



Facile synthesis of highly crystalline EMT zeolite by hydrothermal conversion of FAU zeolite in the presence of 1,1'-(1,4-butanediyl)bis(1-azonia-4-azabicyclo [2,2,2]octane) dihydroxide

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ABSTRACT

Hydrothermal conversion of cubic (FAU) zeolite into hexagonal (EMT) zeolite using 1,1'-(1,4-butanediyl)bis(1-azonia-4-azabicyclo [2,2,2]octane) dihydroxide ([Dab-4]²⁺(OH)₂) instead of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), a well-known organic structure-directing agent (OSDA) for the synthesis of EMT zeolite, was investigated. A systematic study concerning hydrothermal synthesis parameters such as H₂O/SiO₂, NaOH/SiO₂, and [Dab-4]²⁺(OH)₂/SiO₂ ratios in the starting synthesis mixture, and temperature and time of synthesis revealed that pure, highly crystalline EMT zeolite can be easily obtained within a short crystallization period of 6 h.

1. Introduction

The EMT zeolite is a hexagonal polymorph of the cubic FAU zeolite and possesses two types of cages: a hypercage (1.24 nm³, 0.73 nm × 0.73 nm) and a hypocage (0.61 nm³, 0.75 nm × 0.65 nm). Since the successful synthesis of pure EMT zeolite [1], there has been much interest in this potentially useful large-pore mineral because it exhibits better catalytic performance than the FAU zeolite [2]. However, the synthesis of pure, highly crystalline EMT zeolite requires 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), an expensive and toxic compound, as an organic structure-directing agent (OSDA) and a long crystallization period of 7–15 days [3–6]. Therefore, many studies have been conducted to reduce the consumption of the crown ether by using less expensive OSDAs, and additional inorganic and organic auxiliary additives [7–10]. Recently, it has been reported that the EMT zeolite can also be obtained from an OSDA-free system [11,12]. However, 18-crown-6 is still necessary for the synthesis of highly crystalline EMT zeolite.

We have investigated the potential of interzeolite transformation, i.e., hydrothermal conversion of one zeolite into another. This alternative has attracted much attention because it provides information about the crystallization mechanism and is also an outstanding

approach to introduce new zeolites that cannot be crystallized by conventional hydrothermal synthesis methods [13,14]. We succeeded in synthesizing several types of zeolites such as *BEA, CHA, AEI, and LEV from FAU zeolites in the presence of various quaternary ammonium and phosphonium cations [15–18]. The crystallization rates were notably elevated for these syntheses compared with those observed in conventional hydrothermal syntheses that utilize amorphous aluminosilicate gels. Crystallization rate enhancement occurs because the decomposition/dissolution of the starting zeolite generates locally ordered aluminosilicate species (nanoparts) that assemble and evolve into another type of zeolite. Based on several hydrothermal conversions of zeolites, we have concluded that the structural similarity between the starting and crystalline zeolite is a crucial factor in its crystal growth [15].

Here, we report a facile synthesis of highly crystalline EMT zeolite through hydrothermal conversion of FAU zeolite using [Dab-4]²⁺ cation, an OSDA for the synthesis of AFX zeolite, and its characterization. FAU and EMT zeolites have the same composite building units (*d6r* and *sod*).

Abbreviations: CP, Cross-polarized; [Dab-4]²⁺(OH)₂, 1,1'-(1,4-butanediyl)bis(1-azonia-4-azabicyclo[2,2,2]octane) dihydroxide; EDX, Energy-dispersive X-ray; FD, Framework density; OSDA, Organic structure-directing agent; XRD, X-ray diffraction; SEM, Scanning electron microscope

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Table 1
Hydrothermal conversion of FAU zeolite in the presence of [Dab-4]²⁺ + cation.

Run no.	Synthesis conditions						product				
	Si/Al of FAU	[Dab-4] ²⁺ /SiO ₂ ^c	H ₂ O/SiO ₂	NaOH/SiO ₂	Temp./°C	Time/h	Phase	Yield/%	Si/Al ^a	BET surface area/m ² g ^{-1b}	Micropore volume ^c /cm ³ g ⁻¹
1	17	0.1	5.0	0.60	140	48	AFX	39	3.6	819	0.31
2	17	0.1	5.0	0.60	140	6	EMT + AFX				
3	17	0.1	5.0	0.56	140	6	EMT	30	4.7	857	0.33
4	17	0.1	5.8	0.56	140	6	EMT	29	3.5	842	0.34
5	17	0.1	4.0	0.56	140	6	Am.				
6	17	0.1	5.8	0.56	110	6	Am.+AFX + FAU				
7	17	0.05	5.8	0.56	140	6	Am.				
8	17	0.15	5.8	0.56	140	6	EMT + AFX				
9	10	0.1	5.8	0.56	140	6	EMT + FAU				
10	26	0.1	5.8	0.56	140	6	EMT	7	3.4	820	0.34
11	66	0.1	5.8	0.56	140	6	*BEA	6			
12 ^d	17	0.1	5.8	0.56	140	6	Am.+Al(OH) ₃				
13 ^e	19	0.1	5.8	0.56	140	6	Am.				

^a Measured by ICP.

^b Determined by the BET method.

^c Determined by the t-plot method.

^d Synthesized from amorphous hydrogel prepared using fumed silica (Cab-O-Sil M5) and Al(OH)₃.

^e Synthesized from MFI zeolite.

2. Experimental

2.1. Synthesis of EMT zeolite

The starting FAU zeolites used in this work were prepared according to the procedure in previous works [16–18]. NH₄-Y zeolite (Si/Al = 2.8, Tosoh Co., Japan) was dealuminated by steaming at 700 °C and H₂SO₄ (0.40–0.75 M) treatment at 30 °C for 16 h. The powder X-ray diffraction (XRD) pattern of the dealuminated zeolite showed no peaks other than those corresponding to the FAU structure. The particle size of dealuminated FAU zeolite ranges from 0.2 to 0.5 μm. The hydrothermal conversion of FAU zeolite was performed as follows. The dealuminated FAU zeolite alone was mixed with an alkali aqueous solution containing sodium hydroxide (NaOH, > 99%, Kojundo Chemical Laboratory, Japan) and 1'-(1,4-butanediyl)bis (1-azonia-4-azabicyclo [2,2,2]octane) hydroxide ([Dab-4](OH)₂). The mixture was then placed in a 30 cm³ Teflon-lined stainless steel autoclave. [Dab-4](OH)₂ was prepared from [Dab-4]Br₂ (> 98, Wako Pure Chemical, Japan) treated with the hydroxide anion exchange resin, DIAION SA10A0H (Mitsubishi Chemical Co., Japan). The hydrothermal conversion was conducted under static conditions at 100–140 °C for 30 min–3 days in a convection oven. The solid product was collected by centrifugation and washed thoroughly with deionized water until the pH of the washes was near neutral values. Thereafter, it was dried overnight at 70 °C. To remove the [Dab-4]²⁺ cations from zeolitic pores, the as-synthesized EMT zeolites were calcined in open air at 500 °C for 10 h (heating rate of 5 °C min⁻¹).

2.2. Characterization

Powder XRD patterns of the solid products were collected using a powder X-ray diffractometer (Bruker D8 ADVANCE) with graphite-monochromatized Cu Kα radiation at 40 kV and 40 mA. The Si/Al ratio was determined using inductively coupled plasma optical emission spectroscopy (ICP, Seiko SPS7000). The crystal morphology was observed using a Hitachi S-4800 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray (EDX) analyzer. ¹³C, ²⁷Al, and ²⁹Si magic angle spinning (MAS) NMR spectra were recorded at 150.88, 156.33, and 119.17 MHz, respectively, on a Varian 600 PS solid NMR spectrometer, using a 3.2 mm diameter zirconia rotor at 15 kHz for ²⁷Al MAS NMR, and a 6 mm diameter zirconia rotor at 7 kHz for both ¹³C and ²⁹Si MAS NMR. The ²⁷Al MAS NMR spectra were acquired using 2.8

μs pulses, a 1 s recycle delay, and 256 scans. The ²⁹Si MAS NMR spectra were acquired using 6.2 μs pulses, a 100 s recycle delay, and 100 scans. Alk(SO₄)₂·12H₂O and 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt were used as chemical shift references for the ²⁷Al and ²⁹Si MAS NMR, respectively. Prior to the ²⁷Al MAS NMR measurements, the samples were moisture-equilibrated over a saturated solution of NH₄Cl for 24 h. The ¹H–¹³C cross-polarized (CP) MAS NMR spectra were measured with a spinning frequency of 7 kHz, a 90° pulse length of 5.6 μs, and a cycle delay time of 5 s. The ¹³C chemical shifts were compared with hexamethyl benzene. Nitrogen adsorption isotherms were obtained at –196 °C using a conventional volumetric apparatus (BELSORP-mini, Bel Japan). Prior to performing the adsorption measurements, the calcined samples (ca. 50 mg) were heated at 400 °C for 10 h under a N₂ flow. The BET surface area and micropore volume were calculated by the BET method (P/P₀ = 0.05–0.1) and the t-plot method, respectively. The thermal analysis was performed using a TG/DTA apparatus (SSC/5200 Seiko Instruments). Beginning at room temperature, the sample of ca. 7 mg was heated to 800 °C with flowing air (50 mL min⁻¹) at a heating rate of 5 °C min⁻¹.

3. Results and discussion

3.1. Synthesis of EMT from FAU

The hydrothermal conversion of dealuminated FAU zeolite was conducted at 140 °C using [Dab-4]²⁺ cation, a typical OSDA in the synthesis of AFX zeolite. Table 1 lists the hydrothermal conversion conditions and their corresponding results. At a hydrothermal treatment period of 48 h, pure AFX zeolite was obtained (Run no. 1). However, under a shorter treatment time of 6 h with a [Dab-4]²⁺/SiO₂ ratio of 0.1, the formation of EMT zeolite was observed together with that of AFX zeolite (Run no. 2). By decreasing the NaOH/SiO₂ ratio from 0.60 to 0.56 or increasing the H₂O/SiO₂ ratio from 5.0 to 5.8 (a decrease in alkalinity), a pure, highly crystalline EMT zeolite could be obtained (Run nos. 3 and 4). To our knowledge, this is the first report on the synthesis of EMT zeolite under a short crystallization period. When the [Dab-4]²⁺/SiO₂ ratio in the starting synthesis mixture was either 0.05 or 0.15, no pure EMT zeolite was obtained (Run nos. 7 and 8). For comparison, we attempted to synthesize EMT zeolite from an amorphous starting mixture prepared from fumed silica (Cab-O-Sil M5) and Al(OH)₃ (Run no. 12) or MFI zeolite (Run no. 13), whose composite building units (*mor*, *cas*, *mfi* and *mel*) are different from FAU and EMT

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