Synthesis of MCM-48 single crystals

Ji Man Kim, Seong Kyun Kim and Ryong Ryoo*

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

Truncated rhombic dodecahedral crystals of the mesoporous molecular sieve MCM-48 are synthesised by a hydrothermal procedure using sodium silicate, hexadecyltrimethylammonium bromide and various kinds of alcohol.

The materials designated MCM-41 and MCM-48 are large-pore molecular sieves attracting much recent attention in catalysis and nanoscience.[1,2] The structure of MCM-48 consists of two independent and intricately interwoven networks of mesoporous channels,[2–5] while the structure of MCM-41 consists of hexagonal packing of one-dimensional channels. The three-dimensional channel network of MCM-48 is much more desirable than the one-dimensional channel of MCM-41 from a diffusional and catalytic point of view. However, surprisingly little research has been reported on MCM-48, compared with research on MCM-41.[6,7] We believe that this is due to the difficulty of the MCM-48 synthesis.

Here, we present a hydrothermal synthesis procedure to obtain MCM-48 readily using a sodium silicate solution as the silica source, hexadecyltrimethylammonium bromide (HTABr) as the structure-directing agent, and various kinds of alcohol such as methanol, ethanol and 2-methylpropan-2-ol as an additive for the mesophase control. The resultant MCM-48 material exhibits not only excellent structural order but also the unique crystalline morphology of a cube truncated by rhomb dodecahedron.

To prepare the silica source, colloidal silica, Ludox HS40 (39.5 mass% SiO_2, 0.4 mass% Na_2O and 60.1 mass% H_2O, Du Pont), was preheated to 343 K in a Erlenmeyer flask. An aqueous solution of 1.00 M NaOH was slowly added to the heated Ludox with vigorous magnetic stirring, to give a molar composition of $0.25\ Na_2O : 1.0\ SiO_2 : 12.5\ H_2O$ for the resultant mixture. The resultant mixture became a clear sodium silicate solution after stirring continuously for *ca.* 1 h with heating to 343–353 K.[8] After further stirring for 1 h at the same temperature, the solution was cooled to room temp. and stored in a polypropylene bottle until used as the silica source.

In a typical synthesis batch, HTABr (Aldrich) was dissolved, by heating and magnetic stirring if necessary, in a mixture of doubly distilled water and ethanol to give the resulting molar composition of $1.0\ HTABr : 5.0\ EtOH : 120\ H_2O$. The above silica source was added to this surfactant solution at room temp., dropwise with vigorous magnetic stirring. The resulting gel mixture, with a molar composition of $1.4\ SiO_2 : 1.0\ HTABr : 0.35\ Na_2O : 5.0\ EtOH : 140\ H_2O$, was heated for 4 days at 373 K in an autoclave and subsequently cooled to 340 K. The supernatant liquid in the reaction mixture was quickly removed by decantation and filtration before further cooling. The solid product was washed quickly with hot distilled water before cooling. The product was then slurried in EtOH–HCl, filtered, washed with EtOH, dried in an oven, and calcined in air under static conditions, in the same way as described in our recent report.[9]

The product yield in a typical synthesis batch was *ca.* 50% on the basis of the silica recovery. About 50% of silica was dissolved in the supernatant liquid under the hydrothermal reaction condition. The dissolved silica had to be removed from the MCM-48 phase before cooling to below 340 K, because the cooling resulted in the formation of insoluble silicate gel and made it difficult to separate from the MCM-48 phase afterward.

Fig. 1 shows typical powder X-ray diffraction (XRD) patterns and field emission scanning electron micrographs (SEM) for MCM-48 samples obtained following the above procedure. The XRD patterns were obtained with a Cu-Kα X-ray source using a Rigaku D/MAX-III (3 kW) instrument. The field emission SEM images were obtained with a Hitachi S800 instrument. The XRD patterns in Fig. 1(*a*) indicate excellent structural order for the cubic crystallographic space group $Ia\bar{3}d$.[2–5] Fig. 1(*b*) shows a narrow distribution in the particle size around 0.3 μm for the present MCM-48 sample synthesised at 373 K. The SEM image in Fig. 1(*c*) was obtained from a MCM-48 sample after hydrothermal synthesis over 16 h at 413 K. The particle size increased markedly, compared with the sample synthesised at 373 K. It is very remarkable that the MCM-48 particles obtained at 413 K have the crystal shape of a cube truncated by rhomb dodecahedron. An activation energy of 14 kcal mol^{-1} (1 cal = 4.184 J) has been obtained from the Arrhenius plot between the crystallisation rate and the inverse of the synthesis temperature.[10] All these results show remark-

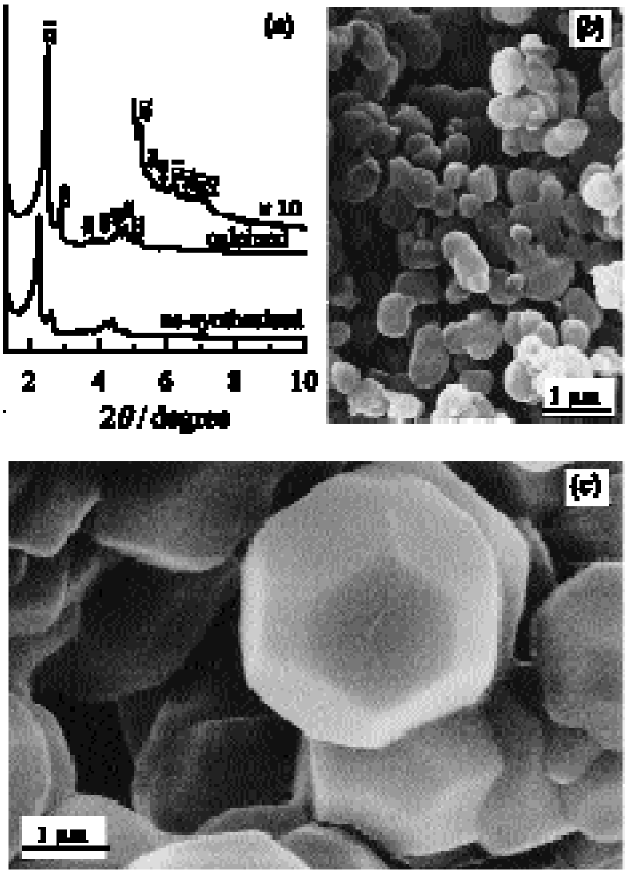

Fig. 1 (*a*) XRD patterns, (*b*) field emission SEM image for MCM-48 synthesised at 373 K and (*c*) at 413 K

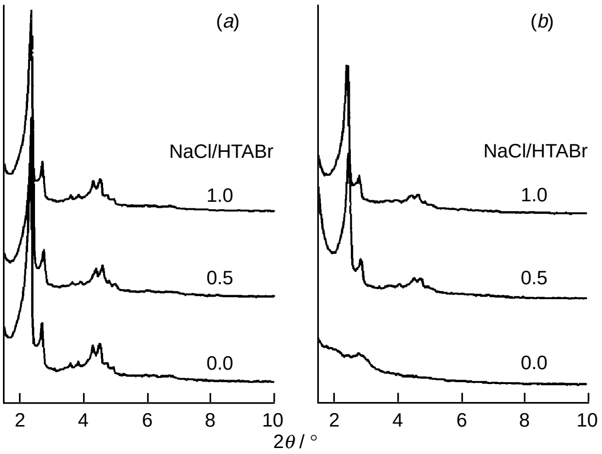

Fig. 2 XRD patterns for MCM-48 samples: (*a*) calcined and (*b*) after heating the calcined samples in distilled water at 373 K for 12 h. Numbers given to XRD patterns denote the NaCl/HTABr molar ratios used for the synthesis.

able similarities between the formation of MCM-48 particles under the present hydrothermal conditions and hydrothermal growth of other conventional zeolite crystals.

The MCM-48 phase was converted to a disordered phase when ethanol was allowed to evaporate under the present hydrothermal synthesis conditions. The role of the added ethanol in the formation of MCM-48 is the ability to cause a systematic rearrangement in the structure of the micelle by penetrating the micelle surface, just the same way as ethanol which is formed by the hydrolysis of tetraethylorthosilicate (TEOS) during the synthesis of MCM-48 with TEOS. The latter has been clarified recently by Huo *et al.*[11] using Cab-o-sil in place of TEOS as the silica source in the presence of other polar organic additives such as $\mathrm{Me_2NCH_2CH_2OH}$ and $\mathrm{N(CH_2CH_2OH)_3}$. The use of tetramethylorthosilicate instead of TEOS did not give MCM-48, and the result was attributed to the high polarity and hydrophilicity of the resulting methanol so that it could not penetrate the micelle surface. However, methanol is more effective for the formation of MCM-48 than ethanol. The substitution of 5.0 EtOH with 3.0 MeOH in our synthesis procedure described above gave just the same high-quality MCM-48 material. The EtOH could also be substituted by appropriate amounts of higher alcohol such as 1.5 $\mathrm{Pr^iOH}$, 0.3 $\mathrm{Bu^sOH}$ and 0.3 $\mathrm{Bu^tOH}$. All MCM-48 materials obtained with the alcohol showed similar BET surface areas in the range of $1000 \pm 50\ \mathrm{m^2\ g^{-1}}$. However, the use of the higher alcohol resulted in a somewhat lower XRD peak resolution, compared with the use of EtOH and MeOH.

MCM-41 or a disordered mesoporous material[12] was obtained instead of MCM-48 when the amount of alcohol was insufficient. The use of excess alcohol resulted, on the other hand, in the formation of a lamellar phase. We have confirmed that MCM-48 can be obtained within a wide range of the gel composition, $x\ \mathrm{SiO_2} : 0.25x\ \mathrm{Na_2O} : 1.0\ \mathrm{HTABr} : 0.035y\ \mathrm{EtOH} : y\ \mathrm{H_2O}$ in a temperature range of 373–413 K, where x and y can be varied over 1.2–3.0 and 70–400, respectively. The formation of the MCM-48 phase followed a typical zeolite crystallisation curve, reaching a maximum in 4 d at 373 K. Subsequently, the MCM-48 phase was converted to a lamellar phase. At 413 K, the MCM-48 formation was accomplished in 16 h.[10]

After heating in boiling water for 12 h, our calcined samples gave no XRD patterns indicating the MCM-48 structure. This was due to the low hydrothermal stability of the MCM-48 samples.[13] The hydrothermal stability of the MCM-48 can be improved by using NaCl, similar to the salt effect for MCM-41.[14] To demonstrate this, the autoclave was cooled to room temp. after heating for 3.5 d at 373 K. The reaction mixture in the autoclave was then added to a conc. NaCl solution with magnetic stirring, to give NaCl/HTA = 0.1–1.0. The autoclave was closed and heated again for 1.5 d. The results are shown in Fig. 2.

This work was supported by Korea Science and Engineering Foundation. The authors thank Korea Material Analysis Co. for field emission SEM.

Footnote and References

* E-mail: rryoo@sorak.kaist.ac.kr

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 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.*, 1992, **114**, 10 834.
3 A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
4 V. Alfredsson and M. W. Anderson, *Chem. Mater.*, 1996, **8**, 1141.
5 R. Ryoo and C. H. Ko, *Chem. Commun.*, 1996, 2467.
6 A. Sayari, *Stud. Surf. Sci. Catal.*, 1996, **102**, 1.
7 X. S. Zhao, G. Q. Lu and G. J. Millar, *Ind. Eng. Chem. Res.*, 1996, **35**, 2075.
8 R. Ryoo and J. M. Kim, *J. Chem. Soc., Chem. Commun.*, 1995, 711.
9 R. Ryoo, S. Jun, J. M. Kim and M. J. Kim, *Chem. Commun.*, 1997, 2225.
10 J. S. Kim, S. K. Kim and R. Ryoo, manuscript in preparation.
11 Q. Huo, R. Leon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.
12 R. Ryoo, J. M. Kim, C. H. Ko and C. H. Shin, *J. Phys. Chem.*, 1996, **100**, 17718.
13 J. M. Kim and R. Ryoo, *Bull. Korean Chem. Soc.*, 1996, **17**, 66.
14 S. Jun and R. Ryoo, *J. Phys. Chem. B*, 1997, **101**, 317.

Received in Cambridge, UK, 23rd October 1997; 7/07677K