Preparation of Mesoporous Silica with Well-Defined Hexagonal Array of Pores by Using Octyltrimethylammonium Chloride

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Hexagonally ordered mesoporous silica MCM-41 was successfully prepared by using titled (OTMA) chloride at OTMA/$SiO_2 = 2.8$–3.5. The BJH pore diameters were 1.4–1.5 nm which was on the prolongation of the correlation line between the chain length of surfactant and the pore diameter.

The synthesis of mesoporous silica MCM-41 with ordered pores between micropore and mesopore regions is of particular interest due to its great scientific and utilitarian importance. The pore diameter of MCM-41 can usually be controlled by the carbon numbers of the template surfactants, the ratios of the template surfactants and the silica source, or the addition of organic compounds.[1–4] The preparation of MCM-41s by using alkyltrimethylammonium (ATMA) bromide or chloride with alkyl chain lengths of C10–C22 has widely been established. In contrast, little success has been reported in the use of short single-chain surfactants, though much effort has been devoted. For example, octyltrimethylammonium (OTMA) salts have indeed been applied to the synthesis of C8-MCM-41,[5,6] but the attempts afforded poorly ordered materials.[6] No hexagonal array of pores was clearly shown by the XRD patterns or electron microscope images.[5] In addition, the pore sizes of C8-MCM-41 obtained[5,6] were far from the correlation line between the carbon number of ATMA and the pore size. At the moment reproducible and reliable preparation of C8-MCM-41 has not yet been developed.[1,7] On the other hand, a few researchers have proposed new types of templates such as adamantamine,[8] short double-chain alkylammonium surfactants[9] or fluorosurfactants.[10] However, the obtained pores were approximately 2.0 nm which is nearly similar to those of prepared by C10 surfactants. The other effort is the solvent evaporation method[11,12] in which pores of 1.65 nm could be prepared but the ordered hexagonal structure was not clarified by the X-ray diffraction patterns. It should be emphasized that the preparation of mesoporous silica with regular arrays of smaller pores than those prepared by C10 surfactants is a long-standing subject but has not yet been achieved.

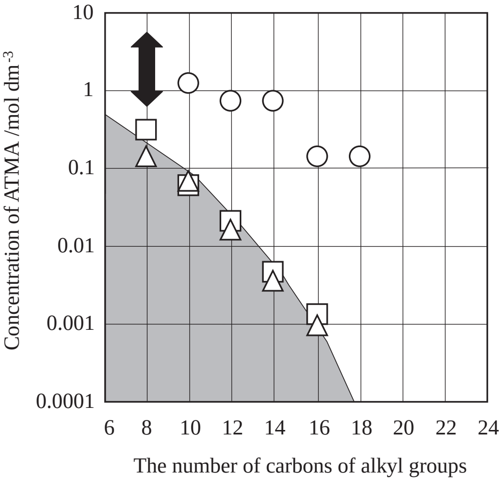

Fig. 1. Correlation between the carbon number of alkyl groups and the critical micelle concentration (CMC) of ATMA. The open triangles indicate the CMC of ATMA bromide. The open squares indicate the CMC of ATMA chloride. The open circles indicate the concentration of ATMA to obtain hexagonally ordered C*n*-MCM-41 ($n =$ 10–18) for the carbon numbers of alkyl groups. The arrow indicates the concentration region of OTMA in this synthesis. The shaded area indicates the region of CMC values smaller than those of OTMA.

In this study, we attempted the preparation of hexagonally ordered C8-MCM-41 by using OTMA. It is well known that the ability of OTMA to self-assemble is relatively low and the CMC values of OTMA are much larger than those of C10–C18 surfactants,[13] as shown in Fig. 1. In the present study, the synthesis conditions were therefore set at the region indicated by the arrow in the figure. We could thus prepare C8-MCM-41 with highly ordered pores and reasonable pore diameters.

All reagents employed here were of commercial origin except for OTMA fluoride (OTMAF). OTMAF was synthesized as follows. Silver fluoride (20.0 g, Kanto Chemical) dissolved into distilled water (100 mL) was added dropwise to an aqueous solution (300 mL) of octyltrimethylammonium chloride (32.8 g) and the mixture was stirred for 30 min. The white precipitate, AgCl, was removed by filtration and OTMAF was yielded as an aqueous solution.

C8-MCM-41 was prepared by the following method. An aqueous solution of sodium hydroxide (96 wt % NaOH, Sigma Aldrich) and colloidal silica (20 wt % SiO_2, Nissan Chemical) was added dropwise to an aqueous solution of OTMA chloride (OTMAC, Tokyo Chemical), bromide (OTMAB, Tokyo Chemical), or OTMAF with vigorous stirring at 313 K. The molar ratios of the respective components were $SiO_2 \cdot 0.14Na_2O \cdot 55H_2O \cdot x$OTMAC (OTMAB, or OTMAF), where the values of x were 0.7–6.0. The mixture was further stirred for 2 h. The resulting white gel was placed into a Teflon autoclave and heated at 413 K for 2 days under static conditions. After the hydrothermal treatment, the solid was filtered, washed, and dried at 353 K for 1 day. The dry powder was suspend-

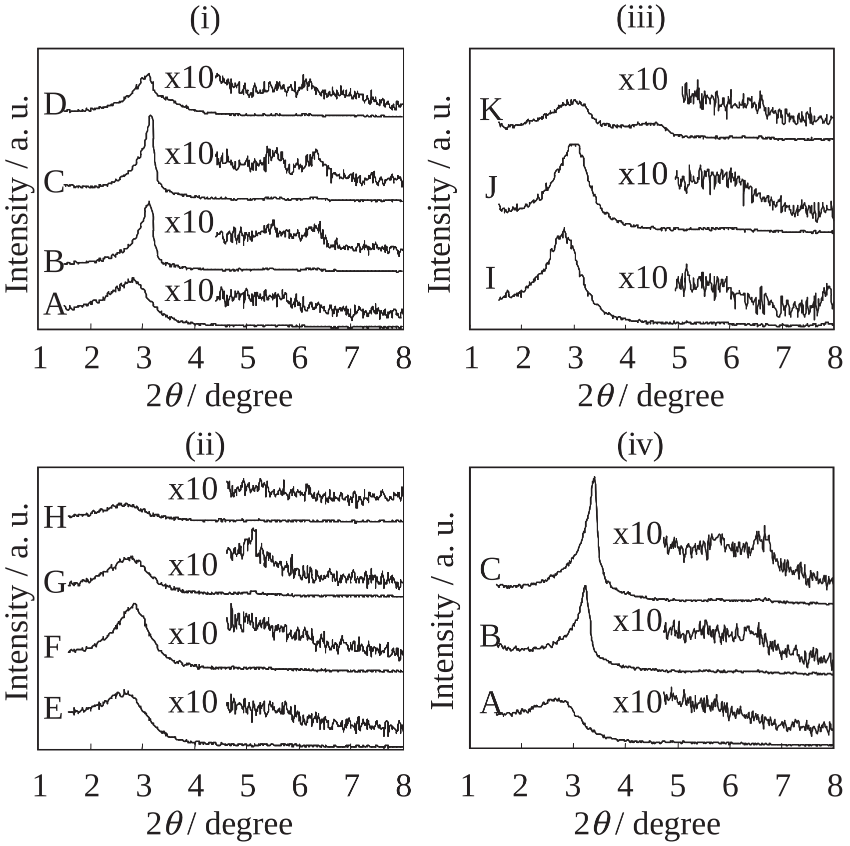

Fig. 2. XRD patterns of as-synthesized samples. The surfactant used was (i) OTMAC ($x = 0.7$ (A), 2.8 (B), 3.5 (C), and 6.0 (D)), (ii) OTMAB ($x = 0.7$ (E), 2.8 (F), 3.5 (G), and 6.0 (H)), or (iii) OTMAF ($x = 0.7$ (I), 1.8 (J), and 3.6 (K)). (iv) The calcined samples A, B, and C.

ed in 30 volumes of distilled water. The pH value of the suspension was adjusted to 6.5 ± 0.5 by the addition of a hydrochloric acid solution. The suspension was allowed to stand at 353 K for 20 h, filtered, washed, and dried at 353 K for 1 day. The resultant white solid was heated to 873 K in flowing air with a heating rate of 5 K min^{-1} and kept at that temperature for 6 h.

X-ray powder diffraction (XRD) patterns were measured on a Rigaku RINT2500VPC diffractometer with Cu Kα radiation and a Ni filter. Nitrogen adsorption–desorption isotherms were determined at 77 K on a Shimadzu ASAP 2020 after the samples were evacuated at 523 K for 5 h. The pore size distribution was evaluated by applying the Barrett–Joyner–Halenda (BJH) method to the adsorption data at 0.01–0.98 of the relative pressure of N_2.

It is widely accepted that the BJH method usually gives smaller values of pore diameters than those determined by other methods. We therefore employed this method only for the relative comparison of the pore diameters. The pore images were observed with a JEM-2000EX transmission electron microscope.

The XRD patterns of the samples were measured before calcination at 873 K and are summarized in Figs. 2(i)–2(iii). Clearly the samples B and C gave a sharp peak at $2\theta = 3.14°$ and two small peaks at 5.48 and 6.38°, which are assignable to the typical (100), (110), and (200) diffractions of hexagonal phase, *p*6*m*. The other samples showed a broad peak at 2.8–3.2° but did not give the peaks resulting from the (110) and (200) diffractions of hexagonal phase. Figure 2 indicates two important findings. First is that the highly ordered hexagonal phase containing silica and OTMA could be constructed only upon using the chloride anion as a counter ion of the template, though the effect of counter ion is not clear. Second is the significance of the concentration of ATMA. We could observe the hexagonal phase only at around $\mathrm{OTMA/SiO_2} = 2.8$–3.5, which is much greater than the conventional values applied in the preparation using C10–C22 surfactants, as shown in Fig. 1. Excessively high concentration of OTMA ($\mathrm{OTMA/SiO_2} = 6.0$) was not good for the synthesis, which could be due to the balance between the amounts of the surfactant cation and the silicate anion.

After calcination, samples B and C again showed XRD patterns originating from the hexagonal structure, though the high angle patterns became somewhat weak, as shown in Fig. 2(iv). The samples D–K did not give any clear diffraction peaks, suggesting destruction of the mesostructure. For comparison the pattern of sample A is depicted in Fig. 2(iv).

Figure 3 displays TEM images of the calcined samples, where samples A, B, and C are shown as typical examples. The highly ordered hexagonal array of pores could be observed on samples B and C. The domain size was dependent on the sample. In contrast, sample A possesses a wormhole-type pore structure. These results are well consistent with those of the XRD patterns in Fig. 2(iv).

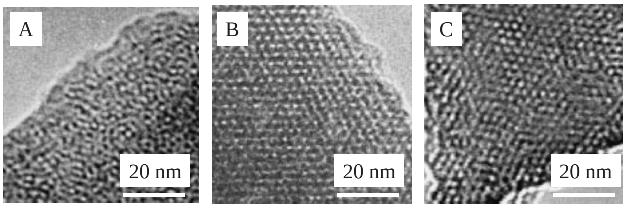

Fig. 3. TEM images of calcined samples A, B, and C.

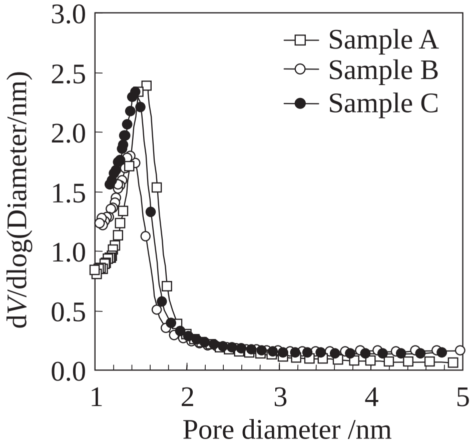

Fig. 4. Pore size distributions of samples A, B, and C determined by the BJH method on the nitrogen adsorption data.

The pore size distributions of samples A, B, and C are shown in Fig. 4. Single sharp peaks were observed on the three samples. The mean pore diameters were 1.52, 1.40, and 1.44 nm on the samples A, B, and C. BET surface areas were 865, 705, and 735 $m^2 g^{-1}$, respectively.

Samples B and C with a hexagonal array of pores showed almost the same pore diameters and surface areas, while those of sample A were rather large. The present results clearly show that we cannot conclude the presence of a hexagonal array of pores on the basis of only appearances of an XRD peak at 2.8–3.5° and of the single pore distribution. That is, the XRD, N_2 adsorption, and TEM measurements should be gathered to reveal the pore structure. Finally, the correlation between the carbon number of ATMA used and the pore size of C*n*-MCM-41 ($n = 10$–18) obtained was examined. The MCM-41s were separately prepared here at the concentrations of ATMA of $x = 1.25$ (C10), 0.71 (C12), 0.71 (C14), 0.14 (C16), and 0.14 (C18) as shown in Fig. 1. All of the XRD patterns of the calcined C*n*-MCM-41s showed clearly three peaks assignable to (100), (110), and (200) planes of hexagonal phase, *p*6*m*. The correlation between the carbon number of ATMA and the pore diameter is summarized in Fig. 5. The excellent correlation could be recognized, indicating that the value obtained here on C8-MCM-41 is quite reasonable.

It follows that the use of OTMA chloride and the adjustment of the template/SiO_2 ratio are very important to achieve the preparation of small pore MCM-41. The linear correlation between the carbon number of ATMA and the pore diameter (Fig. 5) concludes the effectiveness of our method for the preparation of C8-MCM-41. It would be worthy to note that we attempted the preparation of C6-MCM-41 by using hexyltrimethylammonium chloride but the products were amorphous silica or ZSM-5.

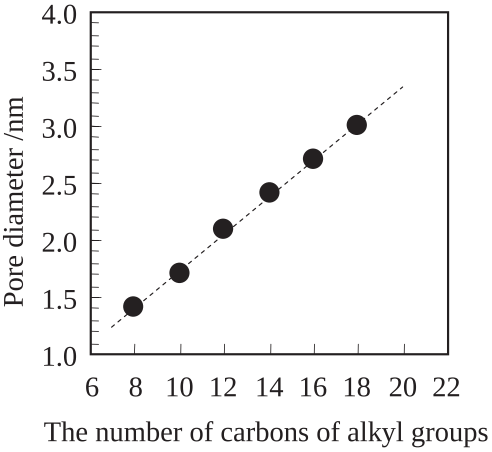

Fig. 5. Correlation between the carbon number of alkyl groups of templates and the pore size of C*n*-MCM-41 prepared.

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