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Synthesis and characterization of large beta zeolite crystals using ammonium fluoride

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Beta zeolite (BEA) is a high-silica microporous material with a large pore, having a three-dimensional system with 12-membered ring channels, and is well known to be one of industrially important zeolites due to its high thermal and chemical stabilities. BEA is usually synthesized in basic medium with tetraethylammonium and alkali metal cations, and the Si/Al ratio is limited in the range of 5–100 [1]. Therefore, a lot of efforts have been carried out in order to exceed this limit. Firstly, van der Waal *et al.*, found that the synthesis of the pure silica BEA was achieved using dibenzyldimethylammonium hydroxide as structure-directing agent and deboronated borosilicate BEA as seeds [2]. Matsukata *et al.*, succeeded in synthesis of BEA with Si/Al ratios, 15:450, by a dry gel conversion technique [3]. Camblor *et al.*, also reported that BEA with a wide range of Si/Al ratio from 10 to infinity was successfully prepared in the presence of tetraethylammonium hydroxide (TEAOH) and fluoride anions at near neutral pH [4–7], and that the obtained pure silica BEA had more hydrophobic and fewer framework defects [8, 9]. Serrano *et al.*, proposed the crystallization mechanism based on solid–solid transformations for the synthesis of pure silica BEA in fluoride medium [10]. However, in the fluoride route, HF was employed as fluoride source in spite of having a difficulty in handling it. Recently, Kim *et al.*, reported the synthesis of BEA (Si/Al = 12.5) using NH_4F as fluoride source in basic media under microwave irradiation [11]. Although they found that addition of NH_4F accelerated the crystallization of BEA, the crystal size of BEA obtained was below 0.5 μm. In general, it is well recognized that the pure silica BEA cannot be synthesized in the presence of sodium cations, which are considered to promote the formation of undesired zeolitic phases. Very recently, Larlus *et al.*, succeeded in the synthesis of pure silica BEA in the presence of a small amount of NaOH ($NaOH/SiO_2 = 0.1$), although the prolonged crystallization time was required [12]. However, the role of NaOH in the synthesis of pure silica BEA was not studied in detail. From such viewpoints, we have now studied the convenient synthesis of large BEA with a wide range of Si/Al ratio and an influence of NaOH addition on their thermal stabilities, and reported the obtained results in this communication.

Precipitated silica (Nipsil, Nippon Silica Ind., Japan, Al_2O_3 = 0.27 wt%, SiO_2 = 88 wt%) or pyrogenic silica (Aerosil, Aerosil Ind. Japan) as silica source was mixed with $Al(OH)_3$ (Wako Pure Chemical, Japan, 98.0%). Pyrogenic silica was used to synthesize the pure silica BEA. Then TEAOH aq. (Aldrich, USA, 40 wt%) and/or NaOH (Merck-Schuchardt, Germany, 99%) were added and mixed well. Finally, NH_4F (Wako Pure Chemical, Japan, 97%) was added and homogenized in a mortar. The gel thus obtained was charged into a 30 cm^3 stainless steel autoclave equipped with a Teflon liner and kept at 140 °C for 6–75 days under static conditions. The solid product was filtered, washed thoroughly with deionized hot water (60 °C), dried overnight in oven at 120 °C and calcined at 500 °C for 10 hr.

Under well-optimized conditions, the highly crystalline BEA was successfully synthesized from the starting gel with the Si/Al ratios from 10 to infinity (Table I). Although BEA could be prepared from the starting gel with Si/Al ratio of over 20 for 6 days of crystallization time, the complete crystallization of zeolite was accomplished after 16 days for the starting gel with the Si/Al

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TABLE I Synthesis results of beta zeolite in the presence of NH_4F

Sample no.	Synthesis starting gel						Time (days)	Phase	Product (by-product)					
	Silica source	Si/Al	TEAOH/ SiO_2	H_2O/ SiO_2	NaOH/ SiO_2	NH_4F/ SiO_2			Average crystal size (μm)	Si/Al XRF	BET surface area (m^2g^{-1}) ICP	Micropore volume (cm3 g^{-1})	F content (wt%)	
1	Aerosil	∞	0.45	5.8	0	0	15	Amorphous (unknown)						
2	Aerosil	∞	0.45	5.8	0	0.40	6	BEA	14		8400	563	0.20	1.6
3	Aerosil	∞	0.30	4.8	0.15	0.40	15	BEA	12			574	0.21	
4	Aerosil	∞	0.30	4.8	0.15	0	15	Layered silicate						
5	Nipsil	250	0.45	5.8	0	0.40	6	BEA	12	267	170			
6	Nipsil	100	0.45	5.8	0	0.40	6	BEA	12	89	79	577	0.22	1.5
7	Nipsil	50	0.45	5.8	0	0.40	6	BEA	11	49		580	0.22	
8	Nipsil	25	0.45	5.8	0	0.40	6	BEA	3.0	29		602	0.23	
9	Nipsil	20	0.45	5.8	0	0.40	6	BEA	1.5	22	21	611	0.24	1.2
10	Nipsil	20	0.35	5.8	0.10	0	6	BEA	0.5	23				
11	Nipsil	10	0.45	5.8	0	0.40	16	BEA	1.0	11	9.8			1.3
12	Nipsil	5	0.45	5.8	0	0.40	75	BEA (amorphous)						

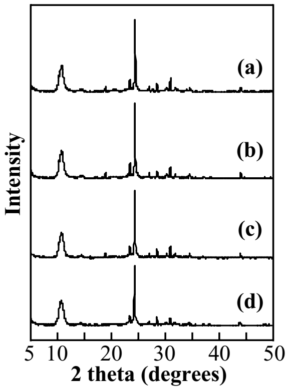

Figure 1 XRD patterns of various BEA. Sample nos.: (a) 2, (b) 3, (c) 7 and (d) 9.

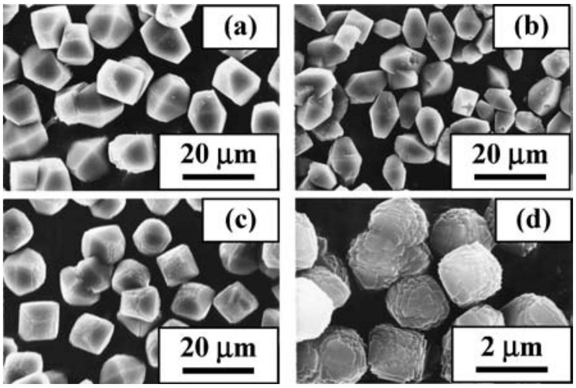

Figure 2 SEM images of various BEA. Sample nos.: (a) 2, (b) 3, (c) 7 and (d) 9.

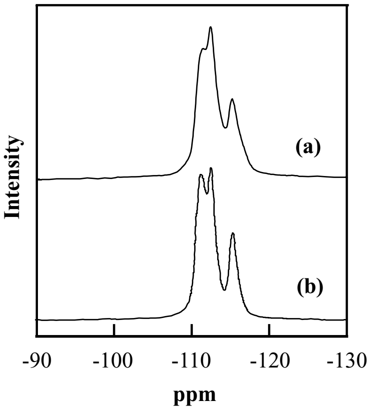

Figure 3 29Si MAS NMR spectra of the pure silica BEA synthesized (a) without (Sample no. 2) and (b) with NaOH (Sample no. 3).

ratio of 10. As compared with the result under stirring (60 rpm) reported by Camblor *et al*., there is almost no difference in the required complete crystallization time. Surprisingly, it was also found that the pure silica BEA could be synthesized in the presence of Na$^+$ cations although the prolonged crystallization time was required (Sample no. 3). When NH_4F was not added into the starting gel, the pure silica BEA could not be obtained (Sample nos. 1 and 4). Therefore, the addition of NH_4F does not only accelerate the crystallization of BEA, but also seems to play the critical role for the crystal growth of BEA.

Fig. 1 shows the XRD patterns of typical zeolites obtained. The XRD patterns exhibited only the typical features of BEA with sharp and broad reflections characteristic of an intergrowth of different polymorphs, indicating the highly crystallinity and no impurities. The typical SEM images are displayed in Fig. 2. No amorphous and impurities phase existed in the all samples. The pure silica BEA showed the well faceted truncated square bipyramid morphology and the crystal size was around 14 μm (Sample no. 2), while the BEA synthesized with NaOH had the elongate morphology (Sample no. 3). The decrease in crystals size was observed when Al content in the sample was increased. However, the crystal size of the BEA with the Si/Al ratio of 49 was still more than 10 μm (Sample no. 7). Although it is well known that the zeolite synthesis in fluoride medium produces larger crystals, which is related to the mineralizing power of F$^-$ as compared to OH$^-$, the crystal size is the largest value among Al-containing BEA reported in literature so far. The characteristics of various BEA are also listed in Table I. The Si/Al ratio of the obtained BEA was measured by XRF and ICP. The fluorine content in the obtained zeolite determined by an ion-selective electrode after the dissolution of as-synthesized samples slightly decreased with a decrease in the Si/Al ratio. Nitrogen adsorption isotherms at −196 °C were measured using a conventional volumetric apparatus, and the surface area and the micropore volume were calculated by the BET method and the *t*-plot method, respectively. The obtained surface area and the micropore volume slightly increased with a decrease in the Si/Al ratio.

In all ^{27}Al MAS NMR spectra of BEA only a sharp signal at ca. 54 ppm was observed (not shown), which is a characteristic resonance of tetrahedrally coordinated framework aluminum species. Also, as can be seen in Fig. 3, only Si(4Si) resonances located at ca. −111.5, −112.5, and −115 ppm were observed in the ^{29}Si MAS NMR spectra of the pure silica BEA synthesized with and with-

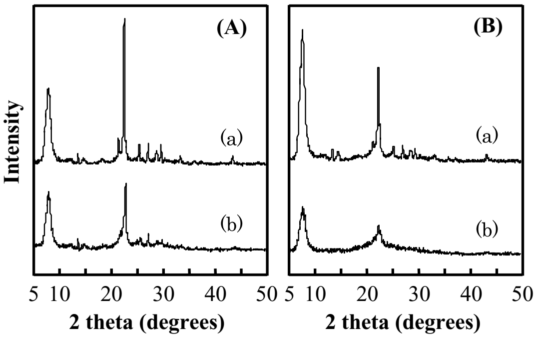

Figure 4 XRD patterns of BEA synthesized (A) without (Sample no. 9) and (B) with NaOH (Sample no. 10) after thermal treatment. Sample nos.: (a) BEA calcined at 500 °C for 10 hr, (b) Sample (a) was calcined at 1000 °C for 1 hr.

out NaOH. No signal assigned to structure defects like $SiOH(OSi)_3$ (approx. -105 ppm) was observed. Therefore, it became clear that the addition of NH_4F in the synthesis of pure silica BEA is also efficient for reducing defect sites in a similar manner as HF addition, regardless of the presence of Na^+ cations [4–6], suggesting the high thermal stability of BEA synthesized with NH_4F. This was confirmed by comparing the structural differences of BEA before and after calcination at 1000 °C for 1 hr using XRD. In the case of the pure silica BEA synthesized with and without NaOH (Sample nos. 2 and 3), there was no difference in the XRD patterns before and after calcination at 1000 °C. On the other hand, as can be seen in Fig. 4, in the case of BEA with the Si/Al ratio of 22, the relative crystallinity of BEA synthesized with NH_4F after calcination at 1000 °C was ca. 68% (Sample no. 9), while BEA synthesized by the conventional method with TEAOH and NaOH was ca. 46% (Sample no. 10).

In summary, the large BEA zeolite crystals with the Si/Al ratios from 9.8 to infinity could be easily prepared by adding NH_4F to the starting gel and showed the high thermal stability. This method was also effective for synthesis of the pure silica BEA.

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