

Synthesis of mesoporous aluminosilicate with zeolitic characteristics using vapor phase transport†

Yiwen Zhang, Tatsuya Okubo and Masaru Ogura‡

Received (in Cambridge, UK) 6th January 2005, Accepted 24th March 2005

First published as an Advance Article on the web 14th April 2005

DOI: 10.1039/b500075k

A mesoporous material with zeolitic characteristics is synthesized by use of a vapor phase transport method for the first time, along with stabilization of the mesostructure during crystallization of the amorphous walls by carbon filling.

Nowadays zeolite microporous molecular sieves have been widely adopted to important industrial applications such as adsorption and catalysis due to their strong acidity and hydrothermal stability. However, the small pore size (less than 1 nm) limits their applications on bulky molecules. Many types of mesoporous material such as M41s and the SBA series have been developed to overcome this difficulty.^{1,2} On the contrary, owing to their poor hydrothermal stability and weak acidity caused by the amorphous nature of the mesopore walls, practical utilization seems to be limited.³ It is thus very attractive to synthesize a material, which has the advantages of both zeolites and mesoporous materials. Several efforts have been made to crystallize the mesopore walls of mesoporous materials, leading to the formation of materials with increased thermal stability and catalytic activity.^{4–7} By the conventional hydrothermal synthesis, however, it is difficult to control the simultaneous nucleation of zeolite and mesoporous material, resulting in the formation in many cases of a physical mixture of each component as reported elsewhere. Moreover in most cases, the mesostructure is partially collapsed and the structural periodicity becomes lower after crystallization of mesopore walls to zeolite, because of shrinkage of the (alumino)silicate framework due to the difference in density of the amorphous and crystal states.

Here we have developed a new route to synthesize mesoporous materials with zeolitic characteristics. The synthesis was carried out through a solid rearrangement process inside the framework of mesoporous materials using a vapor phase transport (VPT) method, which differs completely from the conventional method for the synthesis of zeolites. First, aluminosilicate hydrogel having a chemical composition toward an objective zeolite is prepared, then it is dried up. The dried gel obtained is crystallized in the vapor of the structure directing agent (SDA) as well as water. No continuous liquid phase exists during the final stage of the VPT synthesis for crystallization, meaning that the nucleation and crystal growth of the zeolite can be limited on the accessible surface of the aluminosilicate. Here, mesoporous aluminosilicate is applied as a starting source of Si and Al for zeolites, so that nucleation is

limited on the mesopore walls of the mesoporous materials, as well as avoiding the formation of a physical mixture. Furthermore, carbon materials are introduced into the mesopore channel, which act as a “filler” to restrain the collapse of the mesostructure.

In the typical synthesis of zeolitic mesoporous material, the following steps were carried out: (1) Preparation of mesoporous material; (2) Introduction of Al on the mesopore surface; (3) Filling of carbon inside the mesopores; and (4) VPT for zeolitization. SBA-15 type mesoporous silica was prepared using tetraethylorthosilicate (TEOS) as a silica source, triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF) as a surfactant and HCl aqueous solution according to the procedure in the literature.² 0.074 g of AlCl₃ was dissolved in distilled water and 1 g of SBA-15 was then added. The Si/Al ratio resulting was 30. The mixture was heated at 333 K with stirring to evaporate water until dry, followed by calcination at 813 K for 5 h. Filling of furfuryl alcohol (FA, C₅H₆O₂) into the mesopore channels was carried out using incipient wetness according to the procedure as reported for the preparation of mesoporous carbon, CMK-3.⁸ The Al-SBA-15/FA composite was then heated in Ar flow at 1173 K for 6 h to carbonize FA. The Al-SBA-15/CMK-3 composite was placed into a Teflon cup and was then transferred to a Teflon-lined autoclave, at the bottom of which SDA solution (1.0 ethylenediamine : 7.7 triethylamine : 10 H₂O) for MFI crystallization⁹ was poured and thoroughly separated from the composite. Transformation of amorphous walls of Al-SBA-15 to zeolite was controlled at 448 K in the presence of the SDA steam for five days. Finally the carbonaceous compounds as well as the SDA were removed at 873 K in air for 6 h. The calcined products are denoted as ZMM-1 in this work.

Fig. 1 shows the XRD patterns of various samples. Al-SBA-15 obtained after the impregnation of aluminium retained a highly-ordered hexagonal structure. The CMK-3 obtained by Al-SBA-15 templating showed the typical pattern of hexagonal structure in the region of 2theta = 0.5–5°, confirming sufficient filling of carbon into the mesopore channels. The ZMM-1 exhibited comparably an intense XRD pattern to Al-SBA-15, indicating that the mesostructure is almost retained after the VPT synthesis. No diffraction peaks were observed in the 2theta range of 5–40° on the calcined ZMM-1, indicating the absence of zeolite crystal, suggesting the ZMM-1 sample is a single mesophase. Prolonged VPT synthesis resulted in the apparent formation of a zeolite structure assigned to ZSM-5 by XRD. For the 12 days of VPT, only ZSM-5 was observed, indicating that the excess crystallization caused a collapse of the mesostructure of Al-SBA-15 due to the formation of ZSM-5 large crystal. Nitrogen adsorption was performed to confirm the structural properties of ZMM-1. The ZMM-1 exhibited the typical type IV isotherm with the jump in the

† Electronic supplementary information (ESI) available: TEM images of ZMM-1. Nitrogen adsorption isotherms of Al-SBA-15, ZMM-1, and ZSM-5. See <http://www.rsc.org/suppdata/cc/b5/b500075k/>

‡ Present address: Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan. E-mail: oguram@iis.u-tokyo.ac.jp

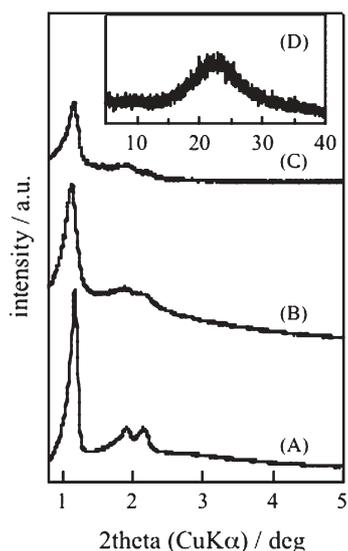


Fig. 1 XRD patterns of (A) Al-SBA-15, (B) CMK-3, and (C,D) ZMM-1.

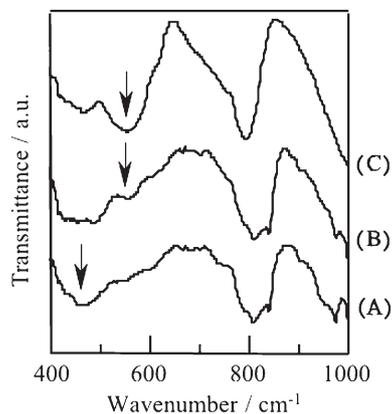


Fig. 2 FT-IR spectra of (A) Al-SBA-15, (B) ZMM-1, and (C) ZSM-5.

adsorption branch at $P/P_0 = 0.65\text{--}0.80$, which is a unique property of such kinds of mesostructure as SBA-15 (see ESI†). The corresponding pore size distribution was found to be narrow and centered at 9.0 nm, and also larger than that of Al-SBA-15, that was at 7.5 nm. It is most likely due to the condensation of mesopore walls of Al-SBA-15 during the crystallization, so that the wall thickness of ZMM-1 (1.5 nm) would be thinner. The wall thickness almost matches the size of the unit cell of ZSM-5.

Fourier-transformed infrared spectra on ZMM-1, Al-SBA-15 and ZSM-5 (Si/Al = 11.9, Tosoh Corp.) are demonstrated in Fig. 2. The Al-SBA-15 showed a broad band at 460 cm^{-1} , which can be assigned to the vibration mode of amorphous silica. It is noted that ZMM-1 displayed another intense absorption at 560 cm^{-1} , which is attributed to the absorption band of the five-membered rings in ZSM-5 framework.^{10,11} These results suggest that ZMM-1 has a zeolitic primary or secondary building unit.

The acidity of ZMM-1, Al-SBA-15, and ZSM-5 were measured by cumene cracking, which is well known as a model reaction to confirm Brønsted acidity. Table 1 summarizes the catalytic

Table 1 Catalytic activity for cumene cracking^a

Sample	Conversion to benzene (%)			
	473 K	503 K	543 K	573 K
Al-SBA-15	0	0	0	0.82
ZMM-1	0	0.13	0.79	2.5
HZSM-5 ^b	0	8.7	20	24

^a Catalyst, 100 mg; cumene pulse, 1 μL . ^b Catalyst, 5 mg.

activities of these samples. The Al-SBA-15 hardly showed catalytic activity below 573 K because of the surrounding amorphous silicate nature of the Al species in its framework. On the contrary, the conversion of cumene into benzene on ZMM-1 could be observed at 503 K, which is the same active temperature as that of H⁺ZSM-5 for this reaction as shown in Table 1. These results indicate that ZMM-1 contains the same type of Brønsted acid site as H⁺ZSM-5 from the activation energy viewpoint. The improved catalytic activity of ZMM-1 compared to Al-SBA-15 is caused by the zeolite primary and secondary building units which exist in the mesopore walls.

In conclusion, a new route for the synthesis of mesoporous materials with zeolitic characteristics has been developed. To the best of our knowledge, this is the first time that the VPT method has been applied to the synthesis of mesoporous materials having zeolitic characteristics. The fabricated composite material exhibited a narrow mesopore size distribution and superior acidity compared to the same type of Al-grafted mesoporous materials. These characteristics suggest that the composites might be useful practically as catalysts for bulky molecules. Moreover, it is believed that a zeolitic building unit is as effective as the zeolite crystal for catalytic reactions, and that the unit the material possesses is considered a “zeolite”.

Yiwen Zhang, Tatsuya Okubo and Masaru Ogura†

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. Fax: 81 3 58003806; Tel: 81 3 58417368

Notes and references

- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
- A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
- K. R. Kloetstra, H. W. Zandbergen, J. C. Jansen and H. van Bekkum, *Microporous Mater.*, 1996, **6**, 287.
- L. Huang, W. Guo, P. Deng, Z. Xue and Q. Li, *J. Phys. Chem. B*, 2000, **104**, 2817.
- Y. Liu, W. Zhang and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 2000, **122**, 8791.
- Z. Zhang, Y. Han, L. Zhu, R. Wang, Y. Yu, S. Qiu, D. Zhao and F.-S. Xiao, *Angew. Chem., Int. Ed.*, 2001, **40**, 1258.
- T.-W. Kim, I.-S. Park and R. Ryoo, *Angew. Chem., Int. Ed.*, 2003, **42**, 4375.
- W. Xu, J. Dong, J. Li, W. Li and F. Wu, *J. Chem. Soc., Chem. Commun.*, 1990, 755.
- J. C. Jansen, F. J. van der Gaag and H. van Bekkum, *Zeolite*, 1984, **4**, 369.
- E. A. Kirschhock, R. Ravishankar, F. Verspeurt, P. J. Grobet, P. A. Jacobs and J. A. Martens, *J. Phys. Chem. B*, 1999, **103**, 4965.