Synthesis of High-silica CHA Zeolite from FAU Zeolite in the Presence of Benzyltrimethylammonium Hydroxide

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A highly crystalline and pure high-silica chabazite zeolite with a Si/Al ratio of ca. 17 was obtained by the hydrothermal conversion of FAU zeolite used as a crystalline Si/Al source in benzyltrimethylammonium hydroxide media.

Aluminosilicate zeolite chabazite (CHA) with a Si/Al ratio of 2–3 has a three-dimensional pore system with ellipsoidal large cages (6.7 × 10 Å^2) that are accessible via eight-membered ring windows (3.8 × 3.8 Å^2). High-silica chabazite SSZ-13 and silicoaluminophosphate zeotype SAPO-34 characterized by CHA topology have attracted great interest as they show a specific shape selectivity for conversion of methanol[1–3] or bioethanol[4,5] to light olefins such as ethylene and propylene. Pure silica chabazite has also potential applications including adsorption and separation of organic molecules and also gas storage because of a larger void space owing to the absence of counter cations in the pores and the extreme hydrophobicity. SSZ-13 and pure silica chabazite have only been synthesized in alkali or fluoride medium and using expensive *N*,*N*,*N*-trimethyladamantammonium cation (TMAda$^+$) as a structure-directing agent (SDA).[6,7] Therefore, a lot of efforts have been paid to the synthesis of high-silica CHA zeolite using a reduced amount of TMAda$^+$ or other inexpensive SDAs.[8,9]

Recently, we have investigated the potential of hydrothermal conversion of one zeolite into another, i.e., interzeolite transformation from the standpoint of an alternative strategy for zeolite synthesis and found that a locally ordered aluminosilicate species may exist in the conversion process and their assembly under a specific structure-directing agent gives rise to a fast crystallization rate and a high selectivity to a particular zeolite. Namely, the highly crystalline and pure *BEA, RUT, and MTN zeolites were obtained from FAU zeolite in the presence of tetraethylammonium hydroxide, tetramethylammonium hydroxide, and benzyltrimethylammonium hydroxide (BTMAOH), respectively.[10–13] Here we report the synthesis of high-silica chabazite from FAU zeolite using BTMAOH. To the best of our knowledge, this is the first high-silica CHA zeolite synthesized with a SDA other than TMAda$^+$ cation, although it is already reported that the conventional aluminous CHA zeolite is obtained from FAU zeolite in a KOH solution.[14]

FAU zeolites with various Si/Al ratios used in this work were prepared from NH$_4$-Y zeolite (Si/Al = 2.8, Tosoh Co., Japan) through dealumination treatment involving a combination of steaming at 700 °C and H_2SO_4 (0.74–0.85 M) treatment at 75 °C for 4 h. The particle size of dealuminated FAU zeolite was 0.4–0.8 µm. The hydrothermal conversion of FAU zeolite into CHA zeolite was performed as follows. The dealuminated FAU zeolite was only mixed well with aqueous BTMAOH 40 wt % (Aldrich, USA), and then the mixture was placed into a 30-cm^3 Teflon-lined stainless steel autoclave. The hydrothermal conversion was conducted at 120–170 °C for 10–21 days in a convection oven. The solid product was collected by centrifugation and washed thoroughly with deionized water until near neutral and then dried overnight at 70 °C. Table 1 lists the chemical compositions of starting gels and the crystallization conditions.

Table 1. Details of hydrothermal conversion conditions and products obtained[a]

Run No.	Synthesis conditions					Product (by-product)	
	Si/Al of FAU	BTMAOH/SiO$_2$	NaCl/SiO$_2$	Temp /°C	Time /d	Phase	Bulk Si/Al
1	21	0.2	0	170	10	Am.	
2	21	0.2	0.05	170	10	MTN	21.5
3	21	0.2	0.05	140	21	MTN(CHA)	
4	21	0.2	0.05	120	21	Am.(FAU)	
5	21	0.2	0.1	120	21	CHA	16.9
6[b]	21	0.2	0.1	120	21	Am.	
7	23	0.4	0.1	120	21	CHA	
8	25	0.4	0.1	120	21	Am.	

[a]$H_2O/SiO_2 = 5$. [b]Amorphous SiO_2/γ-Al_2O_3 (or $Al(OH)_3$) was used instead of FAU zeolite.

The hydrothermal conversion of FAU zeolite without any additives other than BTMAOH gave amorphous materials. When a small amount of NaCl (NaCl/SiO$_2$ ratio of 0.05) was added to the mixture, the highly crystalline and pure clathrasil zeolite MTN was obtained.[13] Under a further increase in the NaCl/SiO$_2$ ratio and lower synthesis temperatures, the pure CHA zeolite was successfully synthesized. Figure 1 shows the XRD pattern and SEM image of calcined CHA zeolite. It shows the typical diffraction pattern of CHA type zeolite, which contains no impurities coming from the unconverted starting FAU zeolite and/or the cocrystallized phase. The obtained CHA zeolite has an ellipsoidal plate-like crystal shape with 1–1.5 µm in size. Figure 2 shows the ^{13}C CP/MAS NMR spectrum of synthesized CHA zeolite. Three resonances were observed at ca. 54, 72, and 132 ppm, which correspond to the methyl carbon, methylene carbon, and phenyl carbon of BTMA$^+$ cation, respectively. It was found that the SDA molecule exists intact within the pores of high-silica CHA zeolite. Although Zones and van Nordstand have already reported the hydrothermal conversions of cubic P zeolite and faujasite to high-silica chabazite SSZ-13, expensive TMAda$^+$ cation was employed as SDA and these zeolites only as the aluminium source.[8,9]

Our previous work concerning the hydrothermal conversion of FAU zeolite into *BEA, RUT, and MTN zeolites showed that the conversion was strongly dependent on the Si/Al ratio of the starting zeolite.[10,11,13] Therefore, in order to investigate the effect of Si/Al ratio on the hydrothermal conversion of FAU zeolite into CHA zeolite, a series of FAU zeolites with

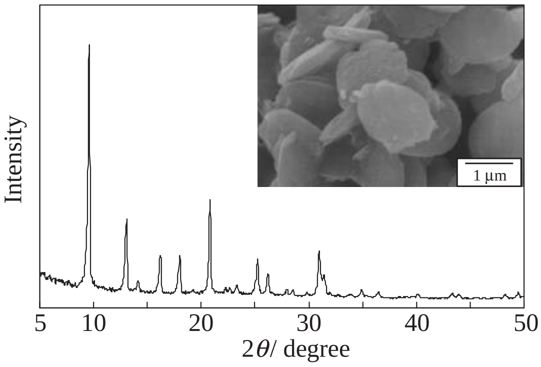

Figure 1. XRD pattern and SEM image of CHA zeolite obtained by hydrothermal conversion of FAU zeolite.

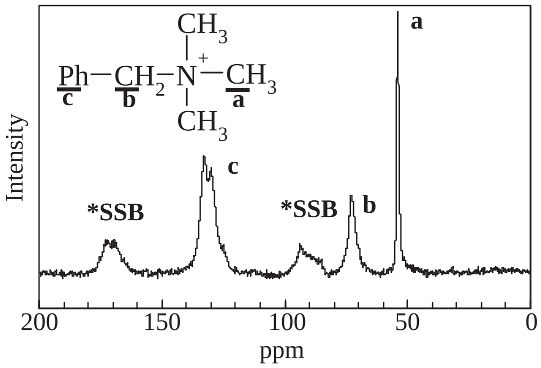

Figure 2. ^{13}C CP/MAS NMR spectrum of CHA zeolite obtained. Asterisks denote spinning sidebands (SSB).

various Si/Al ratios was subjected to the hydrothermal conversion. Only FAU zeolites with Si/Al ratios of 21–23 could be converted into pure CHA zeolites, indicating a very narrow synthesis region. It was also revealed from the previous results that the use of FAU zeolite as a starting material showed an enhanced crystallization rate of the obtained zeolite as compared to starting material from amorphous SiO_2/γ-Al_2O_3 (or $Al(OH)_3$). The enhanced crystallization rate seems to be caused by the assembly of locally ordered aluminosilicate species coming from the decomposition or dissolution of the starting FAU zeolite. For comparison, therefore, the crystallization of high-silica CHA zeolite was tried under the same synthesis conditions using starting gels from amorphous silica powder produced by wet process ($SiO_2 = 88$ wt %, $Al_2O_3 = 0.27$ wt %, Nipsil, Nippon Silica Ind. Japan), γ-Al_2O_3 and $Al(OH)_3$. However, only amorphous materials were obtained, demonstrating the advantage and uniqueness of the hydrothermal conversion of FAU zeolite.

Characteristics of the obtained CHA zeolites were investigated by means of several analytical techniques. The bulk Si/Al ratio of CHA zeolite determined by XRF was 16.9 and slightly smaller than that of the starting FAU zeolite. However, this value is considerably higher as compared to the conventional chabazite, indicating the conversion of FAU zeolite into high-silica CHA zeolite. The surface Si/Al ratio measured by EDX-SEM was 13.1. Moreover, a strong resonance at around 60 ppm was observed in the ^{27}Al MAS NMR spectrum of the calcined CHA zeolite (Figure S1),[15] indicating the presence of tetrahedrally coordinated Al species (framework Al). A trace amount of octahedrally coordinated Al species (nonframework Al) was present as observed at a resonance of 0 ppm. These results strongly suggest that almost all Al species are present in the framework. From N_2 adsorption experiments at $-196\,°C$, the surface area (by the BET method) and micropore volume (by the t-plot method) were ca. $650\,m^2\,g^{-1}$ and ca. $0.34\,cm^3\,g^{-1}$, respectively (Figure S2).[15] These values are consistent with those reported in ref. 6.

The catalytic performance of CHA zeolite (Si/Al ratio of 16.9) obtained was tested through the ethanol (EtOH) conversion reaction using a fixed-bed reactor at atmospheric pressure. The protonated form was prepared by ion exchange with a 1 M NH_4NO_3 solution, followed by calcination at 600 °C for 10 h. Under the reaction conditions of $EtOH/N_2 = 50/50\%$, $W/F = 0.0125\,g\,min\,mL^{-1}$ and temp 400 °C, EtOH was completely converted to hydrocarbons. Nitrogen was used as an internal standard. The product yields on a carbon basis after 0.5 h time on stream were as follows; ethylene 54.7%, propylene 35.1%, and butene 2.8%.

In summary, the high-silica CHA zeolite was effectively prepared from FAU zeolite in the presence of $BTMA^+$ cation. This seems to be due to an existence of locally ordered aluminosilicate species formed by decomposition or dissolution of zeolite. The hydrothermal conversion route was again confirmed to be an alternative strategy for zeolite synthesis.

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