

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

Ryong Ryoo,\* Sang Hoon Joo, and Ji Man Kim

Materials Chemistry Laboratory, Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejeon, 305-701, Korea

Received: April 6, 1999; In Final Form: June 28, 1999

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 SiO<sub>2</sub> 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.<sup>1,2</sup> is one of the most interesting materials among many mesoporous silica molecular sieves found recently.<sup>1–6</sup> The structure of the MCM-48 materials may be described by the gyroid surface discovered by Schoen,<sup>7</sup> and the Q<sup>230</sup> rod structure<sup>8</sup> belonging to the cubic *Ia3d* space group.<sup>1,9,10</sup> 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.<sup>11–15</sup> 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.<sup>11</sup> 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,<sup>1,2</sup> research reports until now on applications of these materials have been severely biased to MCM-41.<sup>16–19</sup> 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.<sup>11–15,20–23</sup> 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.<sup>14</sup> 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 Kim<sup>24</sup> using a pH adjustment. This synthesis method has the advantage of achieving a remarkably high product yield of 4.2 mol of SiO<sub>2</sub> per surfactant, as compared with the production of only 0.8 SiO<sub>2</sub>/surfactants<sup>11</sup> 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 % Na<sub>2</sub>-Si<sub>4</sub>O<sub>9</sub> and 88.6 wt % H<sub>2</sub>O), which was prepared with colloidal silica Ludox HS40 (39.5 wt % SiO<sub>2</sub>, 0.4 wt % Na<sub>2</sub>O, and 60.1 wt % H<sub>2</sub>O, Du Pont), distilled water, and NaOH.<sup>24</sup> 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

\* To whom correspondence should be addressed. E-mail: rryoo@sorak.kaist.ac.kr.

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.<sup>25,26</sup> 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 K $\alpha$  X-ray source.

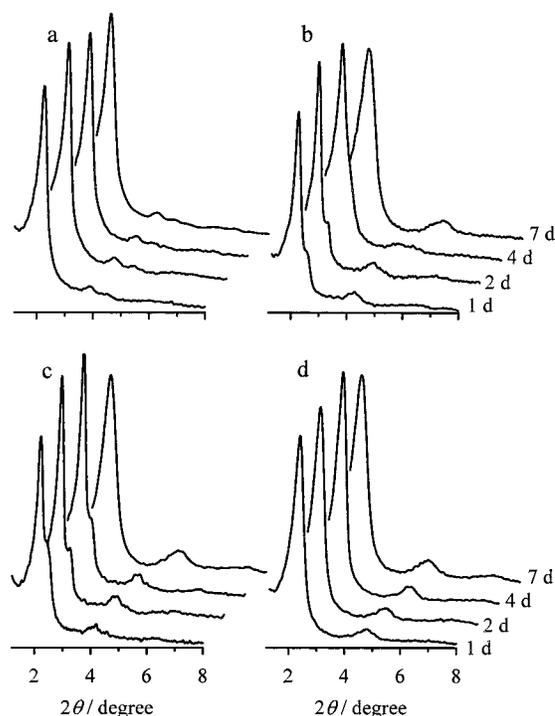
The synthesis and characterization experiments were repeated many times, changing the surfactants, the surfactant mixing ratio, and the hydrothermal reaction time at 373 K. In some experiments, the reaction mixtures were cooled to room temperature after a certain reaction period at 373 K and subsequently added with acetic acid to adjust the pH to 10.<sup>24</sup> The reaction mixtures were heated to 373 K again. The pH adjustment and subsequent heating sometimes was repeated two times, 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 C<sub>12</sub>–C<sub>18</sub>. 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 C<sub>*n*</sub>H<sub>2*n*+1</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>*m*</sub>H [C<sub>*n*</sub>(EO)<sub>*m*</sub> for brevity], where *n* ranges from 12 to 18 and *m* from 3 to 10. These surfactants were donated by Hannong Chemicals.<sup>27</sup> Triton X-100 [CH<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>10</sub>H] received from Daejung was also used as a neutral surfactant.

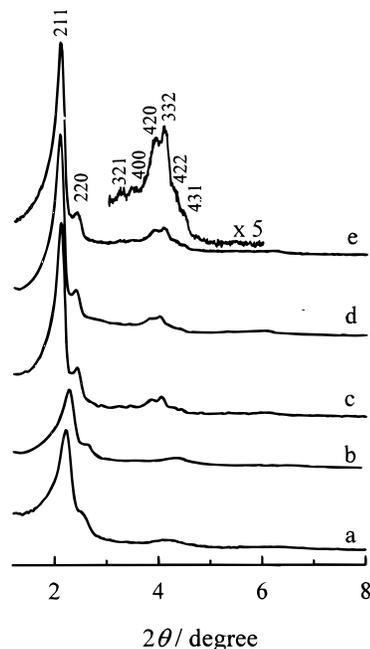
### 3. Results

Figure 1 shows the XRD patterns of the surfactant–silica mesophases obtained from the starting mixtures of 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/*f*<sub>ns</sub> C<sub>12</sub>(EO)<sub>4</sub>/(1 – *f*<sub>ns</sub>) HTMABr/400 H<sub>2</sub>O, where a fraction of the neutral surfactant *f*<sub>ns</sub> 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 synthesized surfactant–silicate mesophases without calcination. The results show that the structure of the mesophase was very sensitive to both *f*<sub>ns</sub> and the hydrothermal reaction time. The structure corresponded to the hexagonal mesophase, MCM-41, when *f*<sub>ns</sub> was given as 0.05. As *f*<sub>ns</sub> 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 *f*<sub>ns</sub> 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 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/0.85 HTMABr/0.15 C<sub>12</sub>(EO)<sub>4</sub>/400 H<sub>2</sub>O. 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.



**Figure 1.** X-ray diffraction patterns for the surfactant–silicate mesophases obtained from 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/*f*<sub>ns</sub> C<sub>12</sub>(EO)<sub>4</sub>/(1 – *f*<sub>ns</sub>) HTMABr/400 H<sub>2</sub>O, as a function of the hydrothermal reaction time: *f*<sub>ns</sub> = (a) 0.05, (b) 0.11, (c) 0.18, and (d) 0.25. Numbers denote the hydrothermal reaction times at 373 K.



**Figure 2.** X-ray diffraction patterns for MCM-48 samples obtained from 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/0.15 C<sub>12</sub>(EO)<sub>4</sub>/0.85 HTMABr/400 H<sub>2</sub>O: (a) after heating the starting mixtures for 2 days at 373 K; (b) after subsequent pH adjustment to 10; (c) after subsequent heating for 2 days; (d) after heating the mixture for 30 days after the pH adjustment; (e) after adjusting the pH of the reaction mixture in (c) to 10 again and subsequent heating again for 2 days.

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  $\text{SiO}_2$  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  $\text{SiO}_2$ /surfactant, which was much more than the 2.5 mol of  $\text{SiO}_2$  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<sup>11–15</sup> 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  $\text{SiO}_2$ /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.<sup>28</sup> 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.<sup>28–32</sup> 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  $\text{C}_{12}(\text{EO})_4$  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  $\text{C}_{12}(\text{EO})_4$  surfactant may be singled out by keeping all other experimental parameters constant, except for the increase in the  $\text{C}_{12}(\text{EO})_4$ /HTMABr molar ratio.

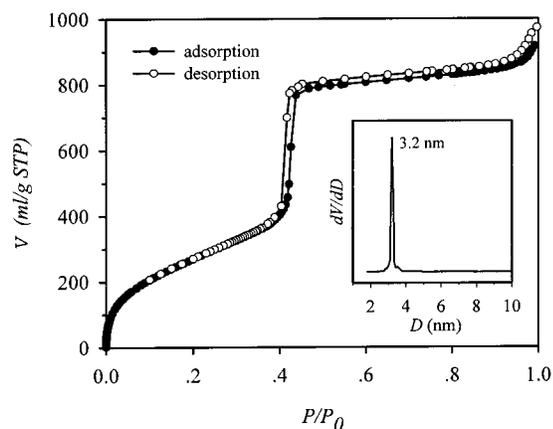
Our results in Figure 1 show that the structure of the silica–surfactant mesostructures in this case changes continuously from hexagonal to lamellar. The *Ia3d* cubic mesophase appears in the middle of the transition. These changes are consistent with the general tendency of the  $\text{H} \rightarrow \text{Q} \rightarrow \text{L}$  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.<sup>33–37</sup> 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  $\text{H} \rightarrow \text{L}$  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.

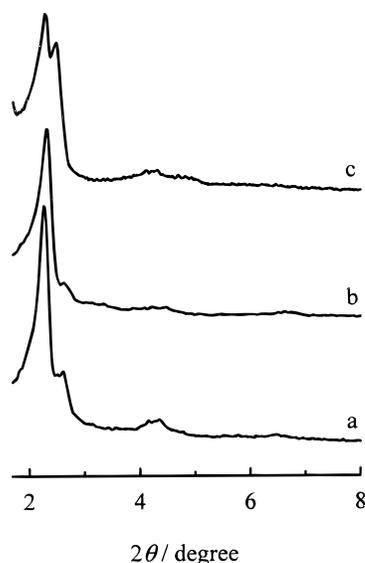
Compared to the strong influence, the effects of the neutral surfactant should decrease if the synthesis is performed under strong acidic conditions via a  $\text{S}^+\text{X}^-\text{I}^+$ -type ionic mechanism,<sup>3</sup> where  $\text{S}^+$  stands for a surfactant,  $\text{I}^+$  for an inorganic silica species, and  $\text{X}^-$  for a counteranion of  $\text{S}^+$ . In this case, the silica species is positively charged due to the adsorption of  $\text{H}^+$ . 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  $\text{S}^+\text{I}^-$ -type ionic mechanism. We have performed synthesis experiments with 5.0  $\text{SiO}_2/\text{HCl}/f_{\text{ns}} \text{C}_{12}(\text{EO})_4/(1 - f_{\text{ns}}) \text{HTMABr}/1000 \text{H}_2\text{O}$ , changing  $f_{\text{ns}}$  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.<sup>11–15,20–23</sup> Further, the cubic mesophase transforms subsequently to a lamellar mesophase. The pH of the reaction mixture increases from 12 to 13 during the first 2 days of reaction, which is due to the  $\text{Na}^+$  released by the silicate condensation.<sup>24</sup> The high pH is a major driving force for the transformation to lamellar. As shown in section 3, the pH adjustment to 10 is not to cause simply a kinetic quenching effect against the transformation but to increase its product yield and purity. The nitrogen adsorption–desorption isotherm and corresponding pore size distribution for the MCM-48 thus obtained exhibited a sharp inflection of the desorption characteristic of the capillary condensation within pores 3.2 nm in diameter, as shown in Figure 3. The product is also characterized by the large BET area (957  $\text{m}^2 \text{g}^{-1}$ ) and the large pore volume (1.26  $\text{cm}^3 \text{g}^{-1}$ ). It is therefore reasonable that the pH adjustment is used to control the hydrothermal reaction within the local energy minimum favorable for MCM-48. Recently, the pH adjustment was briefly mentioned as a means for quenching the transformation of the MCM-48 mesophase to lamellar.<sup>14</sup> The effect of the pH adjustment in the case using HTMABr as a single surfactant is only for kinetic quenching. The MCM-48 stops its transformation to lamellar after the pH adjustment. However, the MCM-48 product becomes contaminated due to the precipitation of hexagonal and disordered mesophases consequent to the pH adjustment. Our experimental results concerning this fact are provided in Figure 4.

Similar results to Figures 1 and 2 can be obtained using other neutral surfactants or amphiphilic species such as dodecylamine (DA,  $\text{C}_{12}\text{H}_{25}\text{NH}_2$ ), other  $\text{C}_n(\text{EO})_m$ , and Triton X-100 instead of LE4. For example, a highly ordered MCM-48 product can be obtained from a mixture of 5.0  $\text{SiO}_2/1.25 \text{Na}_2\text{O}/0.89 \text{HTMABr}/0.11 \text{Triton X-100}/400 \text{H}_2\text{O}$ . The optimum condition for this



**Figure 3.** Nitrogen adsorption–desorption isotherms at 77 K for MCM-48 sample obtained from 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/0.15 C<sub>12</sub>(EO)<sub>4</sub>/0.85 HTMABr/400 H<sub>2</sub>O. Inset: The corresponding pore size distribution curve obtained from the adsorption by Barrett–Joyner–Halenda method.



**Figure 4.** XRD patterns for MCM-48 samples obtained at 373 K from 1.0 TEOS/0.25 Na<sub>2</sub>O/0.65 HTMABr/100 H<sub>2</sub>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).

mixture is as follows: 1 day heating at 373 K, the pH adjustment with 0.3 mol acetic acid per Na, and subsequent heating for 1 more day. The reaction conditions should be adjusted depending on the neutral species. The product should be filtered right after these treatments since the MCM-48 mesophase undergoes the phase transformation from cubic to lamellar afterward. Table 1 summarizes results obtained from the various starting compositions. The pore size of MCM-48 can be varied using other ATMABr's instead of HTMABr, as shown in Table 2.

Our synthesis route to MCM-48 has several advantages over the synthesis methods using HTMABr/tetraethyl orthosilicate (TEOS)/NaOH/H<sub>2</sub>O<sup>9</sup> or HTMABr/sodium silicate/ethanol/H<sub>2</sub>O.<sup>11</sup> 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

**TABLE 1: Surfactant–Silica Mesopores Obtained from Mixtures between HTMABr and Neutral Surfactants<sup>a</sup>**

neutral surfactant <sup>b</sup>	$f_{ns}$ <sup>a</sup>	mesophase <sup>c</sup>	neutral surfactant <sup>b</sup>	$f_{ns}$ <sup>a</sup>	mesophase <sup>c</sup>
C <sub>12</sub> (EO) <sub>4</sub>	0.05	H	DA	0.11	H
	0.11	C		0.20	C
	0.18	C		0.25	L
C <sub>12</sub> (EO) <sub>10</sub>	0.25	L	TX-100	0.05	H
	0.11	H		0.11	C
	0.20	C		0.20	C
	0.25	L		0.25	L

<sup>a</sup> Hydrothermal synthesis was performed at 373 K for 2 days using starting mixtures with the molar composition of 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/ $f_{ns}$  neutral surfactant/(1 –  $f_{ns}$ ) HTMABr/400 H<sub>2</sub>O. <sup>b</sup> C<sub>12</sub>(EO)<sub>4</sub>, C<sub>12</sub>(EO)<sub>10</sub>, DA, and TX-100 indicate C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>4</sub>H, C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>10</sub>H, C<sub>12</sub>H<sub>25</sub>NH<sub>2</sub>, and *i*-C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>10</sub>H, respectively. <sup>c</sup> H, C, and L denote hexagonal, cubic (*Im*3*d*), and lamellar, respectively.

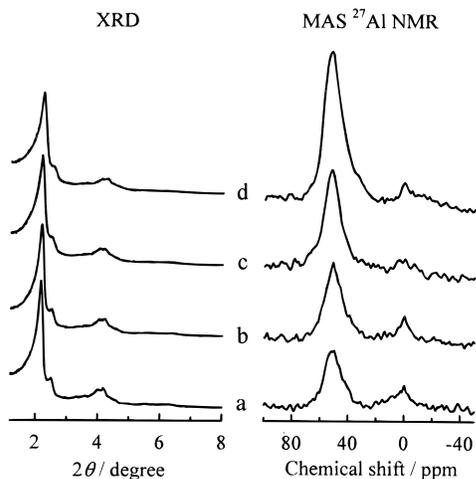
**TABLE 2: Typical Synthesis Conditions<sup>a</sup> for MCM-48 Materials Giving Various Lattice Parameters**

cationic surfactant	neutral surfactant <sup>b</sup>	$f_{ns}$ <sup>a</sup>	$d_{211}$ spacing (nm) <sup>c</sup>	lattice parameter (nm) <sup>c</sup>
C <sub>12</sub> TMABr	C <sub>12</sub> (EO) <sub>3</sub>	0.25	3.79	9.28
C <sub>14</sub> TMABr	C <sub>12</sub> (EO) <sub>4</sub>	0.20	3.99	9.77
C <sub>16</sub> TMABr	C <sub>12</sub> (EO) <sub>4</sub>	0.18	4.18	10.24
C <sub>18</sub> TMACl	TX-100	0.08	4.35	10.66

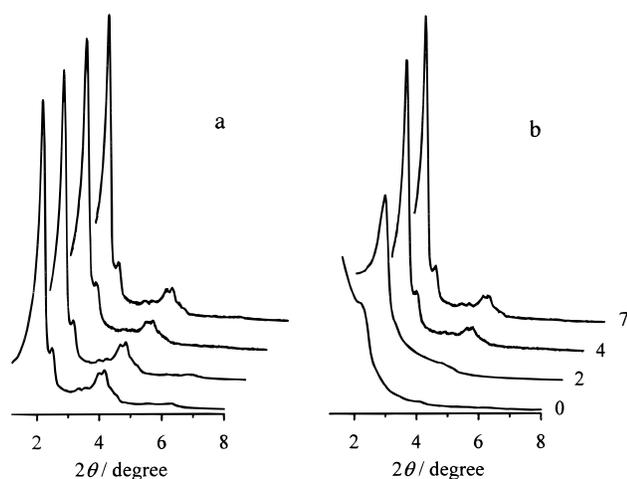
<sup>a</sup> MCM-48 materials were obtained by a hydrothermal reaction at 373 K from the molar composition of 5.0 SiO<sub>2</sub>/1.25 Na<sub>2</sub>O/ $f_{ns}$  neutral surfactant/(1 –  $f_{ns}$ ) cationic surfactant/400 H<sub>2</sub>O. The reaction mixtures were reheated after the pH adjusted to 10. <sup>b</sup> C<sub>12</sub>(EO)<sub>3</sub>, C<sub>12</sub>(EO)<sub>4</sub>, and TX-100 denote C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>3</sub>H, C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>4</sub>H, and *i*-C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>10</sub>H, respectively. <sup>c</sup> The  $d_{211}$  spacings were obtained from as-synthesized samples. Lattice parameters were calculated from the  $d_{211}$  spacings.

formation of the cubic mesophase. Another advantage is its high product yield; 5 mol of SiO<sub>2</sub> are used per surfactant (0.85 HTMABr + 0.15 C<sub>12</sub>EO<sub>4</sub>), among which more than 4 mol are converted to MCM-48. Compared with the high yield, the synthesis procedures using HTMABr/NaOH/TEOS/H<sub>2</sub>O or HTMABr/sodium tetrasilicate/ethanol/H<sub>2</sub>O give a yield corresponding to only 0.8 SiO<sub>2</sub>/surfactant.<sup>9,11</sup> An MCM-48 synthesis procedure using a mixture of HTMABr and anionic surfactants has been reported recently.<sup>15</sup> A high SiO<sub>2</sub>/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<sub>2</sub>/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<sub>2</sub>/1.25 Na<sub>2</sub>O/0.85 HTMABr/0.15 C<sub>12</sub>(EO)<sub>4</sub>/400 H<sub>2</sub>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 AIMCM-41 in our previous study.<sup>38</sup> 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 <sup>27</sup>Al NMR spectra for the AIMCM-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



**Figure 5.** XRD patterns and MAS  $^{27}\text{Al}$  NMR spectra for calcined AIMCM-48 samples displayed against the Si/Al ratios: Si/Al = (a) 44, (b) 24, (c) 15, and (d) 11. Samples were obtained by the addition of sodium aluminate solutions, corresponding to 40, 20, 10, and 5, respectively.



**Figure 6.** The X-ray diffraction patterns for MCM-48 samples: (a) calcined and (b) subsequently boiled in distilled water at 373 K for 12 h. Numbers denote the NaCl/surfactant molar ratios used for the synthesis. See ref 44 for the sample-to-water ratio used in the boiling experiment.

15 Si/Al.<sup>39–41</sup> We believe that other metals such as Zn and Ga can also be incorporated similarly under our synthesis conditions using mixed surfactants.

Various alkali metal salts such as  $\text{EDTANa}_4$ , NaCl, and KCl may be added to the reaction mixture, instead of or simultaneously with, the above aluminum precursor. If the reaction mixture is heated sufficiently long under a proper concentration of the salts, the resultant product can exhibit a significant increase in its hydrothermal stability.<sup>42,43</sup> A brief outline of our results on MCM-48 is shown in Figure 6. The improvement of the hydrothermal stability is very similar to that for MCM-41, which were fully discussed in recent reports.<sup>42,43</sup>

## 5. Conclusions

The use of the surfactant mixture between cationic alkyl-trimethylammonium surfactants and neutral polyoxyethylene/alkyl/ether surfactants has greatly facilitated the synthesis of MCM-48. Reactants are not required to mix drop by drop but can be shaken rapidly in a bottle. The synthesis can be performed at an atmospheric pressure, giving the high-quality

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.<sup>15,45,46</sup>

**Acknowledgment.** The authors thank Hannong Chemicals for donation of neutral surfactants and KOSEF (97-05-02-06-01-3) and Center for Molecular Science for financial support.

## References and Notes

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
- (4) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.
- (5) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.
- (6) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.
- (7) Schoen, A. H. NASA Technical Note D-5541; NASA: Washington, DC, 1970.
- (8) Luzzati, V.; Spet, P. A. *Nature* **1967**, *215*, 701.
- (9) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.
- (10) (a) Alfredsson, V.; Anderson, M. W. *Chem. Mater.* **1996**, *8*, 1141. (b) Alfredsson, V.; Anderson, M. W.; Ohsuna, T.; Terasaki, O.; Jacob, M.; Bojrup, M. *Chem. Mater.* **1997**, *9*, 2066.
- (11) Kim, J. M.; Kim, S. K.; Ryoo, R. *Chem. Commun.* **1998**, 259.
- (12) Voort, P. V. D.; Mathieu, M.; Mees, F.; Vansant, E. F. *J. Phys. Chem. B* **1998**, *102*, 8847.
- (13) Romero, A. A.; Alba, M. D.; Zhou, W.; Klinowski, J. *J. Phys. Chem. B* **1997**, *101*, 5294.
- (14) Xu, J.; Luan, Z.; He, H.; Zhou, W.; Kevan, L. *Chem. Mater.* **1998**, *10*, 3690.
- (15) Chen, F. X.; Huang, L. M.; Li, Q. Z. *Chem. Mater.* **1998**, *9*, 1997.
- (16) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 56 and references therein.
- (17) Corma, A. *Chem. Rev.* **1997**, *97*, 2373 and references therein.
- (18) Sayari, A. In *Recent Advances and New Horizons in Zeolite Science and Technology*; Chon, H.; Woo, S. I.; Park, S.-E., Eds.; Studies in Surface Science and Catalysis, Vol. 102; Elsevier: Amsterdam, 1996; pp 1–46 and references therein.
- (19) Zhao, X. S.; Lu, G. Q. M.; Millar, G. J. *Ind. Eng. Chem. Res.* **1996**, *35*, 2075 and references therein.
- (20) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.
- (21) Corma, A.; Kan, Q. B.; Rey, F. *Chem. Commun.* **1998**, 579.
- (22) Gallis, K. W.; Landry, C. C. *Chem. Mater.* **1997**, *9*, 2035.
- (23) Koyano, K. A.; Tatsumi, T. *Chem. Commun.* **1996**, 145.
- (24) Ryoo, R.; Kim, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 711.

- (25) Kim, J. M.; Kwak, J. H.; Jun, S.; Ryoo, R. *J. Phys. Chem.* **1995**, *99*, 16742.
- (26) Ryoo, R.; Jun, S.; Kim, J. M.; Kim, M. J. *Chem. Commun.* **1997**, 2225.
- (27) Hannong Chemicals, Kunsan Seaside Estate a Block #587, Soryong-Dong, Kunsan City, 573-440, Korea. Phone: +82-654-62-2455. Fax: +82-654-61-5569. E-mail: kunsan@hnchem.com.
- (28) Holland, P. M.; Rubingh, D. N. In *Mixed Surfactant Systems*; Holland, P. M., Rubingh, D. N., Eds.; ACS Symposium Series 501; American Chemical Society: Washington, 1992; pp 2–30.
- (29) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *Faraday Trans. 2* **1976**, *72*, 1525.
- (30) Gruner, S. M. *J. Phys. Chem.* **1989**, *93*, 7562.
- (31) Auvray, X.; Petipas, C.; Anthore, R.; Rico, I.; Lattes, A. *J. Phys. Chem.* **1989**, *93*, 7458.
- (32) Palous, J. L.; Turmine, M.; Letellier, P. *J. Phys. Chem. B* **1998**, *102*, 5886.
- (33) Auvray, X.; Abiyaala, M.; Duval, P.; Petipas, C. *Langmuir* **1993**, *9*, 444.
- (34) Seddon, J. M.; Templer, R. H. *Philos. Trans. R. Soc. London A* **1993**, *344*, 377.
- (35) Nagarajan, R.; Wang, C.-C. *J. Colloid. Interface Sci.* **1996**, *178*, 471.
- (36) Chiruvolu, S.; Zasadzinski, J. A. *J. Phys. Chem.* **1996**, *100*, 5874.
- (37) Kunieda, H.; Ozawa, K.; Huang, K.-L. *J. Phys. Chem. B* **1998**, *102*, 831.
- (38) Ryoo, R.; Ko, C. H.; Howe, R. F. *Chem. Mater.* **1997**, *9*, 1607.
- (39) Romero, A. A.; Alba, M. D.; Klinowski, J. *J. Phys. Chem. B* **1998**, *102*, 123.
- (40) Schmidt, R.; Junggreen, H.; Stöcker, M. *Chem. Commun.* **1996**, 875.
- (41) Kosslick, H.; Lischke, G.; Landmesser, H.; Parltitz, B.; Storek, W.; Fricke, R. *J. Catal.* **1998**, *176*, 102.
- (42) Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317.
- (43) Kim, J. M.; Jun, S.; Ryoo, R. *J. Phys. Chem. B* **1999**, *103*, 6200.
- (44) Kim, J. M.; Ryoo, R. *Bull. Korean Chem. Soc.* **1996**, *17*, 66.
- (45) Namba, S.; Mochizuki, A.; Kito, M. In *Mesoporous Molecular Sieves 1998*; Benneviot, L., Beland, F., Danumah, C., Grasson, S., Kaliaguine, S., Eds.; Studies in Surface Science and Catalysts, Vol. 117; Elsevier: Amsterdam, 1998; pp 257–264.
- (46) Ryoo, R.; Ko, C. H.; Park, I.-S. *Chem. Commun.* 1999, 1413.