Synthesis of Mordenite Nanocrystals by Using a Hydrophobic Structure-directing Agent

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Mordenite nanocrystals of around 80 nm in length along the *c* axis were synthesized successfully by using a hydrophobic structure-directing agent (SDA). The nanometer-sized mordenite catalyst showed higher activity than the micron- or submicron-sized versions in cumene cracking.

Zeolites, microporous crystalline aluminosilicates, are widely used as shape-selective catalysts, ion exchangers, and adsorbents owing to their unique properties such as their solid acidity, large internal surfaces, and molecular sieving and ion-exchange abilities. Over 200 different zeolite framework type codes (FTCs)¹ have been approved so far by the International Zeolite Association (IZA); nevertheless, only a limited number of framework types have been applied for industrial use.

Mordenite (**MOR** topology)¹ is one of the most useful zeolites,^{2–9} and the first synthetic version was reported by Barrer in 1948.¹⁰ The pore system of mordenite consists of two elliptical channels parallel to the *c* axis; one is a 12-membered ring (12-MR) channel with 0.65 nm × 0.70 nm, and the other is an 8-MR channel (0.26 nm × 0.57 nm).¹¹ Although the 12-MR channels are connected with the 8-MR channels (0.34 nm × 0.48 nm) along the *b* axis,¹¹ mordenite can be regarded as a one-dimensional zeolite because the 8-MRs along the *b* axis are too small for most organic molecules.

Since nanosized zeolites generally have the advantages of larger surface areas and fewer diffusion limitations in catalytic and adsorptive applications, the syntheses of many kinds of zeolite nanocrystals have been achieved,^{12–15} and smaller crystals of mordenite are also desired. The most common morphology of mordenite is the needle morphology with *c* axis elongation,¹⁶ and often the length is greater than 5 μm. Although mordenite nanocrystals smaller than 500 nm have been obtained as a result of altering the synthetic routes in the absence or presence of structure-directing agents (SDAs),^{17–24} their morphologies still look like needles with *c*-elongation. In this paper, we report the successful hydrothermal synthesis of mordenite crystals as small as 80 nm along the *c* axis by using a bulky, hydrophobic SDA, *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium (**1**). This is the first example of the use of the organic cation **1** for the synthesis of **MOR**.

In general, the usage of SDAs for zeolite synthesis has great advantages in the control of both the qualitative and quantitative formations of nuclei of a given zeolite structure. In the induction period during zeolite crystallization, the “hydrophobic interaction” between SDA molecules and silicate moieties occurs in aqueous solution, enhancing the frequency of formation of zeolite nuclei and the subsequent crystallization of zeolite nanoparticles.^{25–29} Tetraethylammonium (**2**) is a very common SDA for mordenite synthesis; however, this cation is a little too hydrophilic for the effective nucleation of high-silica zeolites

owing to its *C/N*⁺ ratio of 8.²⁹ The dication **1**, with a *C/N*⁺ ratio of 10, which is a little more hydrophobic than **2**, was expected to cause more frequent nucleation of high-silica zeolites. In fact, the dication **1** is known to be a very effective SDA for the synthesis of nanocrystals of MCM-68 (**MSE**).³⁰

Mordenite samples were synthesized by using the parent mixture with the following typical composition: 1.0·SiO₂–[0.1·**1** or 0.2·**2**]–0.375·KOH–0.1·Al(OH)₃–30·H₂O. The crystallization was carried out in an autoclave at 160 °C for several days under tumbling conditions at 20 rpm. The detailed synthetic procedure, characterization, and reaction scheme are summarized in the Supporting Information.³¹

The time courses of the crystallization at 160 °C were examined by means of powder X-ray diffraction (XRD) of the as-synthesized products (Figure S1).³¹ The crystallization with tumbling for seven days gave an **MOR** phase (Figure S1c),³¹ whereas the product obtained after five or six days was still amorphous (Figure S1a)³¹ or a mixture of amorphous solid and mordenite (Figure S1b),³¹ respectively. The prolonged crystallization time up to 16 days also gave only the **MOR** phase without any other zeolite phases (Figure S1d).³¹ In contrast, the crystallization under static conditions for 16 days produced an **MSE** phase (Figure S1e),³¹ which was consistent with the literature reports.³⁰ Continuous mixing of the synthesis gel by tumbling of the autoclave may have caused the preferential formation of **MOR** nuclei, giving an **MOR** phase. Formation of the **MOR** framework in the presence of **1** is not strange in the light of the fitting of the cationic part into the 12-MR channel and its structural similarity to the known SDA, **2** (Figure 1).

Figure 2 shows the powder XRD patterns of the as-synthesized products crystallized in the presence of **1** (diiodide), **2** (iodide), or **2** (bromide). All three kinds of products were pure mordenite, as confirmed by their XRD peaks. The XRD patterns of the mordenite synthesized by using **1** showed lower intensities and broader peaks than the patterns of the mordenites crystallized in the presence of cation **2**, indicating that smaller crystallites with the **MOR** topology can be obtained by using **1**. On the basis of FE-SEM observation (Figure 3a), the mordenite crystallized in the presence of **1** has a rectangular morphology with dimensions of less than 100 nm on each side. On the other

Figure 1. The structure drawings of *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium (**1**) and tetraethylammonium (**2**) cations, emphasizing the partial similarity of the structure.

Figure 2. XRD patterns of the as-synthesized products crystallized at 160 °C for 7 days with tumbling at 20 rpm by using (a) **1** (diiodide), (b) **2** (iodide), or (c) **2** (bromide) as an SDA.

hand, mordenites synthesized by using **2** also have rectangular morphologies of around 400 nm on each side (Figures 3b and 3c). The particle size distributions of the obtained mordenites were evaluated (Figure S2³¹ and Table 1). The mordenite nanoparticles obtained with the use of **1** gave a narrow particle size distribution from 80 to 200 nm. In contrast, the mordenite crystals assisted by cation **2** had a wide distribution from 300 to 500 nm in particle size.

Table 1 lists the physicochemical properties of the mordenite samples obtained in this study. All three kinds of mordenite samples showed almost the same Si/Al molar ratios (ca. 10) without deviation from the input values. They gave typical type-I nitrogen adsorption–desorption isotherms (Figure S3),³¹ and similar micropore volumes of ca. 0.2 cm³ g^{−1} were estimated by using the *t*-plot method. On the other hand, the BET surface area of the SDA-**1**-assisted mordenite was larger than those of the SDA-**2**-assisted mordenites (Table 1). The isotherm of SDA-**1**-assisted mordenite also gave a typical nitrogen uptake above a relative pressure of 0.98, indicating that intra-mesopores exist in the mordenite nanocrystals. The acidities of the mordenite samples were evaluated by temperature-programmed desorption of ammonia (NH₃-TPD). Niwa and Katada³² have revealed that the ammonia desorption temperature for each zeolite catalyst is consistent with the order of the adsorption heat of ammonia ΔH . The SDA-**1**-assisted mordenite nanocrystals showed a similar NH₃-TPD profile to JRC-Z-HM20 (Figure S4)³¹ and had the usual strong acid sites ($\Delta H = 150$ kJ mol^{−1}).³² Both the **1**-assisted mordenite (Si/Al = 11) and JRC-Z-HM20 (Si/Al = 10) had reasonable numbers of acid sites (1.09 and 1.11 mmol (g-zeolite)^{−1}, respectively).

Figure 3. FE-SEM images of the mordenites synthesized at 160 °C for 7 days with tumbling at 20 rpm by using (a) **1** (diiodide), (b) **2** (iodide), or (c) **2** (bromide) as an SDA.

Table 1. Physicochemical properties of mordenites obtained in this work^{a,b}

SDA used for the synthesis	S_{BET}^c /m ² g ^{−1}	S_{ext}^d /m ² g ^{−1}	V_{micro}^e /cm ³ g ^{−1}	Particle size ^f /nm
1 (diiodide)	596	93	0.212	80–150
2 (iodide)	509	68	0.196	350–400
2 (bromide)	525	57	0.206	400–450

^aSi/Al molar ratio of the starting gel is 10, and the crystallization conditions are described in the text. ^bProduct was pure mordenite with Si/Al molar ratio of 11 for all cases.

^cBET surface area estimated on the basis of nitrogen adsorption–desorption isotherms. ^dExternal surface area estimated by the *t*-plot method. ^eMicropore volume estimated by the *t*-plot method. ^fEstimated by FE-SEM observation.

For the evaluation of the catalytic activities of the mordenites synthesized by using the different SDAs, catalytic cracking of cumene was carried out by using a pulse-type reactor. Figure 4 shows the typical catalytic results for **1**-assisted H⁺-mordenite nanoparticles and **2**-assisted micron- or sub-micron-sized H⁺-mordenite. The benzene yields are used as an indicator of the catalytic activity. At every pulse, the **1**-assisted mordenite nanoparticles exhibited an obviously higher activity than the mordenite synthesized by using **2** iodide. The positive effect of the nanoparticles could be ascribed to the enhanced

Figure 4. Benzene yield in the cracking of cumene by using a pulse-type reactor over (a) mordenite nanoparticles synthesized by using **1** (diiodide) and (b) mordenite synthesized in the presence of **2** (iodide). Reaction conditions: catalyst, 10 mg; temperature, 250 °C; flow rate of helium, 25 cm³ (N.T.P.) min⁻¹; dose amount of cumene, 1.0 μL.

accessibility of the cumene molecules to the acid sites. In both cases, a slight and gradual decrease in activity was observed with each pulse, indicating that the external surface and pore mouths became poisoned, probably by propylene oligomers and dehydrogenated carbonaceous species formed there. However, the deactivation was not serious, and no significant differences in the loss of activity between the current two samples were observed.

In summary, mordenite nanoparticles of around 80 nm in length, especially in the *c*-direction, were synthesized successfully by using a relatively hydrophobic SDA **1**. The obtained mordenite nanoparticles showed typical strong Brønsted acidity and superior catalytic activity to micron- or submicron-sized mordenite in the cumene cracking reaction. The work reported here suggests the possibility of the facile fabrication of zeolite nanocrystals with the aid of appropriate hydrophobic SDA molecules.

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