New Synthesis Route to Uniform-sized β-Zeolite in the Presence of a Cationic Surfactant Containing Siloxane Moiety

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Nanosized β-zeolites (BEA) with different SiO_2/Al_2O_3 ratio were hydrothermally synthesized by using tetraethylammonium hydroxide (TEAOH) as SDA and a small amount of cationic surfactant containing siloxane moiety: [3-(trimethoxysilyl)-propyl]octadecyldimethylammonium chloride (ODSCl). Among them, BEA100 with SiO_2/Al_2O_3 ratio of 100 showed spherical morphology with size of 50–100 nm, and all aluminum species are tetrahedrally incorporated in the framework.

Zeolites are crystalline microporous aluminosilicates and widely been used as a catalyst for petrochemical and petrorefining processings and fine chemical syntheses.[1] The catalytic active surfaces inside the zeolite pores and channels could easily be accessed by reactant molecules if particle sizes are small.[2] Particle morphology is also an important factor to control the diffusion limitations of guest molecules inside micropores. Key factors in catalysis are reasonable reaction rate and good selectivity to desired product. Small-sized zeolite particles with uniformly distributed active sites inside the micropores are concerned to achieve this concept. Tiny crystals have different physicochemical properties compared to the bulk crystals. Recently, nanosized zeolite particles were claimed to improve mass-transfer limitations and selectivity to the desired product. Nanosized zeolite crystals were synthesized by either using a large amount of organic structure-directing agent, a low concentration of alkali metal ion, high aluminum content, cetyltrimethylammonium bromide (CTMABr) added dry-gel conversion, or at a low synthesis temperature.[3–5] It was reported that zeolite crystal size and intercrystalline pores could be tailored by systematic introduction of the siloxane containing amphiphilic surfactant, such as [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride (ODSCl) into the gel composition.[6] Among the zeolites, the synthetic methods of small-sized β-zeolite have been proposed by many researchers, because it is a potential solid acid catalyst for many chemical reactions.[7–9] Mesoporous β-zeolite could also be synthesized using cationic surfactant and small molecular template.[5,10] In this paper, we describe a new synthesis route to obtain discrete and uniformly sized crystals of β-zeolite, of which all aluminum species are tetrahedrally incorporated into the framework.

The typical gel composition for the synthesis of BEA33[11] was: $0.98SiO_2$:0.02ODSCl:0.36tetraethylammonium hydroxide (TEAOH):$0.039Na_2O$:$0.03Al_2O_3$:$15H_2O$ in molar ratio. After mixing all the reagents, the gel was aged for 6 h at 80 °C, then transferred into a Teflon-lined autoclave (100 mL) and subjected to hydrothermal treatment at 175 °C for 3 d.

The addition of ODSCl onto the synthesis gel of β-zeolite probably induces the formation of amorphous aluminosilicate domains containing organic-rich and inorganic-rich nanoclusters held together by means of strong chemical bonding between organosiloxane moiety and silica and van der Waals force between organic surfactant molecules. These amorphous aluminosilicate domains are converted into tiny crystals upon further hydrothermal treatment. Initially, the addition of ODSCl to the synthesis gel would establish equilibrium between cationic organic species and anionic inorganic silicate species and hence forms nano domains. The effective incorporation of amphiphilic surfactant through strong bonding with silicates via siloxane bridge not only controls the growth of particle size but also permits maximum number of Al to be inserted into the framework as evident from ICP analysis.

Figure 1 shows XRD patterns of as-synthesized nanosized β-zeolite samples showing pure β-zeolite phase with high crystallinity. The intensity of the peaks decreased in all samples after the calcination; however, the peak pattern remained the same in H^+-form of β-zeolite (Figure S1).[13] BEA100 has been synthesized at 150 °C as different phases as impurity were observed when it was synthesized at 175 °C.

As shown in Figure 2, the SEM images of BEA15, BEA20, and BEA33 showed tiny crystals clustered together as spongy morphologies. As the SiO_2/Al_2O_3 ratio increased, the crystal morphology became distinct in nature, and regular spherical morphology was obtained for BEA100. The surface of BEA100 shows surface roughness and porosity due to the removal of coated organosiloxane during calcination. Particle sizes are in the range of 50–150 nm in all the samples. BEA100N showed clear square-bipyramidal morphology that was commonly reported for β-zeolite (Figure S2).[13]

Table 1 summarizes the textural properties and ICP analysis of nanosized β-zeolite samples. The BET surface areas were in the range of 336–411 $m^2\cdot g^{-1}$ and the external surface area of 46–86 $m^2\cdot g^{-1}$. The ICP analysis of BEA20, BEA33, and BEA100 showed that the SiO_2/Al_2O_3 ratio was similar to initial

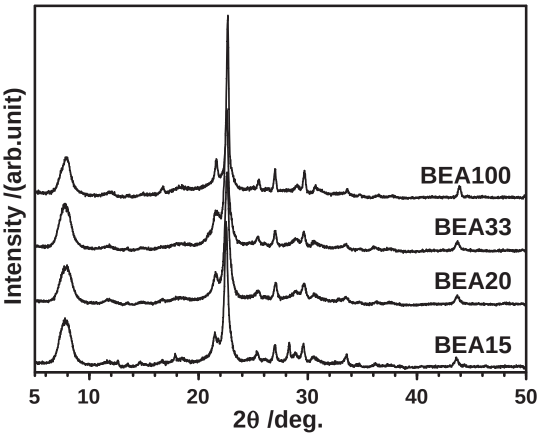

Figure 1. XRD patterns of β-zeolites (as-synthesized) synthesized in the presence of ODSCl.

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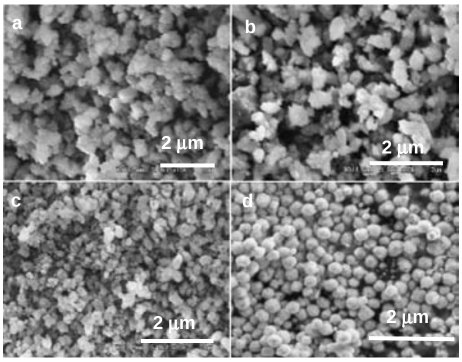

Figure 2. SEM images of β-zeolites: a: BEA15, b: BEA20, c: BEA33, and d: BEA100.

Table 1. Properties of nanosized β-zeolites synthesized in the presnec of ODSCl

Sample[a]	SiO_2/Al_2O_3 ratio[b]	Surface area/$m^2 \cdot g^{-1}$ BET[c]	External[d]	Total[d]	Pv[e] /$cc \cdot g^{-1}$	Acidity /$mmol \cdot g^{-1}$
BEA15	8.0	362	68	646	0.18	0.91
BEA20	21.5	336	86	552	0.11	0.78
BEA33	37.5	411	85	586	0.15	0.69
BEA100	98.0	402	46	608	0.18	0.59
BEA100N[f]	43.7	482	60	682	0.16	0.42

[a]The integer indicates the input SiO_2/Al_2O_3 ratio. [b]Measured by ICP. [c]BET method. [d]t-plot method. [e]Pore volume. [f]Synthesized in the absence of ODSCl.

gel composition. However, BEA15 showed less SiO_2/Al_2O_3 ratio that could be due to higher dissolution of silica under this reaction conditions. BEA100N also showed less SiO_2/Al_2O_3 ratio ($\approx$43.7) and low yield. Hence, the present method showed advantage over conventional hydrothermal method to get good yield of β-zeolite, where the entire Al atoms are tetrahedrally incorporated into zeolite framework.

^{29}Si MAS NMR spectrum of nanosized BEA100 showed the signal at -111 ppm that can be assigned to siliceous sites (Q^4; Si(0Al)), and additional broad low-field signals centered at -103.6 ppm can be assigned to possible interference of (Si(1OH) and Si(1Al) signals (Figure 3).[12] ^{27}Al MAS NMR spectrum of calcined BEA100 showed only one symmetrical signal at around 56 ppm, which is characteristic of tetrahedral Al^{3+} species in the framework, whereas BEA100N showed both octahedral (0 ppm) and tetrahedral Al^{3+} (57 ppm) in the samples. These results show that tetrahedral Al^{3+} species were uniformly incorporated into the framework of BEA100. However, high aluminum containing samples BEA15, BEA20, and BEA33 showed small octahedral Al^{3+} peak in addition to tetrahedral ones.

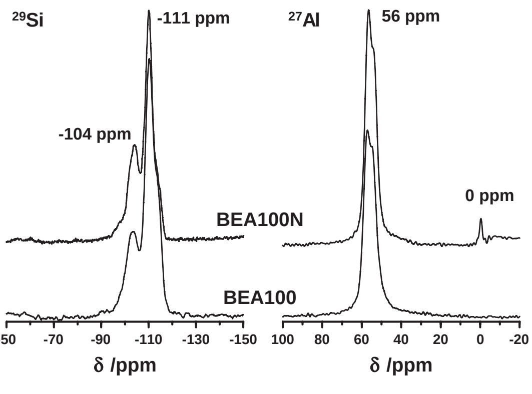

Figure 3. ^{29}Si and ^{27}Al MAS NMR spectra of BEA100 and BEA100N.

NH_3-TPD profiles of the H^+-form of β-zeolite with different SiO_2/Al_2O_3 ratio showed two stages of NH_3 desorption peaks appeared at around 200 and 310 °C. The first peak (l-peak) is due to desorption of physisorbed NH_3, and the second peak (h-peak) is due to NH_3 desorption from strong Brønsted acid sites (Figure S3).[13] BEA15 and BEA20 showed higher intense peak at 200 °C due to the presence of more Al in the samples. BEA100N showed less intense peak profile compared to BEA100.

All the synthesized β-zeolite samples were studied on vapor-phase isopropylation of m-cresol with 2-propanol at 210 °C (Table S1).[13] Comparable conversion (45–70%) with the selectivity for thymol, the desired product was 70–80%. The activity remained the same for all the samples for 6 h reaction time.

In summary, nanosized β-zeolites with SiO_2/Al_2O_3 (= 15–100) having higher surface area were synthesized in the presence of cationic surfactant containing siloxane moiety and found that BEA100 has quite uniformly sized spherical morphology and is active for the isopropylation of m-cresol with good selectivity for thymol. The detailed studies are underway and will be discussed in near future.

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11 Abbreviation of the zeolite sample shows by BEA33, where 33 is input SiO_2/Al_2O_3 ratio.
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13 Supporting Information is available electronically on CSJ-Journal web site: http://www.csj.jp/journals/chem-lett/.

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