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Rapid Crystallization of Mesoporous Silica with Highly Stable 2D-Hexagonal Structure

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We investigated the synthetic parameters of MCM-41, prepared through the evaporation-to-dryness treatment of alkali-free surfactant–silicate mixture, and their thermal stability and water resistance. The product obtained by this method gave a well-ordered 2D-hexagonal structure after the removal of surfactant molecules by either solvent-extraction or calcination. It is noteworthy that the d_{100} value of MCM-41 remained almost the same after calcination, indicating that the pore walls of the as-made product were dense and rigid. This MCM-41 shows a high degree of thermal stability and water resistance due to the highly dense silicate framework in the mesopore walls.

Mesoporous inorganic materials templated by surfactant molecular assemblies have attracted a great deal of attention because of their potential applications as adsorbents, molecular sieves, catalysts, and sensors.[1] Mesoporous silica materials are one of the most useful materials due to wide varieties of mesopore dimensions and crystalline structures, such as 2D-hexagonal, cubic, and 3D-hexagonal, and their high thermal stability compared to other mesoporous metal oxides. Yanagisawa et al.[2] and Kresge et al.[3] first reported the synthesis of ordered mesoporous silica materials with 2D-hexagonal structure, so-called MCM-41, using hexadecyltrimethylammonium salts as templates, and subsequently great efforts have been dedicated to improving the synthesis of mesoporous MCM-41 by lowering the temperature and shortening the crystallization time as well as controlling the particle size.[4]

As MCM-41-type mesoporous materials are generally prepared by hydrothermal reactions of silicate gels in aqueous NaOH solution at temperatures ranging from 100 to 150 °C,[3] the products are thermally or hydrothermally unstable, due to the amorphous nature within the pore wall.[5] To achieve highly stable MCM-41, thickening the pore wall in order to obtain a more condensed and longer range ordered framework, either by modifying the assembly pathways[6–8] or by post-synthetic treatments[9,10] have been attempted. Alternatively, some groups have investigated the synthesis of MCM-41 in alkali-free systems.[11–13] Zhao et al.[11] synthesized a highly ordered MCM-41 using aqueous ammonia solution in the absence of organic or inorganic salts over a 72 h period at 100 °C. Recent studies examined the synthesis of mesoporous silica using aqueous ammonia solution at room temperature.[12,13] Wang et al.[12] reported the preparation of double-mesoporous silica with pore sizes of 2.6–3.0 and ca. 19 nm using aqueous ammonia in an alkali-free system at room temperature. Tsutsumi and co-workers[13] reported that stirring mixtures of tetraethyl orthosilicate (TEOS), surfactant, and aqueous ammonia solution for only 1 h at room temperature yielded silica precipitates with a 2D-hexagonal structure. Brinker et al.[14] have reported the preparation of a thin film of mesoporous silica during an evaporation-induced self-assembly process and studied the formation mechanism of mesoporous silica thin films. Moreover, under acidic conditions, mesoporous silica SBA-3 with a 2D-hexagonal structure was also formed in 1 h at room temperature using cetyltrimethylammonium salts.[15] Although these synthetic investigations have advanced the process of applying mesoporous silica materials as catalysts, adsorbents, and supports, an easier and more rapid technique for the preparation of mesoporous silica materials would be desirable.

Evaporation-to-dryness is a useful technique for the rapid formation of mesoporous silica materials. Endo and co-workers[16] have developed an evaporation-to-dryness technique for the syntheses of some kinds of mesoporous silica materials under acidic conditions. We have recently reported rapid crystallization of MCM-41 using an evaporation-to-dryness technique.[17] In this method, a well-ordered 2D-hexagonal structure was obtained in two steps: (1) aging a mixture of TEOS, hexadecyltrimethylammonium bromide, and water with an aqueous ammonia solution for a short period of 30 min, and (2) subsequent evaporation-to-dryness of the resultant mixture at 80 °C for about 2 h.[17] In this study, we investigated the synthetic conditions of our rapid crystallization treatments in detail and formation mechanism of 2D-hexagonal structure. The stability of the 2D-hexagonal structure produced by this method was also investigated.

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Table 1. Synthetic Conditions of MCM-41 via the Aging and Successive Drying[a)]

Entry	Synthetic conditions		pH	Remaining solvent /vol %
	Aging period /min	Drying period /min		
1	5	—	11.2	—
2	30	—	10.7	96.8
3	30	5	9.2	81.8
4	30	30	8.1	68.7
5	30	60	7.1	45.5
6	30	90	7.0	10.5
7	30	120	—	—

a) Aging and drying treatments were carried out at 20 and 80 °C, respectively. The solid products (Nos. 1–6) were recovered by filtration, and the dried product (No. 7) was directly recovered without filtration.

Experimental

Synthetic Procedure for Preparation of MCM-41. Mesoporous silica, MCM-41, was prepared by an evaporation-to-dryness technique using hexadecyltrimethylammonium bromide (C_{16}TMABr, >98%, Aldrich) as a template. The TEOS/H_2O molar ratio was varied from 0.001 to 0.1, and the surfactant concentration was varied from 0.005 to 0.5 mol dm^{-3}. In a typical procedure, first, 1.15 g of C_{16}TMABr was added to 43.5 mL of distilled water in a 100-mL polypropylene beaker. The solution was mixed with 5.2 g of TEOS (>98%, Merck) followed by the addition of 2.0 g of an aqueous ammonia solution (28%, Kanto Chem.) in a dropwise manner under static conditions at 20 °C. The molar composition of the resultant mixture was SiO_2:C_{16}TMABr:NH_3:H_2O = 1.0:0.125:1.30:100. The mixture was aged at 20 °C for 30 min with stirring, followed by heating at 80 °C for 120 min with stirring until dry. To investigate the crystallization behavior, the aging treatments only were performed for 5 or 30 min (designated as sample 1 and 2, respectively); aging for 30 min and the following heating for 5, 30, 60, 90, or 120 min (sample 3, 4, 5, 6, and 7, respectively) were also carried out (Table 1). The dried solid product 7 obtained after 120 min of drying was directly recovered without filtration, whereas the solid products 1–6 in a suspension was recovered by filtration and then dried at room temperature. For comparison, a synthesis using an aqueous NaOH solution instead of aqueous ammonia solution was carried out according to the procedure described above. Hydrothermal synthesis of MCM-41 in aqueous ammonia solution was also performed at 80 °C for 24 h using a parent mixture with SiO_2:C_{16}TMABr:NH_3:H_2O = 1.0:0.125:1.30:100.

Removal of surfactant molecules from as-made MCM-41 products was carried out by two different methods: solvent-extraction using HCl–pyridine solution[18] and calcination in air. The first method was carried out as follows: 22.0 g of pyridine (99.5%, Kanto Chem.) was added to 10.0 mL of 1.0 M aqueous HCl solution (Kanto Chem.) and stirred gently for 10 min at room temperature, followed by the addition of 0.20 g of as-made sample. The suspension was stirred at 80 °C for 24 h to remove surfactant molecules from as-made MCM-41. The solid was recovered by filtration, washed with distilled water and acetone, and then dried at room temperature. The removal of water from solvent-extracted MCM-41 was carried out at 200 °C for 5 h. In the second method of template removal, as-made products were calcined at 550 °C for 6 h in a furnace after heating from room temperature to 550 °C for 9 h.

The yield of MCM-41 was calculated by the following equation:

$$\text{Yield of Si-MCM-41/wt\%} = \frac{\text{Amount of Si in calcined product/g}}{\text{Amount of Si in TEOS used/g}} \times 100 \qquad (1)$$

Water vapor resistance of calcined MCM-41 was tested at 20 °C for 24 h under saturated vapor pressure of water in a glass desiccator. The MCM-41 exposed to water vapor was recovered at room temperature, and then dried at 200 °C for 5 h to remove water adsorbed on MCM-41.

Characterization. The crystallinity and phase purity of all products before and after calcination were checked by X-ray powder diffraction (XRD) on a RINT 2100 (Rigaku) diffractometer using Cu Kα radiation at 40 kV and 30 mA. The textural properties of the calcined mesoporous products were determined from N_2 sorption experiments at −196 °C on a BELSORP-mini (Bel Japan Inc.) apparatus. Specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method.[19] Mesopore size distributions of the calcined products were determined from adsorption branches using the Barrett–Joyner–Halenda (BJH) method.[20] The contents of water in products prior to calcination were determined by thermogravimetric analysis (DTG-50H, Shimadzu) under 60 cm^3 min^{-1} of air flow rate and 2.0 °C min^{-1} of ramping rate. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) measurements of the products were performed using an EX270 (JEOL) with a magnetic field of 6.3 T. ^{29}Si MAS NMR spectra for the products were recorded at 79.4 MHz with a pulse width of 2.2 µs, a pulse interval of 60 s, and a spinning rate of about 5 kHz.

Results and Discussion

Product Phases of Silica Depending on the Synthetic Procedures. We prepared three series of silica products using C_{16}TMABr surfactants by adding an aqueous solution of ammonia or NaOH. The first series of silica materials was prepared by the evaporation-to-dryness (ETD) method in aqueous ammonia solution, whereas the second series was obtained by the same method but in aqueous NaOH solution. The third method was the hydrothermal synthesis (HTS) of mesoporous silica in aqueous ammonia solution. Figure 1 presents the XRD patterns of the products synthesized in the present study. In the first method, i.e., ETD with aqueous ammonia solution, the evaporation of ammonia, water, and ethanol, produced by the hydrolysis of TEOS, required a period of only 120 min in a typical synthesis using a mixture with composition of SiO_2:C_{16}TMABr:NH_3:H_2O = 1.0:0.125:1.31:100. As Figure 1b shows, the reflection peaks corresponding to [100], [110], and [200] faces in the XRD results indicated that the solid product obtained by ETD with ammonia had a 2D-hexagonal structure. On the other hand, Figure 1a indicates that a lamellar structure was obtained under the second synthetic conditions, i.e., ETD with aqueous NaOH solution. NaOH in the synthetic mixture caused the increase of pH value during drying and remained in the drying product, resulting in the collapse of rod-like micelles of silica–surfactant complexes leading to the formation of a lamellar structure. These observations were in agreement with results reported previously.[21] On the other hand, when ammonia was used, a decrease in pH value in the course of the evaporation-to-dryness process led to stabilization of the 2D-hexagonal

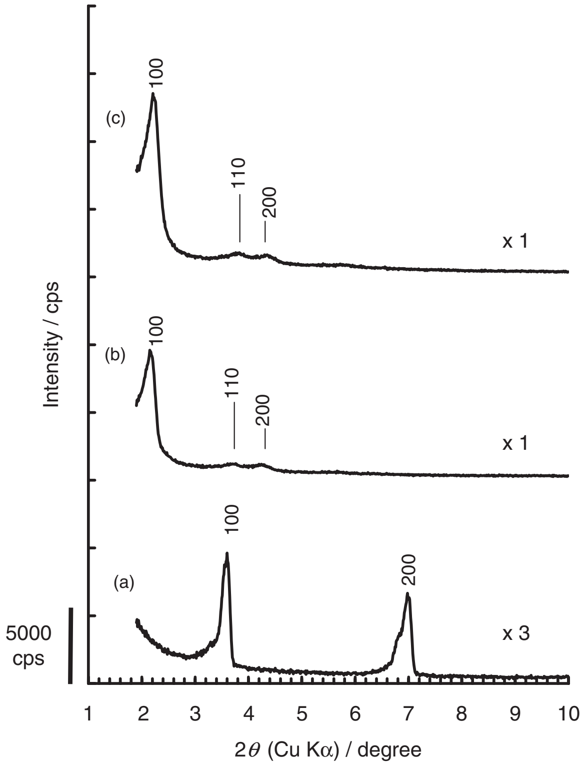

Figure 1. XRD patterns for (a) product prepared by the evaporation-to-dryness (ETD) with NaOH solution, (b) product prepared by the ETD with aqueous NH_3 solution, and (c) product prepared by the hydrothermal synthetic method with aqueous NH_3 solution.

structure. The third method, hydrothermal synthesis in aqueous ammonia solution, yielded a 2D-hexagonal structure after 24 h of crystallization at 80 °C, as shown in Figure 1c.

The ETD syntheses of mesoporous silica in aqueous ammonia solution were performed under various synthesis conditions. Figure 2 shows the distribution of product phases depending on the concentrations of TEOS and C_{16}TMABr in the synthetic mixture. A 2D-hexagonal structure was formed under a wide range of conditions: molar ratios of TEOS/H_2O from 0.001 to 0.05, and concentrations of C_{16}TMABr from 0.005 to 0.10 mol dm^{-3}. A lamellar structure was obtained when the concentration of the surfactant exceeded 0.10 mol dm^{-3}, regardless of the concentration of TEOS. Because an increasing concentration of surfactant in the synthetic mixture causes the formation of plate-like micelles of silica–surfactant complexes, the silica product possessed a lamellar structure. No periodic structure was obtained with the concentration of C_{16}TMABr <0.005 mol dm^{-3} at TEOS/H_2O molar ratios >0.05. With an excess amount of silica to surfactants, although a small amount of silica was consumed in the formation of silica–surfactant complexes, most of the silica became amorphous. In addition, the ETD synthesis using C_{14}TMABr or C_{12}TMABr in aqueous ammonia solution also yielded a 2D-hexagonal structure. When using surfactant with short alkyl chains, a 2D-hexagonal structure was yielded for a narrow distribution of concentrations of TEOS and surfactant in the synthetic mixture, in comparison to the usage of C_{16}TMABr.

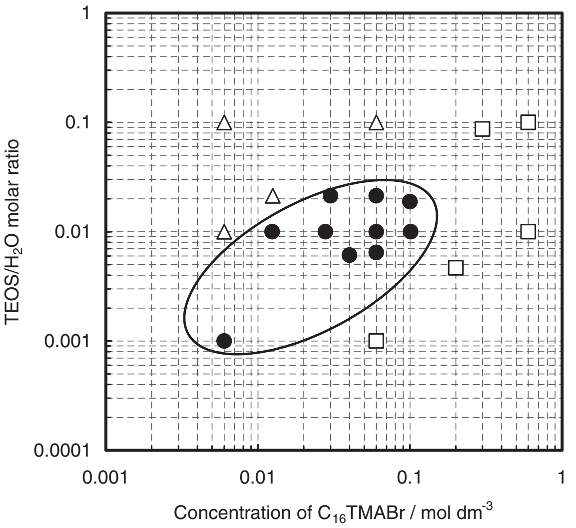

Figure 2. Product phases synthesized by using the parent mixtures having various concentrations of TEOS and C_{16}TMABr. ●: 2D-hexagonal, □: lamellar, and △: amorphous.

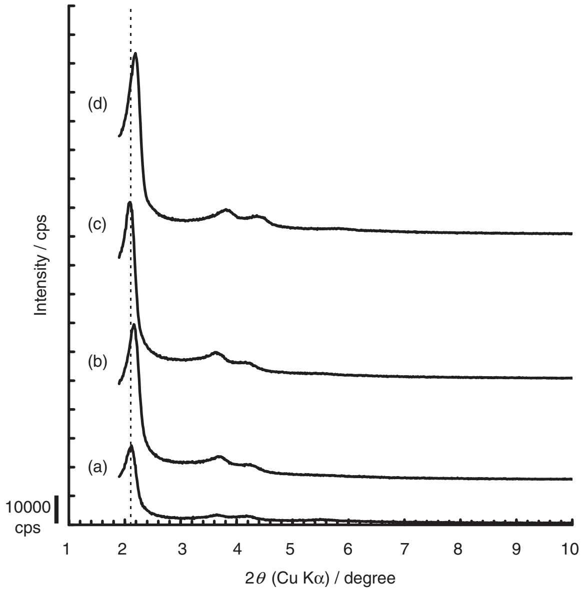

Figure 3. XRD patterns for ETD-MCM-41 prepared with aqueous ammonia solution. (a) The as-made product, (b) the product obtained after the solvent-extraction of surfactant in product (a), (c) the product obtained after drying the product (b) at 200 °C, and (d) the calcined product of (a).

Stability of 2D-Hexagonal Structure after Template Removal. We investigated the stability of the 2D-hexagonal structure during two different methods of removal of surfactant from the MCM-41 products: (1) solvent-extraction using HCl–pyridine solution followed by drying at 200 °C, and (2) calcination in air. We confirmed that more than 80% of the initial amount of surfactant in as-made MCM-41 was removed via solvent-extraction. Figure 3 shows the XRD patterns of as-made, solvent-extracted, solvent-extracted and dried, and calcined MCM-41 materials prepared by ETD methods in

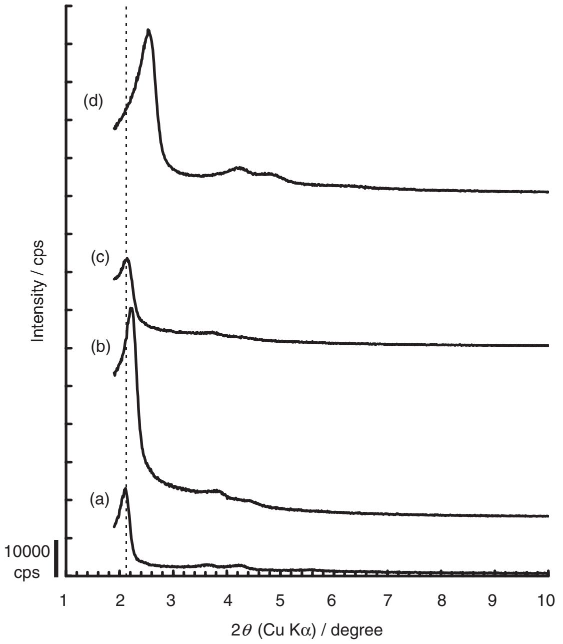

Figure 4. XRD patterns for HTS-MCM-41 prepared with aqueous ammonia solution. (a) The as-made product, (b) the product obtained after the solvent-extraction of surfactant in product (a), (c) the product obtained after drying the product (b) at 200 °C, and (d) the calcined product of (a).

aqueous ammonia solution. Figure 4 shows the XRD patterns of the hydrothermally-synthesized products in the same order as in Figure 3. In Figure 3b, the XRD patterns for MCM-41 obtained by the ETD method (ETD-MCM-41) clearly indicate preservation of a 2D-hexagonal structure upon template removal by the solvent-extraction. Remarkably, the drying step following the solvent-extraction for ETD-MCM-41 did not affect the crystallinity of the product (Figure 3c). On the other hand, the XRD reflection peaks in Figures 4b and 4c indicate that MCM-41 prepared by the HTS method (HTS-MCM-41) mostly collapsed after the solvent-extraction and the following drying, although a 2D-hexagonal structure was preserved after the solvent-extraction. The solvent-extracted ETD-MCM-41 had a high BET surface area (905 $m^2 g^{-1}$) and uniform mesopores (diameter, 2.9 nm), whereas BET surface area of the solvent-extracted HTS-MCM-41 became remarkably low. These observations imply that the evaporation-to-dryness treatment to prepare MCM-41 silica produces a more fully cross-linked silicate framework in the 2D-hexagonal structure, leading to high stability of the mesoporous structure during the solvent-extraction and subsequent drying.

This consideration is also supported by ^{29}Si MAS NMR measurements. Figure 5 displays the ^{29}Si MAS NMR spectra of as-made ETD- and HTS-MCM-41. Both possess Q^3 and Q^4 species, as evidenced by the presence of peaks at around −100 and −110 ppm, respectively. The ETD-MCM-41 involved 97% of Q^4 species (Figure 5a), whereas the Q^4 species in HTS-MCM-41 was 52% (Figure 5b). These NMR results support the conclusion that ETD-MCM-41 shows a high stability to solvent-extraction of templates due to the formation of a highly cross-linked silicate framework in the course of the ETD treatment.

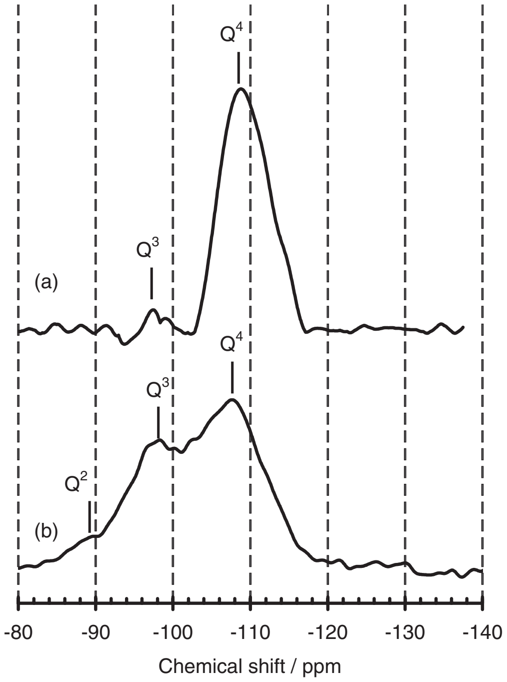

Figure 5. ^{29}Si MAS NMR spectra for (a) as-made ETD-MCM-41 and (b) as-made HTS-MCM-41.

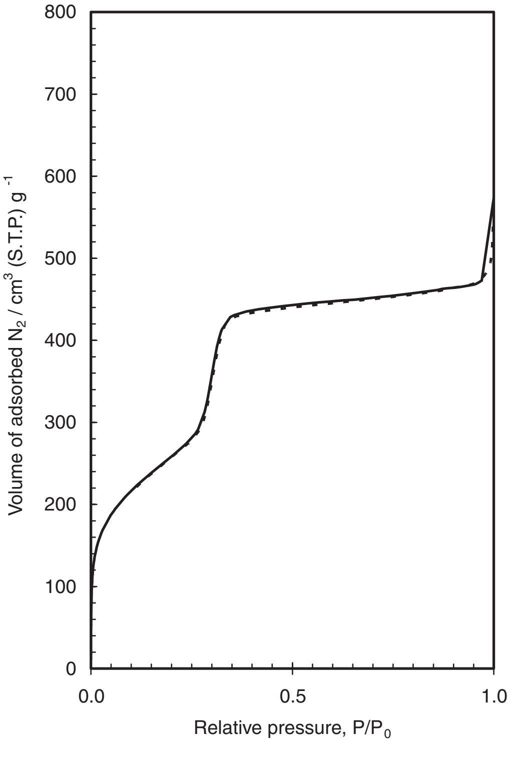

Figure 6. A nitrogen adsorption isotherm for calcined ETD-MCM-41. Solid line: adsorption and dash line: desorption.

We also studied the physicochemical properties of calcined ETD- and HTS-MCM-41. Figures 3d and 4d show the XRD patterns of calcined ETD- and HTS-MCM-41, respectively. The 2D-hexagonal structures remained after calcination of both as-made MCM-41 samples. Figures 6 and 7 show the nitrogen

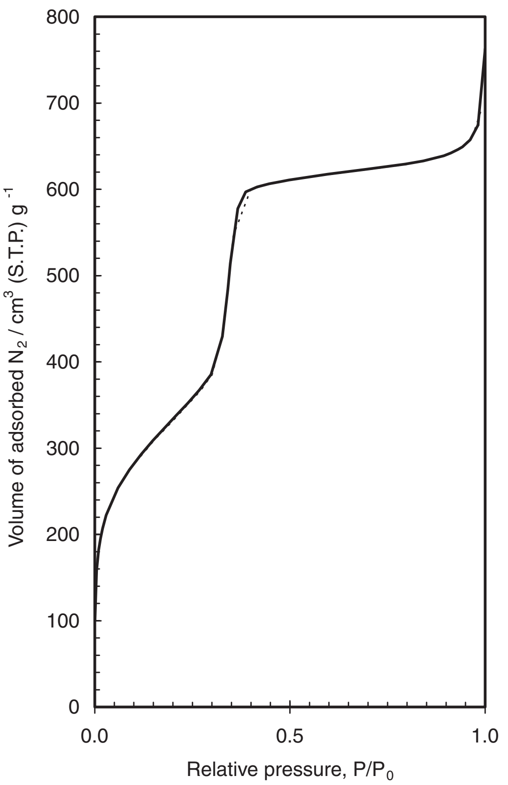

Figure 7. A nitrogen adsorption isotherm for calcined HTS-MCM-41. Solid line: adsorption and dash line: desorption.

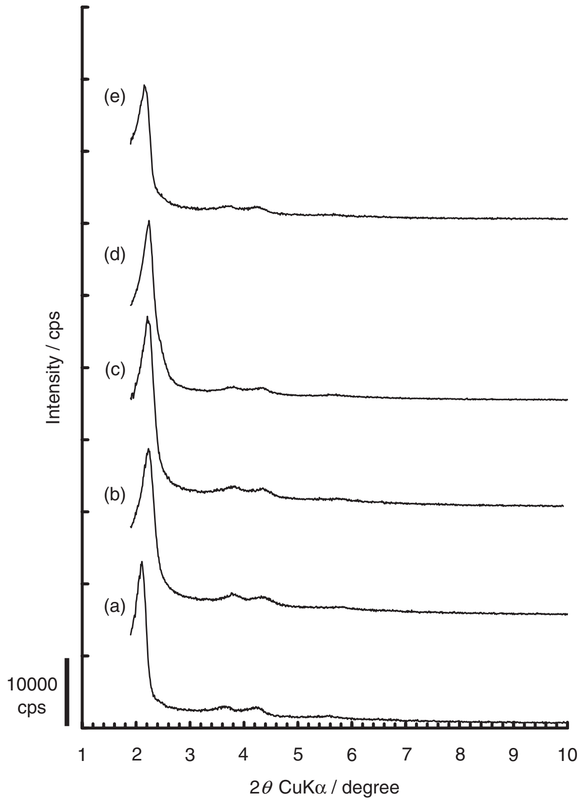

Figure 8. XRD patterns for the products after aging and drying of the mixture of silica and surfactant in aqueous ammonia solution. (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4, and (e) No. 7.

Table 2. Structural Properties of As-Made and Calcined MCM-41 Prepared by the ETD and HTS Methods

Preparation	Treatment	XRD		Nitrogen adsorption		Thickness of mesopore wall /nm
		2θ (100) /degree	d_{100} /nm	BET surface area /$m^2\,g^{-1}$	Mesopore diameter[a] (BJH)/nm	
Evaporation-to-dryness	As-made	2.15	4.11	—	—	—
	Calcination	2.19	4.03	1233	2.6	2.0
Hydrothermal synthesis	As-made	2.12	4.16	—	—	—
	Calcination	2.95	2.99	1211	2.8	0.8

a) Mesopore diameter of MCM-41 was determined from the adsorption branch using the BJH method.

adsorption data of calcined ETD- and HTS-MCM-41, respectively. These isotherms also indicate preservation of mesoporous structures after calcination due to the appearance of an increase in uptake at around 0.3 of relative pressure in the isotherm. On the basis of the XRD and nitrogen adsorption data, Table 2 summarizes the structural properties of calcined MCM-41 prepared by the two different methods. Calcination of HTS-MCM-41 caused a reduction in the d_{100} value from 4.16 to 2.99 nm due to shrinking of the mesoporous structure during calcination. This behavior was generally observed in hydrothermally synthesized MCM-41.[22] On the other hand, the d_{100} values of ETD-MCM-41 changed little during calcination, indicating the high thermal stability of ETD-MCM-41. When ETD- and HTS-MCM-41 were exposed to saturated water vapor at 20 °C for 24 h, ETD-MCM-41 retained a well-ordered 2D-hexagonal structure during exposing, compared to HTS-MCM-41. These high degrees of thermal stability and water resistance of ETD-MCM-41 were probably due to the formation of dense mesoporous silica walls.

Formation of 2D-Hexagonal Structure by the Evaporation-to-Dryness Method. We now discuss formation pathways of the 2D-hexagonal structure in the course of the evaporation-to-dryness treatment. As described above, drying the mixture with composition SiO_2:C_{16}TMABr:NH_3:H_2O = 1.0:0.125:1.31:100 and initial pH 11 took about 120 min. Table 1 lists aging and drying conditions and pH of suspension, and Figure 8 shows typical XRD patterns for solid products obtained for different aging and drying periods. In aqueous ammonia solution, a suspension of silica–surfactant complexes was rapidly formed after aging for 5 min at 20 °C, whereas the formation of such silica precipitates hardly occurred in aqueous NaOH solution at 20 °C. Figure 8a indicates that the solid product recovered by filtration from the suspension already had a 2D-hexagonal structure. These results imply that, after the addition of aqueous ammonia solution to the parent mixture at room temperature, a part of the silica–surfactant complexes rapidly assembled to form a 2D-hexagonal structure. Figures 8b–8e indicate that the 2D-hexagonal structure was stable during crystallization. Although the yield of MCM-41 obtained after the filtration following aging for 30 min was as low as 43.4%, successive drying for 5 min (sample 3) gave MCM-41 in more than 90 wt % yield, and prolonged drying for 120 min (sample 7) also produced a highly ordered 2D-hexgonal structure with 99 wt % yield. During the drying treatment in the ammonia route, the conspicuous decrease in pH of the suspension occurred from 9.2 to 7.0 due to the evolution and evaporation of ammonia gas. In a previous study,[23] change of pH was very important for the synthesis and the quality of a MCM-41 product. At the initial stages of crystallization, the high alkalinity affords a relatively high solubility of the silica, favoring negatively charged silica species. As ammonia is released, the pH and the solubility of the silica also decrease, resulting in an enhanced condensation of silicates and a high yield of MCM-41. Eventually, as the pH is close to neutral due to the complete evaporation of ammonia and solvents, the improved condensation of silicate network occurred. In contrast, in the NaOH route, the evaporation to dryness cannot afford a decrease in pH by the removal of any basic species. As such a high alkalinity should be preserved throughout the drying treatment, a large number of highly charged silica species, which favor formation of a lamellar phase reacted with surfactant molecules, probably exist in suspension. Therefore, the evaporation to dryness in the NaOH route gave a lamellar phase as the final product.

As described above, the d_{100} values of as-made and calcined MCM-41 obtained by complete drying (No. 7) hardly changed during calcination, leading to a high thermal stability. On the other hand, the calcination of MCM-41 recovered by filtration after aging for 30 min and drying for 5 min (No. 3) showed a relatively low thermal stability, causing a decrease in d_{100} values from 3.99 to 3.49 nm (see Supporting Information, Figure S1). We, therefore, deduce that the condensation of siliceous species was probably enhanced by the evaporation of water from the solid product during the course of drying, and such improved condensation of silica species would be essential to form a stable mesoporous structure. Additionally, the use of C_{14}TMABr or C_{12}TMABr for the ETD synthesis of mesoporous silica also gave thermally stable 2D-hexagonal structure.

Figure 9 shows a plausible scheme for the formation of MCM-41 in the rapid crystallization method. We suppose that the formation of the 2D-hexagnal structure in this method takes place by the following pathway. In the early stage of crystallization, a silica–surfactant complex was formed. Then, dehydration condensation of this complex occurred at room temperature and part of the complex was self-assembled to form a 2D-hexagonal structure. Upon heating the suspension, rapid assembly of rod-like micelles caused the formation of a 2D-hexagonal structure. Successive drying of the aged suspension would enhance the dehydration condensation of the micelles. Through this pathway, a well-ordered and highly stable 2D-hexagonal structure was formed in high yield.

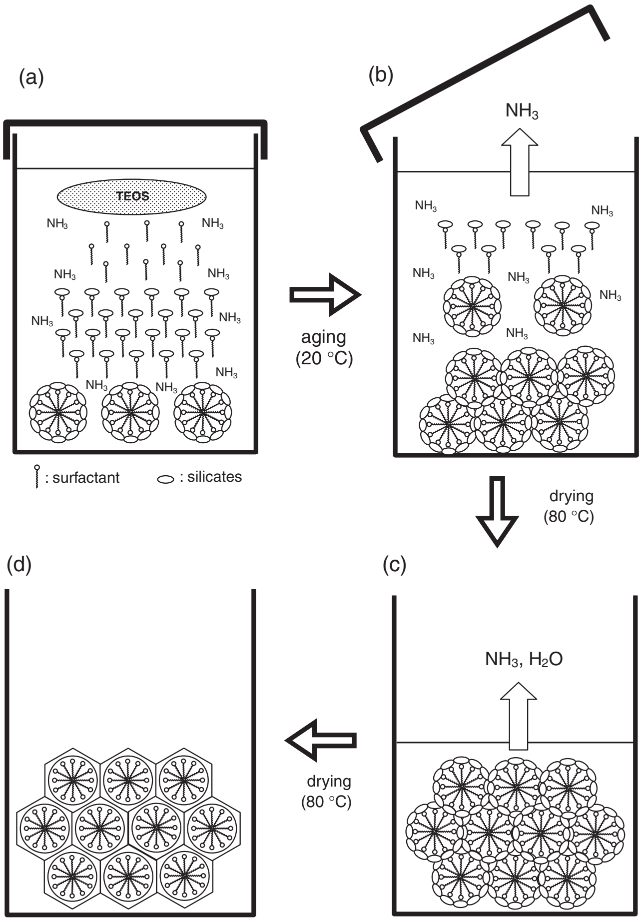

Figure 9. A plausible scheme of the formation of MCM-41 by the evaporation-to-dryness method with aqueous ammonia solution. (a) The formation of silicate–surfactant complexes; (b) the self-assembly of rod-like micelles; (c) the dehydration condensation during the evaporation of NH_3 and water; and (d) the formation of highly-condensed MCM-41.

Conclusion

A well-ordered and highly stable MCM-41 was rapidly crystallized by the evaporation-to-dryness technique using aqueous ammonia solution in a wide range of TEOS/H_2O molar ratios and the concentrations of surfactant molecules. A 2D-hexagonal structure prepared by the ETD method remained after solvent-extraction of a surfactant, whereas the solvent-extraction of HTS-MCM-41 gave rise to spoiling the 2D-hexagonal structure, suggesting that the evaporation-to-dryness treatment causes the formation of a highly-condensed silicate network in MCM-41. It is noteworthy that the d_{100} values of as-made and calcined ETD-MCM-41 changed little, and calcined ETD-MCM-41 showed a high degree of thermal stability and water resistance, probably due to the formation of a highly dense silicate framework. We have concluded that aqueous ammonia solution used in the ETD synthesis of MCM-41 plays an important role to form a highly dense silicate network, causing rapid assembly of rod-like micelles in the aging step and an enhancement of the dehydration condensation of the micelles in the drying step.

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Supporting Information

Figure S1 shows the XRD patterns of as-made and calcined ETD-MCM-41. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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