



Textural and Catalytic Properties of MCM-22 Zeolite Crystallized by the Vapor-Phase Transport Method

Satoshi Inagaki,* Kohei Kamino, Masahiro Hoshino, Eiichi Kikuchi, and Masahiko Matsukata

Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

Received November 17, 2003; E-mail: sinagaki_dr@ruri.waseda.jp

MCM-22 zeolite crystallized by the vapor-phase transport (VPT) method showed a higher shape-selectivity to *p*-xylene in the alkylation of toluene with methanol, compared with MCM-22 crystallized by the hydrothermally synthetic (HTS) method, because VPT-MCM-22 has a smaller external surface area and a smaller number of acid sites thereon than HTS-MCM-22. Such textural properties of VPT-MCM-22 are caused by the fact that the spherical particles of VPT-MCM-22 are composed of hexagonal plates as thin as 55 nm; they are larger than those of HTS-MCM-22, which are 30 nm thick. The acidic properties, characterized by NH₃-TPD and FT-IR using a pyridine adsorption technique, showed no significant difference between VPT- and HTS-MCM-22, except for the acidity on the external surface.

Hydrothermally synthesized MCM-22 zeolite using hexahydro-1*H*-azepine (hexamethyleneimine, HMI) as a structure-directing agent¹ is designed as an MWW structure, and has the same topology as PSH-3,² SSZ-25,³ ERB-1,⁴ and ITQ-1⁵ (*three letter codes representing the zeolite structures are defined by the International Zeolite Association⁶). This type of zeolite has a large pocket (inner diameter of 0.71 nm) on the external surface and two independent pore systems with 10-membered ring (10MR): one is defined by a two-dimensional sinusoidal channel, and the other by the 12MR supercages.^{7,8} Much attention has been paid to the unique crystalline structure due to possibilities of being applied to many catalytic reactions, such as the selective production of *p*-xylene in the disproportionation of toluene⁹ and the aromatization of *n*-butane.¹⁰ This zeolite has recently enabled commercial processes of ethylbenzene and cumene production by the alkylation of benzene with ethylene and propylene.^{11,12}

The morphologies of zeolite catalysts have been demonstrated to significantly change the catalytic activity and selectivity. For instance, larger ZSM-5 particles with smaller external surface area showed higher *p*-xylene selectivity than smaller ZSM-5 particles in the alkylation of toluene with methanol and the disproportionation of toluene.^{13,14} The crystal morphologies (size, aspect ratio, shapes) of zeolites could be changed by controlling the hydrothermal conditions of crystallization, for example, the compositions of the parent hydrogel, aging temperature and period, crystallization temperature and period and stirring/rotating speed.

The hydrothermal synthesis of MCM-22 zeolite has been studied in detail^{15–18} using HMI. In early reports,^{15,16} MCM-22 having SiO₂/Al₂O₃ ratios of around 30 could be obtained as a pure phase for a relatively broad range of OH/SiO₂ ratios, whereas crystallization from a parent mixture with low aluminum contents (i.e., SiO₂/Al₂O₃ = 70) yielded a mixture of the MWW phase with the MFI¹⁵ or the FER¹⁶ phase. Mochida and co-workers¹⁶ reported that seeding in the hydrothermal synthesis of MCM-22 zeolite could avoid the formation of an unde-

sired phase. These early reports,^{15,16} as well as the original patent,¹ indicate that stirring or rotating during hydrothermal crystallization is necessary to obtain a high-quality MWW phase. Crystallization by using HMI under static conditions yielded a pure phase of MCM-22 for narrow ranges of synthetic parameters, such as the gel composition, crystallization period and temperature.^{15,17,18}

The stirring/rotating crystallization yielded isolated hexagonal thin plates (around 1 μm in width) of MCM-22 crystals, whereas static crystallization gave crystals composed by the aggregation of hexagonal thin plates. Güray et al.¹⁸ suggest that the aggregation of thin plates resulted in a limitation on the mass transfer of nutrients from the solution to the growing crystals during static crystallization, if compared with the rotating/stirring conditions.

In our previous research,¹⁹ MCM-22 zeolite crystallized by the vapor-phase transport (VPT) method, which is one of the dry gel conversion techniques for zeolite synthesis,^{20–23} consisted of aggregates of hexagonal thin plates, similarly to a crystal crystallized by the hydrothermally synthetic (HTS) method under static conditions. In this study, we investigated the physicochemical and catalytic properties of MCM-22 zeolite crystallized by the VPT method compared with the crystal obtained by the HTS method.

1. Experimental

1.1 Synthesis of an MCM-22 Precursor by the VPT Method.

An MCM-22 precursor having an MWW-type framework was synthesized by the VPT method according to our previous report,¹⁹ using HMI as a structure-directing agent. In a typical procedure, the hydrogel was prepared by mixing appropriate amounts of fumed silica (99.8% purity, Aldrich), NaAlO₂ (Al₂O₃: 36.5 wt %, Na₂O: 33.0 wt %, Kanto Chem.), NaOH pellet (96.0% purity, Kokusan Chem.) and distilled water. The composition of the mixture was SiO₂:Na₂O:Al₂O₃:H₂O = 1.0:0.075:0.028:44. The hydrogel was stirred vigorously for 30 min at room temperature, followed by drying on a hot stirrer at 80 °C overnight. Dry gel weighing 0.5

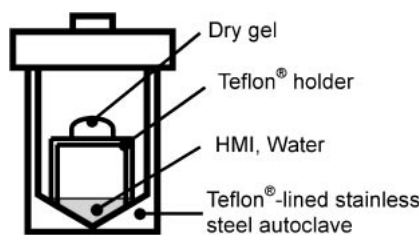


Fig. 1. Setup of autoclave for the vapor-phase transport (VPT) method.

g was crushed to a powder and placed in a 50 mL autoclave. The autoclave was set up so as to separate the dry gel from a liquid mixture of HMI (>97.0% purity, Kanto Chem.) and distilled water, as shown in Fig. 1. In this study, 1.5 g of HMI and 2.0 g of distilled water were added to the bottom of the autoclave. The dry gel was crystallized under autogeneous pressure at 150 °C for 3–7 days. The products were filtered, washed with distilled water, and dried at 110 °C.

1.2 Synthesis of MCM-22 Precursor by HTS Method. MCM-22 precursor was also synthesized hydrothermally according to the following procedure. A mixture of fumed silica, NaAlO₂, NaOH, HMI, and distilled water was prepared and stirred vigorously for 30 min at room temperature. The mixture was composed of SiO₂:Na₂O:Al₂O₃:H₂O:HMI = 1.0:0.075:0.028:44:0.5, and was transferred into an 100 mL autoclave and crystallized at 150 °C for 5–7 days under rotating conditions. The rotating speed was 20 rpm. The products were filtered, washed with distilled water, and dried at 110 °C.

1.3 Preparation of H⁺-MCM-22 Zeolite. The formation of MCM-22 zeolite requires the calcination of an as-synthesized product, defined as an MCM-22 precursor. The precursor was calcined in an air flow at 540 °C for 12 h (ramping rate = 5 °C min⁻¹). The calcined product, defined as MCM-22 zeolite, was treated by repeated ion exchange in 1 M NH₄NO₃ aqueous solution at 80 °C for 1 h with stirring four times. The NH₄⁺-MCM-22 zeolites were calcined again in air at 540 °C for 12 h (ramping rate = 5 °C min⁻¹) in order to degas NH₃, and then H⁺-MCM-22 zeolites were obtained.

In this report, the as-synthesized MCM-22 precursor and the calcined MCM-22 zeolite are designated as MCM-22(P) and MCM-22, respectively. In the cases of crystallization using the VPT and HTS methods, VPT- and HTS- are prefixed to MCM-22(P) or MCM-22; for instance, the MCM-22 precursor crystallized by the VPT method is designated as VPT-MCM-22(P).

1.4 Characterization. All of the as-synthesized and calcined products were checked concerning their crystallinity and phase purity by X-ray powder diffraction (XRD) on an RINT 2000 (Rigaku) equipped monochromator and scintillation counter, using Cu Kα radiation at 40 kV and 20 mA.

The scanning micrographs for the products were obtained on an S-4500S field-emission scanning electron microscope (FE-SEM, Hitachi) at an accelerating voltage of 15 kV. The samples were sputtered with a mixture of platinum and palladium before taking the images.

The textural properties of MCM-22 zeolites were determined from a N₂ sorption experiment at -196 °C on AUTOSORB-1 (Quantachrome Inst.). The sample was evacuated at 350 °C for 3 h prior to a measurement. The external surface area and the micropore volume were determined from the adsorption branch by using the *t*-plot method.²⁴

The amount of Al in MCM-22 zeolites was measured by using inductively coupled plasma spectrometry (ICP, CIROS-120, Rigaku).

The number of acid sites was measured by using the temperature-programmed desorption (TPD) of ammonia. The catalyst employed was evacuated at 500 °C prior to the measurement. The TPD data were collected at a ramping rate of 1 °C min⁻¹. A mass spectrometer was used to monitor the desorbed ammonia. The number of acid sites was determined from that of the desorbed ammonia.

Brönsted and Lewis acid sites on MCM-22 zeolite were characterized by pyridine adsorption with Fourier transform infrared spectrometry (FT-IR). Self-supporting pressed wafers (diameter, 2 cm; weight, 20 mg) were prepared and activated by heating under a dynamic vacuum for 1 h at 500 °C, in an IR cell allowing in situ thermal treatments and low-temperature gas dosage. After cooling to 150 °C, adsorbing pyridine vapor (ca. 2.6 kPa) and evacuating gases, IR spectra were recorded on the FT-IR (FT-610, JASCO) with a resolution of 4 cm⁻¹.

1.5 Catalytic Tests. The alkylation of toluene with methanol was performed under atmospheric pressure in a downflow quartz-tube microreactor with 8 mm of inner diameter. Prior to running the reaction, 10 or 20 mg of a catalyst was packed in a fixed-bed of the reactor with 2.0 g of silicon nitride as a diluent, and preheated at 350 °C for 1 h in a stream of argon. After reducing the temperature to 250 °C, the feed was switched over to an argon stream containing an equimolar mixture of toluene and methanol. The argon stream contained 5% of methane as an internal standard material. The reactants and products were separated by using a packing column with Bentone 34 (5%) + diisodecylphthalate (DIDP) (5%) (GL Science) and analyzed by using GC-8A (Shimadzu) with a flame-ionization detector.

The cracking of 1,3,5-triisopropylbenzene (TIPB) at 200 °C was carried out by a pulse method as a catalytic test to evaluate the number of acid sites on the external surface of the MCM-22 zeolite. Before the reaction, 10 mg of a catalyst was packed in a fixed-bed of a stainless-tube microreactor with a 4 mm inner diameter, and preheated at 350 °C for 1 h in a stream of helium (30 cm³ min⁻¹). After reducing the temperature to 200 °C, 1.0 μL of TIPB was pulsed into the catalyst-bed with a stream of helium (30 cm³ min⁻¹). The reactant and the products of cracking were separated by using a packed column with OV-1 (GL Science), and detected by using GC-8A (Shimadzu) with a thermal-conductivity detector.

2. Results and Discussion

2.1 Morphologies and Textural Properties of VPT- and HTS-MCM-22 Zeolites. As confirmed by XRD, shown in Fig. 2c, VPT-MCM-22(P) was crystallized at 150 °C for 7 days with the addition of 1.5 g of HMI and 2.0 g of H₂O in the liquid phase in a 50 mL autoclave. A shorter crystallization period of only 3 days gave an amorphous product (Fig. 2a), and a crystallization period of 5 days was sufficient to crystallize an MWW structure (Fig. 2b). The crystallization of HTS-MCM-22(P) also required 5 days, as confirmed by XRD (shown in Fig. 2d). The intensities of the XRD patterns for the products after more than 5 days of crystallization were hardly changed (Fig. 2e). Hereafter, the MCM-22 products obtained by crystallization for 7 days either by the VPT or by the HTS method are characterized.

The XRD pattern for VPT-MCM-22 gave sharper peaks than that of HTS-MCM-22, if compared to Figs. 3a and 3b, suggesting that VPT-MCM-22 consisted of larger crystallites than HTS-MCM-22. The crystallinity of HTS-MCM-22, however, was comparable to that of VPT-MCM-22, if we considered no appreciable difference in the micropore volume between VPT- and HTS-MCM-22, as shown in Table 1 to be $0.150 \text{ cm}^3 \text{ g}^{-1}$ and $0.144 \text{ cm}^3 \text{ g}^{-1}$. The micropore volume and the external surface area were determined by using *t*-plot curves, as shown in Fig. 4. In contrast, the external surface area of HTS-MCM-22 ($262 \text{ m}^2 \text{ g}^{-1}$) was much larger than that of VPT-MCM-22 ($150 \text{ m}^2 \text{ g}^{-1}$), caused by a difference in the thickness of the thin plates composing MCM-22 crystals, as demonstrated by the FE-SEM images given in Fig. 5. VPT-MCM-22 had the shape of a sphere with a diameter of around $15 \mu\text{m}$ (Fig. 5a); these spherical particles were actually the aggregate of thin plates with about $45\text{--}65 \text{ nm}$ thickness (Fig. 5b). On the other hand, HTS-MCM-22 had a hexagonal shape,

which was composed of isolated thin plates with a $25\text{--}35 \text{ nm}$ thickness isolated and about $1 \mu\text{m}$ length (Figs. 5c and 5d).

2.2 Catalytic Properties of VPT- and HTS-MCM-22.

The number of Brönsted acid sites on the external surface, which depends on the external surface area, was considerably different between the VPT- and HTS-MCM-22 zeolites. This difference was confirmed by comparing the activity for TIPB cracking. The proton-type HTS-MCM-22 showed a 74% conversion of TIPB at 200°C , higher than that of VPT-MCM-22 (41%), as shown in Table 1. Only the number of acid sites on the external surface was different between these two MCM-22 catalysts. There were no significant difference in the acidic properties, which have so far been characterized by NH_3 -TPD and FT-IR using the pyridine adsorption technique. These MCM-22 zeolites had almost the same amount of whole acid sites, which was proved by NH_3 -TPD, as shown in Fig. 6 and Table 1. In both MCM-22 zeolites, the acid sites measured by NH_3 -TPD originated from Al species included in MCM-22 powder, because the amount of Al in MCM-22 was equal to that of the acid sites, as listed in Table 1. The relative number of Brönsted to Lewis acid sites on VPT-MCM-22 was almost the same as that on HTS-MCM-22, since the relative intensities of two peaks at 1540 and 1450 cm^{-1} , respectively, corresponding to pyridine adsorbed on Brönsted and Lewis acid sites, were not significantly different between VPT- and HTS-MCM-22

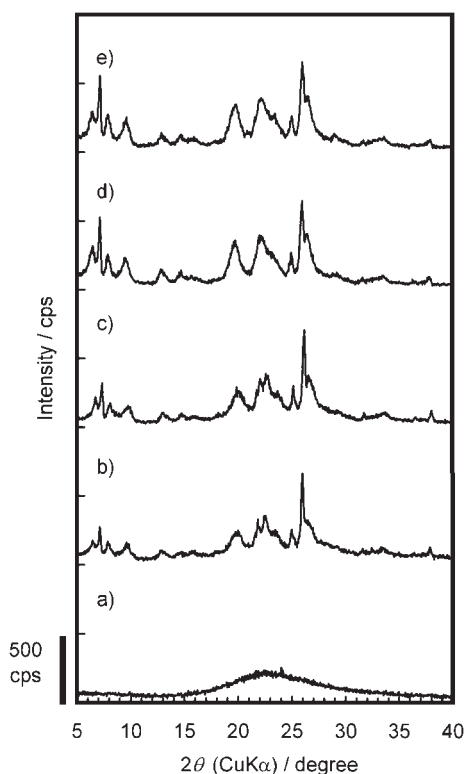


Fig. 2. XRD patterns for as-made products crystallized at 150°C by the VPT method for a) 3 days, b) 5 days, c) 7 days and by the HTS method for d) 5 days, e) 7 days.

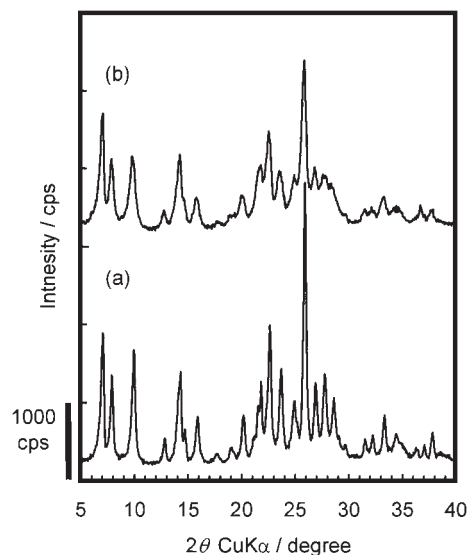


Fig. 3. XRD patterns for calcined MCM-22 zeolites crystallized at 150°C for 7 days by the VPT (a) and HTS (b) methods.

Table 1. Textural, Acidic, and Catalytic Properties of MCM-22 Zeolites

Catalyst	Micropore volume $/\text{cm}^3 \text{ g}^{-1}$	External surface area $/\text{m}^2 \text{ g}^{-1}$	Average of thickness of thin plate $/\text{nm}$	% Conversion of TIPB ^{a)}	Number of acid site ^{b)} $/\text{mmol g}^{-1}$	Number of Al in MCM-22 ^{c)} $/\text{mmol g}^{-1}$
VPT-MCM-22	0.150	150	55 ± 10	41	0.97	1.09
HTS-MCM-22	0.144	262	30 ± 5	74	1.13	1.02

a) Reaction conditions for cracking of 1,3,5-triisopropylbenzene (TIPB): temperature, 200°C ; weight of catalyst, 10 mg; He flow rate, $30 \text{ cm}^3 \text{ min}^{-1}$; pulse width of TIPB, $1.0 \mu\text{L}$. b) The amount of acid sites was determined by NH_3 -TPD. c) The amount of Al in MCM-22 was determined by ICP.

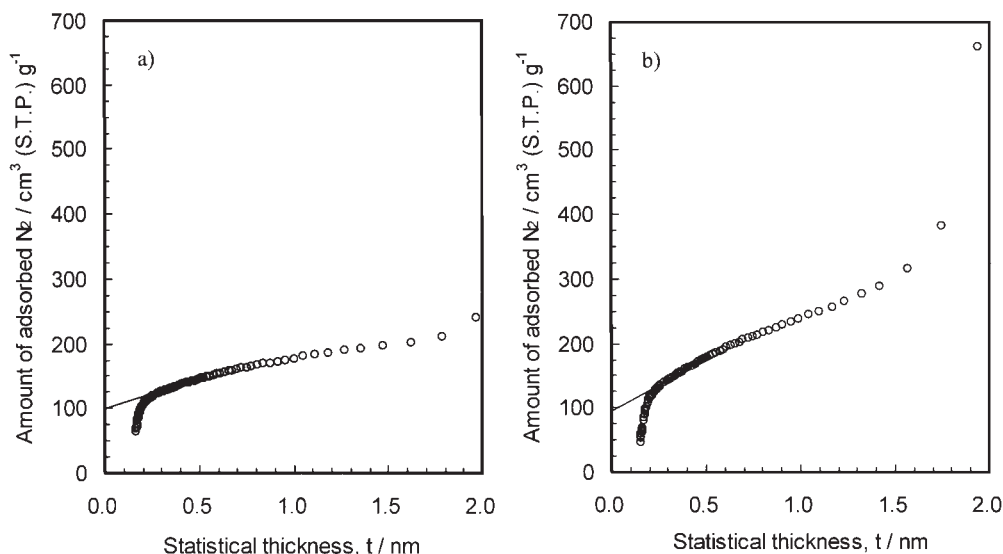


Fig. 4. t -Plot curves calculated from nitrogen adsorption isotherm for a) VPT-MCM-22 and b) HTS-MCM-22 zeolites.

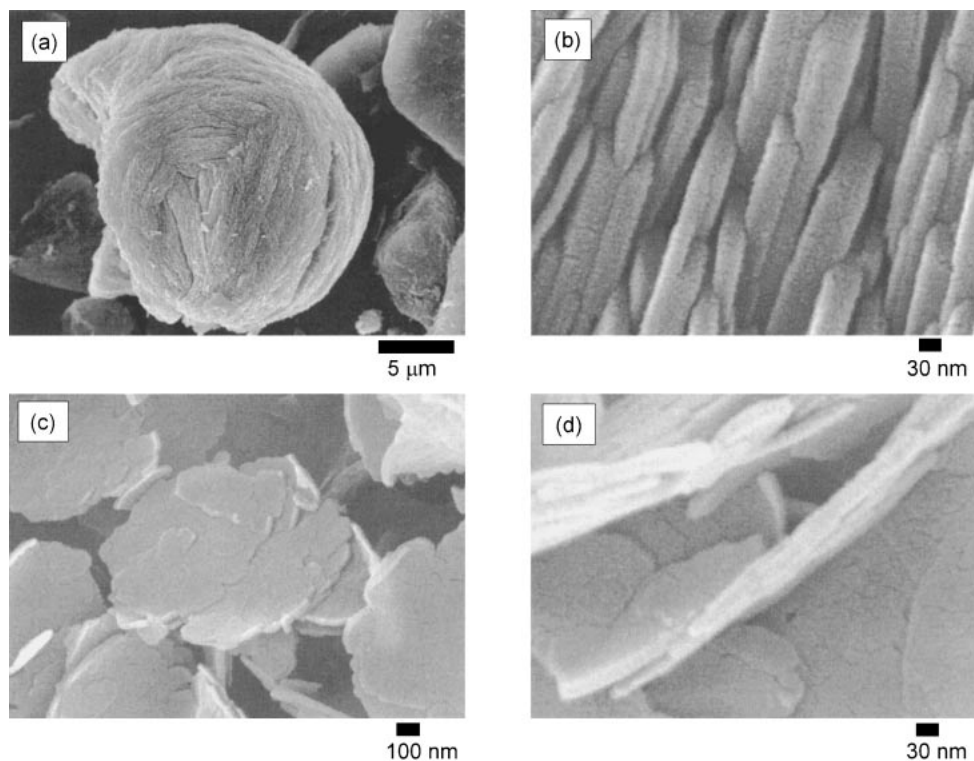


Fig. 5. FE-SEM images for calcined MCM-22 zeolites crystallized at 150 °C for 7 days by the VPT (a, b) and HTS (c, d) methods.

zeolites, as demonstrated by the FT-IR spectra (Fig. 7).

As shown in Table 2, the MCM-22 catalyst showed a high selectivity to *p*-xylene in the alkylation of toluene with methanol at 250 °C, as attributed to shape-selective alkylation in 10MR micropore of the MWW structure, similarly to ZSM-5.¹³ Moreover, the *p*-xylene selectivity of VPT-MCM-22 was always higher than that of HTS-MCM-22, over the whole range of W/F studied, due to a smaller number of acid sites on the external surface of VPT-MCM-22. The smaller fraction of the external surface acidity on the VPT-MCM-22 gave lower levels of conversion, based on either toluene or methanol, than did HTS-MCM-22, in spite of almost the same total number of acid

sites.

On either MCM-22 catalyst, dimethyl ether (DME) was formed by the intermolecular dehydration of methanol, which was faster than the alkylation of toluene with methanol, as shown in Table 2. The yield of DME was determined by the following Eq. 1:

$$\begin{aligned} \text{Yield of DME (\%)} &= \frac{(\text{Amount of DME formed}) \times 2}{\text{Amount of methanol in a mixture of reactants}} \times 100. \\ (1) \end{aligned}$$

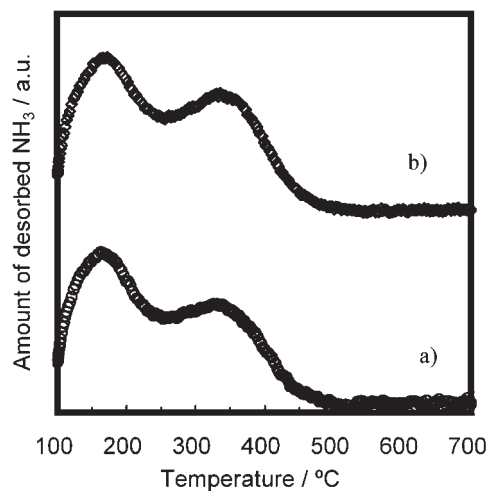


Fig. 6. NH_3 -TPD spectra for a) VPT-MCM-22 and b) HTS-MCM-22 zeolites.

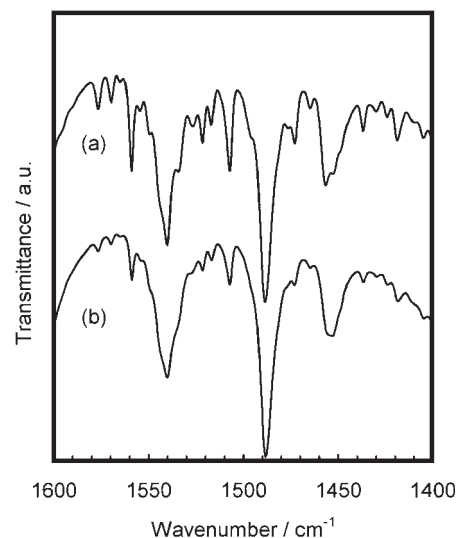


Fig. 7. FT-IR spectra of adsorbed pyridine on the VPT (a) and HTS (b) MCM-22 zeolites.

Table 2. Product Distributions in the Alkylation of Toluene with Methanol over MCM-22 Zeolites

Catalyst	(W/F)/g h (mol-methanol) ⁻¹	% Conversion of toluene	% Conversion of methanol	Yield of DME/%	Product distribution in alkylated products/%					
					<i>p</i> -X	<i>m</i> -X	<i>o</i> -X	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB
VPT-MCM-22	0.66	1.4	30.0	28.5	63.6	12.7	20.9	0.0	2.8	0.0
	1.37	2.9	40.9	38.4	57.4	14.2	20.7	0.0	6.5	1.2
	2.02	3.9	59.3	55.0	55.3	14.5	20.7	0.0	8.2	1.2
HTS-MCM-22	0.69	1.8	36.9	34.9	44.0	14.7	37.9	0.0	3.4	0.0
	1.35	3.1	49.9	46.5	41.8	14.3	36.1	0.0	5.1	2.6
	2.08	5.4	65.8	59.8	40.4	15.2	32.5	0.0	8.9	3.1

Reaction conditions: temperature, 250 °C; weight of catalyst, 10 or 20 mg; partial pressure of methanol, 9 kPa; partial pressure of toluene, 9 kPa; time on stream, 5 min. DME, dimethyl ether; X, xylene; TMB, trimethylbenzene.

As shown in Fig. 8, there was no appreciable difference in the selectivity to DME on the basis of methanol between VPT- and HTS-MCM-22, since there was no significant difference in the acidic properties, as confirmed by NH_3 -TPD and FT-IR.

3. Conclusions

The main results from our studies can be summarized as follows:

- VPT-MCM-22 zeolite has the shape of a sphere composed of hexagonal plates as thin as 55 nm, which are larger than those of HTS-MCM-22 (30 nm thick).
- Thus, VPT-MCM-22 has a smaller external surface area, and the number of acid sites thereon compared with HTS-MCM-22.
- In the alkylation of toluene with methanol at 250 °C, the *p*-xylene selectivity of VPT-MCM-22 catalyst was always higher than that of HTS-MCM-22, due to a smaller number of acid sites on the external surface of VPT-MCM-22.
- In contrast, the acidic properties characterized by NH_3 -TPD and FT-IR using the pyridine adsorption technique showed no significant difference between VPT- and HTS-MCM-22, except for the acidity on the external surface.

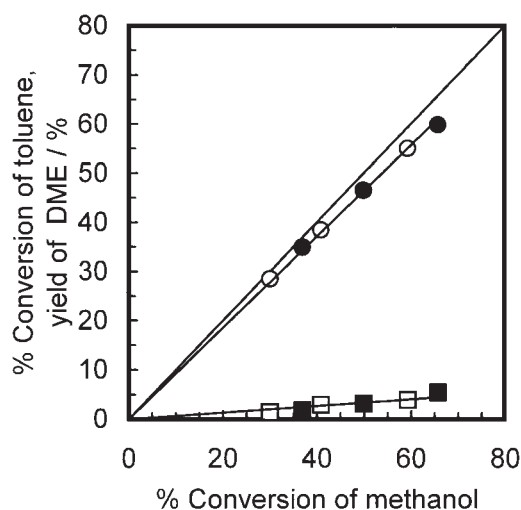


Fig. 8. Conversion of toluene (□, ■) and yield of DME (○, ●) against conversion of methanol in alkylation of toluene with methanol on MCM-22 zeolites. Blank mark means VPT-MCM-22; filled mark means HTS-MCM-22.

References

- 1 M. Rubin and P. Chu, U. S. Patent 4954325 (1990).
- 2 L. Puppe and J. Weisser, U. S. Patent 4439409 (1984).
- 3 S. I. Zones, D. I. Holtermann, R. A. Innes, T. A. Pecoraro, D. S. Santilli, and J. N. Ziemer, U. S. Patent 4826667 (1989).
- 4 G. Bellussi, G. Perego, M. G. Clerici, and A. Giusti, European Patent Application, 293032 (1988).
- 5 M. A. Camblor, A. Corma, M.-J. Díaz-Cabañas, and Ch. Baerlocher, *J. Phys. Chem. B*, **102**, 44 (1998).
- 6 Ch. Baerlocher, W. M. Meier, and D. H. Olson, "Atlas of Zeolite Framework Types," 5th ed, Elsevier, Amsterdam (2001).
- 7 M. E. Leonowicz, J. A. Lawton, S. L. Lawton, and M. K. Rubin, *Science*, **264**, 1910 (1994).
- 8 S. L. Lawton, M. E. Leonowicz, R. D. Partridge, P. Chu, and M. K. Rubin, *Microporous Mesoporous Mater.*, **23**, 10 (1998).
- 9 P. Wu, T. Komatsu, and T. Yashima, *Microporous Mesoporous Mater.*, **22**, 343 (1998).
- 10 N. Kumar and L.-E. Lindfors, *Appl. Catal., A*, **147**, 175 (1996).
- 11 P. Chu, M. E. Landis, and Q. N. Le, U. S. Patent 5334795 (1994).
- 12 A. Corma, V. Martínez-Soria, and E. Schnoefeld, *J. Catal.*, **192**, 163 (2000).
- 13 D. H. Olson and W. O. Haag, "ACS symposium series 248," ed by T. E. Whyte, Jr., R. A. Dalla Betta, E. G. Derouane, and R. T. K. Baker, American Chemical Society, Washington, D.C. (1984), Chap. 14.
- 14 J.-H. Kim, T. Kunieda, and M. Niwa, *J. Catal.*, **173**, 433 (1998).
- 15 A. Corma, C. Corell, and J. Pérez-Pariente, *Zeolites*, **15**, 2 (1995).
- 16 I. Mochida, S. Eguchi, M. Hironaka, S. Nagao, K. Sakanishi, and D. D. Whitehurst, *Zeolites*, **18**, 142 (1997).
- 17 I. Güray, J. Warzywoda, N. Baç, and A. Sacco, Jr., *Microporous Mesoporous Mater.*, **31**, 241 (1999).
- 18 A. L. S. Marques, J. L. F. Monteiro, and H. O. Pastore, *Microporous Mesoporous Mater.*, **32**, 131 (1999).
- 19 S. Inagaki, M. Hoshino, E. Kikuchi, and M. Matsukata, *Stud. Surf. Sci. Catal.*, **142**, 53 (2002).
- 20 X. Wu, J. Dong, J. Li, and F. Wu, *J. Chem. Soc., Chem. Commun.*, **1990**, 755.
- 21 M. H. Kim, H. X. Li, and M. E. Davis, *Microporous Mater.*, **1**, 191 (1993).
- 22 M. Matsukata, N. Nishiyama, and K. Ueyama, *Microporous Mater.*, **1**, 219 (1993).
- 23 M. Ogura, S. Nakata, E. Kikuchi, and M. Matsukata, *J. Catal.*, **199**, 41 (2001).
- 24 R. S. Mikhail, S. Brunauer, and E. E. Bodor, *J. Colloid Interface Sci.*, **26**, 45 (1968).