Novel Route to Synthesize Nanosized β-Zeolite with High Surface Area

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Nanosized β-zeolite was synthesized in presence of two templates viz., tetraethylammonium hydroxide and cetyltrimethylammonium bromide by steaming dry-gel precursors.

Because zeolites and their related molecular sieves have uniform channel size, unique molecular shape selectivity, as well as strong acidity and good thermal/hydrothermal stability, they have been used for various catalytic applications.[1–3] In particular, β-zeolite with a three-dimensional large-pore system is one of potential catalysts used in petro-refining and other chemical industries.[4] However, the poor diffusion efficiency through their pores leads easily to insufficient activity and fast deactivation.[5] Such a diffusion limitation in the zeolites can be avoided by the short diffusion paths by reducing the crystal size.[5–8] Several methods have been developed during the last decades for the preparation of nanosized zeolites from colloidal precursors under mild hydrothermal conditions.[5–9] Recently, Naik et al.[10] synthesized nanosized ZSM-5 zeolites via two templates by three step (hydrothermal–flocculation–steaming) procedures. On the other hand, dry gel conversion (DGC) method, in which an aluminosilicate gel dried in advance is crystallized into a zeolitic phase in a water steam environment, has been much interested as the new synthetic method for zeolites and zeotype materials in recent years.[11,12] It is interesting to introduce dual template on DGC method for the synthesis of nanosized microporous materials.

In the present investigation, we have examined the introduction of two templates, tetraethylammonium hydroxide (TEAOH) and cetyltrimethylammonium bromide (CTMABr) for the synthesis of nanosized β-zeolite by DGC method.

The gel composition was used for the synthesis of nanosized β-zeolite: $1.0SiO_2$:0.37TEAOH:0.041CTMABr:0.072NaOH:(0.01–0.02)Al_2O_3:$17H_2O$. A typical synthesis procedure is as follows: 15.57 g (37 mmol) of TEAOH solution (35 wt %) was mixed with 1.12 g (7.2 mmol) of a 25.2 wt % aqueous NaOH solution, followed by the addition of 15.02-g colloidal silica (Ludox HS-40 (40 wt %)) containing 6.01 g (100 mmol) of SiO_2. Then, the mixture was stirred for 30 min. An appropriate amount of $Al_2(SO_4)_3 \cdot 6H_2O$ dissolved in 10.2 mL of warm water was added to the mixture, and the resultant mixture was stirred for further 1 h. 1.49 g (4.1 mmol) of CTMABr dissolved in 80 mL of ethanol was added to the mixture and stirred for further 2 h. The gel was then dried for about 6–7 h over an oil bath at 90 °C with continuous stirring. The dried gel was transferred to a Teflon cup (55 mm × 37 mm i.d.) placed in a Teflon-lined autoclave (100 mL) with the support of a Teflon holder with a small amount of external bulk water (ca. 0.2 g per 1 g (dry gel)) at the bottom of the autoclave.[12]

The crystallization of the dried gel was carried out at 175 °C for 1 day. The addition of CTMABr on the synthesis of β-zeolite helps to produce nanoprecursors and to convert them into nanocrystals via steaming final dry-gel.[10] The surfactant (in particular, CTMABr) was helpful to assemble nanosized crystals by its interaction with silanol group of zeolite precursor in the synthesis of nanosized ZSM-5 by flocculation method.[10] Similar kind of interaction occurred in the present case and, thus, results in the formation of uniform nanosized β-zeolite. However, there may be no interaction between CTMABr and TEAOH.

Figure 1 shows XRD patterns of calcined nanosized β-zeolites with different SiO_2/Al_2O_3 ratios (50, 75, and 100) in the initial gel composition. They have pure β-zeolite phase with high crystallinity. The crystallinities decreased slightly with increasing SiO_2/Al_2O_3 ratio. The intensity of the peaks was also decreased in all samples after the calcination; however, the peak pattern remains after the protonation by using NH_4NO_3 solution (see Figure S1 in Supporting Information).[14] All the samples in H-form were free from impurity phases. The broadening of main peaks indicates that particle sizes are in nanolevel. Further, the low angle XRD of H-form samples (Figure S1 in Supporting Information)[14] showed the absence of any mesostructural periodicity.

SEM image of nanosized β-zeolite ($SiO_2/Al_2O_3 = 100$) in Figure 2 shows that the β-zeolite has uniform particle size of ca. 30–50 nm; however, the β-zeolite synthesized in the absence of CTMABr has the particle size of ca. 100–150 nm.

Table 1 summarizes the textural properties and ICP analysis of β-zeolites. Their BET surface areas were in the range of 412–602 $m^2 \cdot g^{-1}$ and the external surface areas of 124–136 $m^2 \cdot g^{-1}$: cumulative surface areas were in the range of 602–875 $m^2 \cdot g^{-1}$; however, conventional β-zeolite had surface are of 100–200 $m^2 \cdot g^{-1}$. The observed high surface areas of nanosized β-zeolite are mainly due to particle size. The surface area of the β-zeolites increased with the decrease in aluminum content. ICP analysis shows that all β-zeolites have the SiO_2/Al_2O_3 ratios similar to initial gel composition.

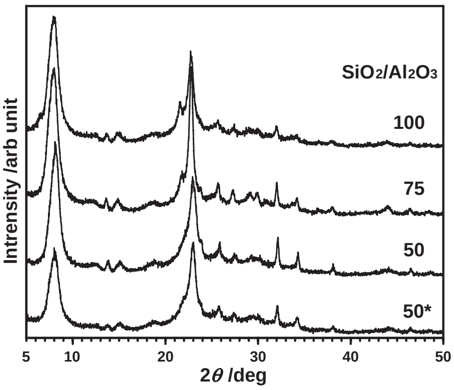

Figure 1. XRD patterns of nanosized β-zeolite. *: synthesized in the absence of CTMABr.

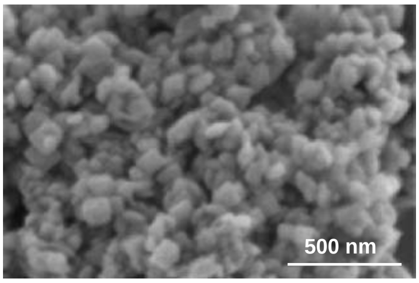

Figure 2. SEM image nanosized β-zeolite ($SiO_2/Al_2O_3 = 100$).

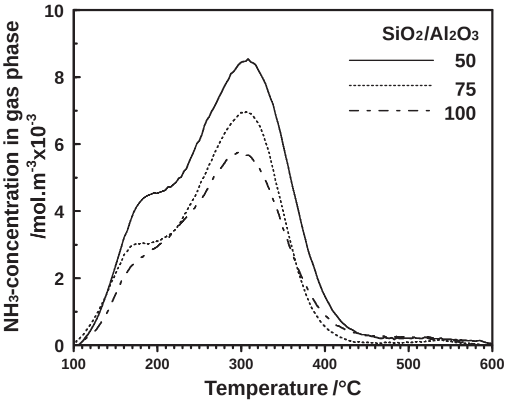

Figure 3. NH_3-TPD of nanosized β-zeolite.

Table 1. Textural properties of nanosized β-zeilote

SiO_2/Al_2O_3 ratio		N_2 adsorpion/$m^2 \cdot g^{-1}$			Acid amount /$mmol \cdot g^{-1}$
Input	Product[a]	BET SA[b]	External SA[c]	Total SA[c]	
50[d]	50	104	ng.[e]	224	0.15
50	54	603	136	875	0.43
75	63	516	124	726	0.12
100	93	412	124	602	0.06

[a]Measured by ICP. [b]BET method. [c]*t*-Plot method. [d]Sample synthesized in the absence of CTMABr. [e]Negligible.

NH_3-TPD profiles of β-zeolites in the H-form with different SiO_2/Al_2O_3 ratios are shown in Figure 3. In all cases, two stages of NH_3 desorption peaks appeared at around 160 and 300 °C similar to conventional β-zeolite. The first peak (*l* peak) is due to the desorption of physisorbed NH_3, and the second peak (*h* peak) is due to NH_3 desorption from Brønsted acid sites. The acid amounts increased with the increase in aluminum content (Table 1). Further, observed difference in acidity of β-zeolites with similar aluminum content synthesized in the presence and absence of CTMAB is mainly due to amount of acid sites exposed on the surface. The presence of surfactant (CTMAB) during β-zeolite synthesis helps much to increase the total and external surface areas and decreased the particle size of 3–5 times. The influence of the surfactant may cause the difference in acidity of nano sized β-zeolite.

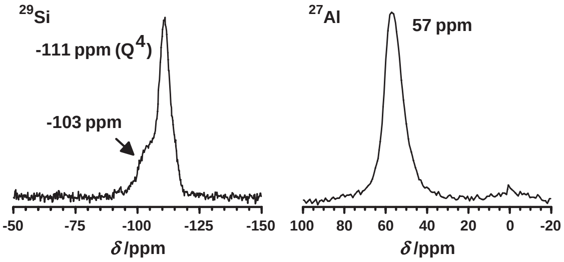

Figure 4. ^{29}Si and ^{27}Al MAS NMR spectra of nanosized β-zeolite ($SiO_2/Al_2O_3 = 50$).

Figure 4 shows ^{29}Si and ^{27}Al MAS NMR spectra of nanosized β-zeolite ($SiO_2/Al_2O_3 = 50$). The ^{29}Si NMR spectrum shows the signals assigned to siliceous sites (Si(0Al)) at -111 ppm and additional broad low-field signals centered at -103 ppm. The latter signals are assigned to a superposition of signals of silanol groups and/or of Si(1Al) sites.[13] The observed broadening of low-field signal is due to the incorporation of tetrahedral Al^{3+} sites in the framework and also to small particle size of the β-zeolite. The ^{27}Al NMR spectrum shows only one symmetrical signal at around -57 ppm, which is characteristic of tetrahedral Al^{3+} species in the framework (Figure 4). However, there is no octahedral Al^{3+} species in the zeolite. These results show that Al^{3+} species were uniformly dispersed in the nanosized β-zeolite.

Nanosized β-zeolite ($SiO_2/Al_2O_3 = 50$) was applied for the isomerization of hexane at 350 °C (see Table S1 and Figure S2 in Supporting Information).[14] The selectivities for isomerized products, viz. methylpentanes (2- and 3-methylpentanes, and 2,2-dimethylbutane), methylbutanes (2- and 3-methylbutanes and 2,2-dimethylpropane), and 2-methylpropane at comparable conversion were 65–70% accompanying the cracking with the selectivities in the range of 35–30%.

In summary, nanosized β-zeolites with various SiO_2/Al_2O_3 ratios having high surface area were synthesized by DGC method in the presence of dual template (TEAOH and CTMABr). The increase of CTMABr in the initial gel composition resulted in further increase in surface area. They were active for the isomerization of hexane with good selectivity for branched isomers.

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14 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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