



Nanosized CHA zeolites with high thermal and hydrothermal stability derived from the hydrothermal conversion of FAU zeolite



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ABSTRACT

Nanosized CHA zeolites approximately 100 nm in size with high thermal and hydrothermal stability were synthesized by hydrothermal conversion of FAU zeolites in the presence of *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH) as a structure-directing agent. The crystal size of CHA zeolites depended strongly on the silica/alumina source (FAU zeolite or amorphous aluminosilicate hydrogel) and the Si/Al ratio of starting material. An increase in the hydrothermal synthesis temperature enhanced the thermal stability of nanosized CHA zeolites without increasing the crystal size, and the structural framework of the nanosized CHA zeolites was maintained even after thermal treatment at 1000 °C for 1 h. The potential of nanosized CHA zeolites as solid acid catalysts and as catalyst supports was evaluated by the ethanol conversion reaction and the selective catalytic reduction (SCR) of NO_x with NH₃, respectively. A protonated nanosized CHA zeolite catalyst effectively produced propylene from ethanol by suppressing catalytic deactivation arising from carbonaceous deposition. A Cu-loaded nanosized CHA zeolite catalyst exhibited good performance for the NH₃-SCR of NO_x even after hydrothermal treatment at 900 °C for 4 h. The results indicate that hydrothermal zeolite conversion is very effective in producing nanosized CHA zeolites with high thermal and hydrothermal stabilities.

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1. Introduction

Low density crystalline aluminosilicate zeolites with regular molecular-level micropores are important industrial materials. Due to their high surface area, solid acidity, and molecular sieve and ion-exchange properties, they have been used as catalysts and as a separation medium in environmentally friendly and economically beneficial applications such as hydrocarbon conversion in the petroleum industry and separation and refining processes in chemical industries [1–3]. However, their regular microporous channel systems lead to severe mass transport limitations, which limit catalytic efficiency. Reducing the size of a zeolite crystal can solve the problem by shortening the effective diffusion path length and enhancing the accessibility of micropores [4–6]. Significant effort

has been devoted to improve the accessibility of zeolite micropores. Methods include synthesis of nanosized zeolite crystals [7–14], formation of zeolite nanosheets [15–18], creation of mesopores in zeolite crystals [19–23], and other synthetic approaches [24–27]. However, mesopore creation by post-synthetic treatments such as desilication, dealumination, or steaming or by direct zeolite synthesis in the presence of organic additives leads to the formation of structural defects and inhomogeneous chemical compositions as well as an uncontrolled broad distribution of mesopores within the zeolite crystal. In addition, nanosized zeolites have a lower crystallinity than micrometer-sized zeolites, resulting in lower thermal and hydrothermal stabilities. This drawback strongly restricts their application under severe conditions. Although several reports have focused on a solution to this problem, a multistep post-synthetic treatment [26,27] and the use of a complex organic structure-directing agent (OSDA) [15] are required. However, the expensive cost of OSDA and relatively low yield in the synthesis of nanosized zeolites hinder their wide applications.

To overcome such limitations, herein, we attempt an alternative synthetic approach involving the hydrothermal conversion of FAU

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zeolite, which is employed as a silica/alumina source, to crystalline nanosized CHA zeolite. CHA zeolite is a promising small-pore zeolite. It has a three-dimensional pore system with large cages that are accessible via eight-membered ring (8-MR) windows measuring around $3.8 \text{ \AA} \times 3.8 \text{ \AA}$. It has been utilized as a support for the selective catalytic reduction (SCR) of NO_x by ammonia [28–31], as a separation membrane for the dehydration of aqueous organic solutions [32–35] and gas separations [36,37], and as a solid acid catalyst for the conversion of methanol or ethanol into light olefins such as ethylene or propylene [38–42]. Despite its attractive structural features and potential applications, there are few reports concerning the synthesis of nanosized CHA zeolites [14,22,42].

We have investigated the potential of hydrothermal conversion of one zeolite into another (interzeolite conversion or transformation) [43–46] and have found that this approach is an attractive strategy for zeolite synthesis [35,41,46–53]. Recently, we succeeded in obtaining mesoporous MFI zeolite with a hierarchical pore structure via *BEA-MFI interzeolite transformation by carefully tuning hydrothermal conversion conditions and the Si/Al ratios of the starting *BEA zeolites [49]. The porosity of the MFI zeolite crystals obtained is strongly affected by the hydrothermal treatment time, with the BET surface area varying from 370 to $510 \text{ m}^2 \text{ g}^{-1}$. It also was found that the mesoporous MFI zeolite with a high aluminum content (Si/Al = 9.0) exhibited high catalytic activity for the dehydration of lactic acid to acrylic acid. Furthermore, we successfully synthesized high-silica CHA zeolites with high crystallinity from FAU zeolite in the presence of benzyltrimethylammonium hydroxide (BTMAOH) or *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH) as an OSDA. The number of structural defects in CHA zeolite obtained by hydrothermal conversion was smaller than that in CHA zeolite obtained from amorphous aluminosilicate hydrogel (the conventional hydrothermal synthesis method), resulting in greater acid stability [35,50]. These results strongly indicate the potential of interzeolite conversion for synthesis of nanosized CHA zeolite with a high degree of crystallinity. However, the relationship between the hydrothermal conversion condition and the crystal size of zeolite is not still clarified.

Herein, we report the synthesis of highly crystalline nanosized CHA zeolites by hydrothermal conversion of FAU zeolite in the presence of TMAdaOH as an OSDA. The crystal size of the CHA zeolite produced depends strongly on the Si/Al ratio of starting FAU zeolite. We also found that the thermal stability of nanosized CHA zeolites is greater than that of CHA zeolites synthesized conventionally from amorphous aluminosilicate hydrogel. We also confirmed the high catalytic performance of nanosized CHA zeolites for the conversion of ethanol into propylene and for the NH_3 -SCR reaction.

2. Experimental

2.1. Hydrothermal conversion of FAU to CHA zeolites

The FAU zeolites used in this work were prepared from NH_4 -Y zeolites (Si/Al = 2.8, Tosoh Co., Japan) through a dealumination treatment that involved a combination of steaming at 700–800 °C and H_2SO_4 (0.40–0.75 M) treatment at 30 °C for 16 h. The XRD pattern of the dealuminated zeolite showed no peaks other than those corresponding to the FAU structure. The particle size of the dealuminated FAU zeolite was 0.2–0.5 μm . The hydrothermal conversion of FAU zeolite into CHA zeolite was conducted as follows. Dealuminated FAU zeolite was thoroughly mixed with an aqueous solution containing sodium hydroxide (>99%, NaOH, Kojundo Chemical Laboratory, Japan), *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH, 25 wt%, SACHEM,

Inc.) as an OSDA, and calcined seed crystals (CHA zeolite, Si/Al = 16). The mixture was placed in a 30 cm^3 Teflon-lined stainless steel autoclave, and hydrothermal conversion was conducted at 125–170 °C for 3 h to 21 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, and then dried overnight at 110 °C. Table 1 lists the chemical compositions of the starting reaction mixtures and the hydrothermal conversion conditions. Conventional CHA zeolite was synthesized as a reference using an amorphous aluminosilicate hydrogel prepared from fumed silica (Cab-O-Sil M5, Cabot) and $\text{Al}(\text{OH})_3$ (Wako Pure Chemical Ind. Ltd., Japan) as Si and Al sources and TMAdaOH. The yield of product was defined as follows:

$$\text{Yield}(\%) = \frac{\text{Product/g} - \text{seeds/g}}{\text{Starting Si and Al source/g}} \times 100 \quad (1)$$

2.2. Preparation of the Cu-loaded CHA zeolite catalyst

Before metal loading, the Na^+ cations in the CHA zeolite were removed by ion exchange with an aqueous solution of NH_4NO_3 . The resulting NH_4^+ form was calcined at 450 °C for 6 h to yield the H^+ form. The Cu-loaded zeolite catalyst was prepared by the following impregnation method. An aqueous solution containing a measured amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Kishida Chemical Co. Ltd., Japan) was added to the H^+ form zeolite and mixed thoroughly in a ceramic mortar. After mixing at room temperature, an excess of water was removed under reduced pressure. The resultant wet powder was dried at 110 °C, followed by calcination at 550 °C for 1 h.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the solid products were collected using a powder X-ray diffractometer (Rigaku Mini Flex) with graphite-monochromatized Cu K α radiation at 30 keV and 15 mA. The Si/Al, Na/Al, and Cu/Al ratios were determined by 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. ^{13}C , ^{27}Al , and ^{29}Si magic angle spinning (MAS) NMR spectra were recorded at 150.88 MHz, 156.33 MHz, and 119.17 MHz, respectively, on a Varian 600PS solid NMR spectrometer using a 3.2-mm diameter zirconia rotor at a rotation speed of 15 kHz for ^{27}Al MAS NMR and a 6-mm diameter zirconia rotor at 7 kHz for ^{13}C MAS NMR and ^{29}Si MAS NMR. The ^{27}Al spectra were acquired using 2.8 μs pulses, a 1 s recycle delay, and 256 scans. The ^{29}Si spectra were acquired using 6.2 μs pulses, a 100 s recycle delay, and 100 scans. $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt were used as chemical shift references for ^{27}Al and ^{29}Si MAS NMR, respectively. Prior to the ^{27}Al MAS NMR measurements, the samples were moisture-equilibrated over a saturated solution of NH_4Cl for 24 h. ^1H – ^{13}C 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. ^{13}C chemical shifts were referenced to hexamethylbenzene.

Thermal analyses were carried out by use of a thermogravimetric/differential thermal analysis (TG/DTA) apparatus (SSC/5200, Seiko Instruments). A sample (ca. 3 mg) was heated in a flow of air (50 mL min^{-1}) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C. Nitrogen adsorption isotherms were obtained at –196 °C using a conventional volumetric apparatus (BELSORP-mini, Bel Japan). The calcined samples (ca. 50 mg) were heated at

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