

Fine Control of Pore Size of Highly Ordered MCM-41 by Using Template Mixtures of Dodecyltrimethylammonium Bromide/Hexadecyltrimethylammonium Bromide with Various Molar Ratios

Seitaro Namba,* Atsushi Mochizuki, and Muneharu Kito

Department of Materials, Teikyo University of Science & Technology, Uenohara, Kitatsuru-gun, Yamanashi 409-0193

(Received March 4, 1998; CL-980156)

MCM-41 materials were prepared hydrothermally by using template mixtures of hexadecyltrimethylammonium/dodecyltrimethylammonium (C_{16} TMABr/ C_{12} TMABr) with various molar ratios. The MCM-41 materials thus prepared were highly ordered and their pore sizes can be finely controlled by changing the C_{16} TMABr/ C_{12} TMABr molar ratio.

Recently a variety of methods for synthesizing mesoporous silica molecular sieves have been developed.¹⁻³ One of them is called "MCM-41", which has a hexagonal structure, uniform one-dimensional mesopores and a very high surface area.^{2,3} It has been also reported that pore size of MCM-41 materials can be tailored in the range of 1.5-10 nm through the choice of surfactant agents as templates and addition of auxiliary chemicals.^{2,3} Moreover MCM-41 materials exhibit high thermal and hydrothermal stabilities.^{4,5} Therefore much attention is being devoted to MCM-41 materials as catalytic materials.

When MCM-41 materials are synthesized with a template mixture of two kinds of *n*-alkyltrimethylammonium cations with different alkyl-chain length, the questions may be raised whether highly ordered MCM-41 materials form or not, whether two kinds of MCM-41 materials with different pore size form or not, whether the product has uniform pores or two kinds of pores, and so on.

MCM-41 materials were synthesized hydrothermally at 373 K by using water glass (Na_2O ; 9.5 wt%, SiO_2 ; 28.6 wt%, Nippon Chemical Industry Co.), sulfuric acid, pure water, and a template which was dodecyltrimethylammonium bromide (C_{12} TMABr, Tokyo Chemical Industry Co.), hexadecyltrimethylammonium bromide (C_{16} TMABr, Tokyo Chemical Industry Co.), or their mixture. The procedure was as follows. (1) The template was dissolved in pure water at 333-343 K. (2) The waterglass (56.1 g) was dissolved in pure water (120 g). (3) The solution prepared in (2) was added to the solution prepared in (1). (4) Diluted sulfuric acid ($H_2SO_4/H_2O = 3.6$ g/60 g) was added to the

mixture and the resulting mixture was stirred vigorously for 0.5 h. (5) The pH was adjusted to the prescribed value with a small amount of diluted sulfuric acid. (6) Then the mixture was put into a polytetrafluoroethylene vessel and allowed to stand for 5-7 days at 373 K. (7) The solid product was washed with a large amount of warm water ($500\text{ cm}^3 \times 6$ times) and dried at 373 K. (8) The dried product was heated to 813 K in air at a rate of 1 K/min and then calcined in air at the same temperature for 6 h. The gel composition, optimum pH value, and days for hydrothermal treatment for each run are summarized in Table 1.

MCM-41 materials were characterized by XRD (JEOL JDX-8030), and N_2 adsorption (ASAP 2000) for determining surface areas and pore size distributions (BJH method).

The MCM-41 materials were prepared by using mixtures of C_{16} TMABr/ C_{12} TMABr with various molar ratios under the

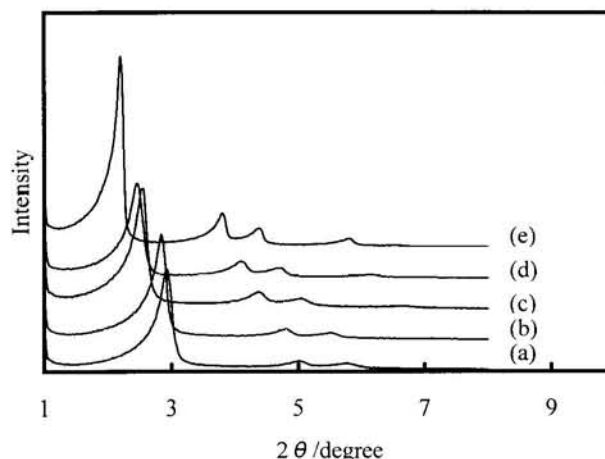


Figure 1. XRD patterns of MCM-41 materials prepared with C_{16} TMABr/ C_{12} TMABr with various molar ratios. C_{16} TMABr/ C_{12} TMABr molar ratios; (a) 0/1, (b) 1/2, (c) 1/1, (d) 2/1, (e) 1/0.

Table 1. Gel compositions, optimum pH values, days for hydrothermal treatment and specific surface areas of MCM-41.

Run	Gel composition in molar base						pH	Days for hydrothermal synthesis	Specific surface area / m^2g^{-1}
	SiO_2	C_{16} TMABr	C_{12} TMABr	H_2SO_4	Na_2O	H_2O			
1	1		0.51	0.14	0.32	70	11	5	1584 ^a
2	1	0.17	0.34	0.14	0.32	75	11	5	1194
3	1	0.26	0.26	0.14	0.32	75	11	5	1105
4	1	0.34	0.17	0.14	0.32	75	10	5	1015
5	1	0.51		0.14	0.32	75	10	7	1045

^aThis value may be too large because capillary condensation took place at low P/P_0 .

conditions of Runs 1-5 (Table 1). The pH values in Table 1 were optimum values for preparation of MCM-41 from each gel composition. XRD patterns of MCM-41 materials prepared with the template mixture are shown in Figure 1. The four peaks characteristic of hexagonal structure were observed for every sample. XRD peaks shifted toward lower degrees with increasing $C_{16}TMABr/C_{12}TMABr$ molar ratios.

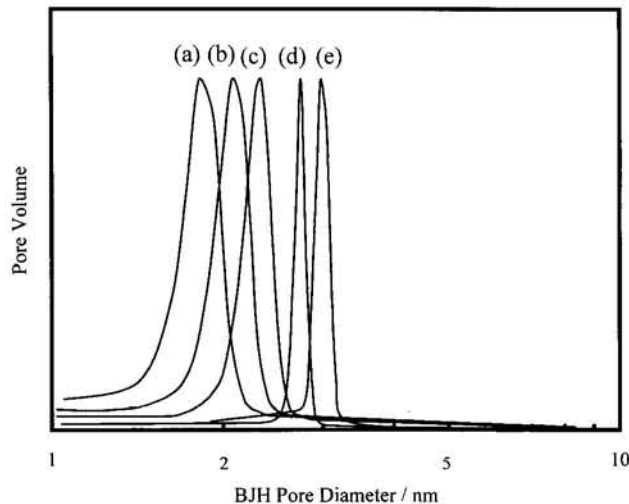


Figure 2. BJH pore size distributions for MCM-41 materials prepared with $C_{16}TMABr/C_{12}TMABr$ with various ratios. $C_{16}TMABr/C_{12}TMABr$ molar ratios; (a) 0/1, (b) 1/2, (c) 1/1, (d) 2/1, (e) 1/0.

The BJH pore size distributions are shown in Figure 2. All the samples showed a sharp distribution and the pore size increased with increasing $C_{16}TMABr/C_{12}TMABr$ molar ratios. The specific surface areas of MCM-41 materials are summarized in Table 1. The surface area of every sample was very high ($>1000 \text{ m}^2/\text{g}$). Hence MCM-41 materials prepared with the mixture of $C_{12}TMABr/C_{16}TMABr$ have uniform pores and are highly ordered.

Figure 3 shows the relation between the BJH pore size or d_{100} spacing and the molar fraction of $C_{16}TMABr$ [$C_{16}TMABr/(C_{16}TMABr + C_{12}TMABr)$]. The BJH pore size and d_{100} spacing increased monotonously with increasing fraction of $C_{16}TMABr$.

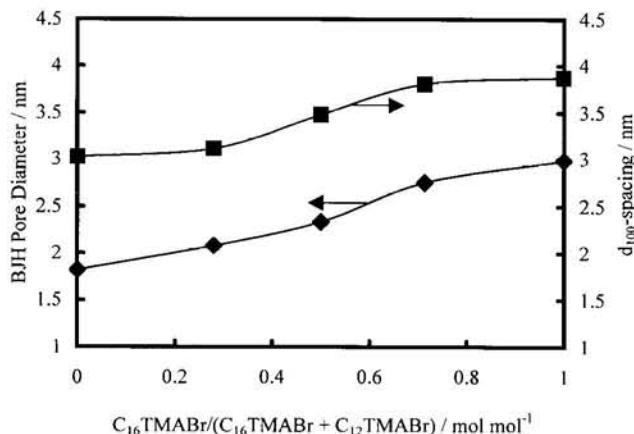


Figure 3. Relation between BJH pore size or d_{100} spacing and fraction of $C_{16}TMABr$.

These results indicate MCM-41 materials prepared with the mixtures of $C_{16}TMABr/C_{12}TMABr$ are highly ordered and their pore sizes can be finely controlled by changing the $C_{16}TMABr/C_{12}TMABr$ molar ratios.

The results obtained here can be explained by assuming that the only cylindrical micelles are formed in each gel and both surface concentration of ammonium cations on the micelles and hydrocarbon concentration in the micelles are constant.

This work has been carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the support of the Ministry of International Trade and Industry.

References

1. T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990).
2. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, *Nature*, **359**, 710 (1992).
3. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
4. S. Namba, N. Sugiyama, M. Yamai, I. Shimamura, S. Aoki, and J. Izumi, *Stud. Surf. Sci. Catal.*, **105**, 1981 (1997).
5. S. Namba and A. Mochizuki, *Res. Chem. Intermed.*, **24**, 561 (1998).