
<td>9.77</td>
</tr>
<tr>
<td>C$_{14}$TMABr</td>
<td>C$_{12}$ (EO)$_4$</td>
<td>0.18</td>
<td>4.18</td>
<td>10.24</td>
</tr>
<tr>
<td>C$_{16}$TMABr</td>
<td>TX-100</td>
<td>0.08</td>
<td>4.35</td>
<td>10.66</td>
</tr>
</tbody>
</table>

$^b$ Neutral surfactant/(1 - $f_m$) cationic surfactant/400 H$_2$O. The reaction mixtures were reheated after the pH adjusted to 10. $^c$ C$_{12}$ (EO)$_4$, C$_{12}$ (EO)$_3$, and C$_{16}$TMABr are denoted as the neutral surfactant. $^d$ The $d_{211}$ spacings were obtained from as-synthesized samples. Lattice parameters were calculated from the $d_{211}$ spacings.

**Figure 4.** XRD patterns for MCM-48 samples obtained at 373 K from 1.0 TEOS/0.25 Na$_2$O/0.65 HTMABr/100 H$_2$O: (a) after hydrothermal reaction for 4 days; (b) after pH adjustment to 10 and heating again for 2 days; (c) after pH adjustment to 11 and heating again for 2 days. Note that the (211)/(220) peak ratio in (b) is significantly lower than that in (a). This is due to the formation of a hexagonal and/or disordered surfactant–silica mesophase that gives a strong XRD line overlapping with the (211) peak for MCM-48, from the silica sources remaining in the reaction mixture after the pH adjustment. The XRD line from the disordered mesophase overlaps with the (220) line in (c).

Our synthesis route to MCM-48 has several advantages over the synthesis methods using HTMABr/tetraethyl orthosilicate (TEOS)/NaOH/H$_2$O or HTMABr/sodium silicate/ethanol/H$_2$O. The present synthesis is performed at an atmospheric pressure, while the others require autoclave to prevent a loss of ethanol, since the ethanol concentration is critical for the formation of the cubic mesophase. Another advantage is its high product yield: 5 mol of SiO$_2$ are used per surfactant (0.85 HTMABr + 0.15 C$_{12}$ EO$_4$), among which more than 4 mol are converted to MCM-48. Compared with the high yield, the synthesis procedures using HTMABr/NaOH/TEOS/H$_2$O or HTMABr/sodium tetrasilicate/ethanol/H$_2$O give a yield corresponding to only 0.8 SiO$_2$/surfactant. An MCM-48 synthesis procedure using a mixture of HTMABr and anionic surfactants has been reported recently. A high SiO$_2$/surfactant molar ratio around 6 was claimed as a significant merit for the synthesis procedure. However, we have confirmed that approximately 2 mol of SiO$_2$/surfactant are converted to the form of MCM-48.

As stated in section 1, the long-term product stability under the synthesis reaction conditions increases our opportunities for the metal incorporation within the siliceous framework of MCM-48. Let us demonstrate the aluminum incorporation, for example. A starting mixture with 5.0 SiO$_2$/1.25 Na$_2$O/0.85 HTMABr/0.15 C$_{12}$ (EO)$_4$/400 H$_2$O was heated for 2 days at 373 K, and the pH of this mixture was adjusted to 10. The reaction mixture was heated for 2 more days following the pH adjustment in order to complete the formation of the MCM-48 mesophase. This mixture was heated for 7 more days after adding an aqueous solution of sodium aluminate. These experiments are the same as those used for the preparation of AlMCM-41 in our previous study. As Figure 5 shows, aluminum up to 11 Si/Al can be incorporated within MCM-48 by this procedure. The XRD patterns and the magic-angle spinning $^{27}$Al NMR spectra for the AlMCM-48 samples indicate the incorporation of tetrahedral aluminum maintaining the excellent structural order of pure silica MCM-48. The Si/Al ratio of 11 achieved in the present work is comparable with the previous record of...
product in high yield. The MCM-48 mesophase becomes energetically favorable, if the surfactant mixture is used and the pH of the reaction mixture is adjusted to 10. The mesophase can be maintained longer than 1 month, preventing subsequent transformation to lamellar mesophases under these synthesis conditions. The inhibition of the phase transformation increases our opportunities for aluminum (and probably other metals, too) incorporation into the siliceous framework of MCM-48. In addition, the hydrothermal stability of MCM-48 is greatly improved if a suitable amount of alkali metal salts is added to the reaction mixture after completing the formation of the MCM-48 mesophase. The present synthesis strategy for MCM-48 including the pH adjustment, the aluminum incorporation, and the salt addition is very similar to that of the MCM-41 synthesis reported by Ryoo and Kim, except for the use of the mixed surfactant. Thus, the simple addition of the neutral surfactant to the cationic surfactant solution has allowed us to synthesize MCM-48 very easily. Mixed surfactants can exhibit very complex phase behaviors in an aqueous solution. Therefore, the use of other mixed surfactants may be considered for finding mesoporous silica molecular sieves of new structures as well as for improving synthesis procedures for known materials.15,45,46

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