Synthesis of Nanosized A-type Zeolites from Sodium Silicates and Sodium Aluminates in the Presence of a Crystallization Inhibitor

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Nanosized A-type zeolites (primary particle size: 30–40 nm), which exhibit higher cationic exchange rate than commercially available A-type zeolites (primary particle size: 2 μm), have been synthesized from sodium silicates and sodium aluminates by using a crystallization inhibitor such as a nonionic surfactant and polyethylene glycol.

Nanosized zeolites with the primary particle size of less than 100 nm have attracted considerable attention because of their improved properties based on the large external surface area-to-volume ratios and reduced mass transfer resistance, compared with ordinary micron-sized zeolites. Several nanosized zeolites including silicalite-1,[1] ZSM-5,[2] Y,[3] L,[4] and Beta[5]-type zeolites have been synthesized. Also for A-type zeolites whose production is the most among various types of zeolites, many attempts have been made to reduce the primary particle size. For example, addition of organic cations to synthesis solutions results in a marked reduction in the primary particle size compared to similar syntheses in the absence of such cations. However, by this method nanosized A-type zeolites can be obtained from neither sodium silicates nor sodium aluminates which are low cost and common starting materials.[6] In synthesis methods using the sodium silicates and the sodium aluminates, the primary particle size of A-type zeolites decreases with increasing the alkaline concentration in the synthesis solution.[7] However, the primary particle size of A-type zeolites is at least 150 nm, because the higher alkaline concentration leads to quick transformation of A-type zeolites (metastable phase) into hydroxysodalites (stable phase).[7] Recently, nanosized A-type zeolites have been synthesized from the sodium silicates or the sodium aluminates in the presence of mesoporous carbon blacks as inert matrices.[8] However, the synthesis concentration is very low (the molar Al_2O_3/H_2O ratio of 0.0062) to avoid uncontrolled growth in the pore system. Although it is desirable that nanosized A-type zeolites can be synthesized from the sodium silicates and the sodium aluminates in a high concentration range for the industrial application, to the best of our knowledge, no report has been published on the high concentration synthesis of nanosized A-type zeolites. We expected that not only the control of the alkaline concentration in the synthesis solution but also the use of a crystallization inhibitor which interacts with reactive sites of zeolite precursors and zeolites to inhibit crystal growth and the phase transition should be a key to success in the high concentration synthesis. Here we described successful synthesis of nanosized A-type zeolites in a high concentration range (the molar Al_2O_3/H_2O ratio of 0.042) from the sodium silicates and the sodium aluminates by using a nonionic surfactant and polyethylene glycol as the crystallization inhibitors.

A nonionic surfactant (polyoxyethylene lauryl ether, Emulgen-108, Kao Corp., abbreviated as C12E6) and polyethylene glycol (PEG 600, Wako Pure Chemical Industries, abbreviated as PEG) were used as the crystallization inhibitors. The composition of a synthesis gel (molar basis) was 1.9 Na_2O:2.0 SiO_2:1 Al_2O_3:24 H_2O. In a typical recipe, 200 g of C12E6 was added to 400 g of an aqueous sodium aluminate solution (Na_2O: 21%, Al_2O_3: 28%) which was obtained by dissolving $Al(OH)_3$ and NaOH in water with heating. 445 g of sodium silicate solution (Na_2O: 10%, SiO_2: 30%, Osaka Keiso) was added dropwise to the resulting solution at 50 °C over 5 minutes while stirring. Then, the mixture was further stirred for 10 minutes, and heated to 80 °C over 30 minutes while stirring. Thereafter, the mixture was further aged at 80 °C for 60 minutes. The resulting aqueous slurry of zeolite particles was filtered, and washed with deionized water until pH of the filtrate became less than 12. The filter cake was dried at 100 °C for 13 h, and crushed for 1 minute with a cooking cutter, resulting in a white powder (abbreviated as NZ).[9]

Figure 1 shows X-ray diffraction (XRD) patterns of micron-sized A-type zeolite (primary size: 1.8 μm, chemical analysis: 1.1 Na_2O:2.0 SiO_2:1 Al_2O_3:4.0 H_2O) commercially available from Tosoh and NZ. The XRD patterns confirmed that NZ had A-type crystalline structure. Note that the diffraction lines of NZ were broadened, suggesting that NZ should have smaller crystalline size than the micron-sized zeolite. The crystalline size of NZ was estimated to be 40 ± 10 nm by the XRD peak ($2\theta = 30$ deg) broadening using Scherrers equation. Figure 2 shows SEM and TEM images of NZ. It was shown that NZ consisted of nanosized spherical primary particles which were aggregated. It was revealed that NZ had the narrow primary particle size distribution (variation coefficient: 16%) with the mean diameter of 32 nm which was consistent with the estimated value by the XRD peak broadening. The spherical shape and the nano-size of the primary particles of NZ were nearly the same with those of the zeolite precursors (amorphous aluminosilicates),[10] indicating that the growth of the zeolite crystallites should be almost perfectly inhibited.

The nitrogen gas adsorption measurement (Shimadzu Micrometrix Flowsorb 2300) revealed that NZ had larger external surface area (BET surface area: 28 m^2/g) than the micron-sized zeolite (BET surface area: 4 m^2/g). This should be explained in terms of the smaller primary particle size of NZ.[11] In ^{27}Al NMR spectra[12] only one signal was observed at 60 ppm assignable to the tetrahedral Al atoms for both the micron-sized zeolite and NZ. In ^{29}Si NMR spectrum[12] of NZ, two peaks were detected with chemical shifts of −90 ppm and −85 ppm (area ratio 89:11) assigned to Q4(4Al) and Q3(3Al), respectively,[13] in contrast to only one peak at −90 ppm for the micron-sized zeolite. These NMR results indicate that NZ should have more silanolate (Si-O$^-$) groups than the micron-sized zeolite, which coincides with the system of nanosized silicalite-1.[14]

It was evidenced that the cationic exchange capacity (CEC) of NZ was the same as that of the micron-sized zeolite (210 mgCaCO$_3$/g).[15] This result indicates that the amounts of impurities, such as amorphous aluminosilicates and hydroxysodalites (Figure 1, $2\theta = 14$ deg) contained in NZ, should be negligible, since their CECs were very low (amorphous aluminosilicates: 80 mgCaCO$_3$/g, hydroxysodalites: 30 mgCaCO$_3$/g). Furthermore, NZ exhibited higher cationic exchange rate (CER, 200 mgCaCO$_3$/gmin) than the micron-sized zeolite (140 mgCaCO$_3$/gmin).[15] Note that the ratio of CER to CEC of NZ (95%) was nearly 100%. This should be due to the smaller primary particle size (nano-size) of NZ, taking account of dependence of the ratio of CER to CEC on the primary particle size of zeolites.[16]

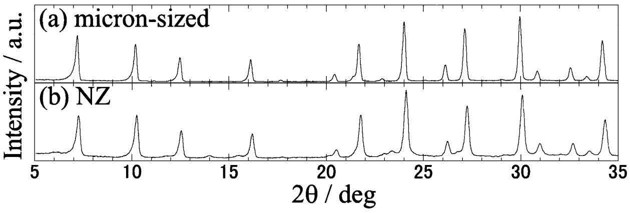

Figure 1. XRD patterns (Rigaku RINT 2500 VPC, light source: CuKα) of (a) micron-sized A-type zeolite commercially available from Tosoh and (b) NZ.

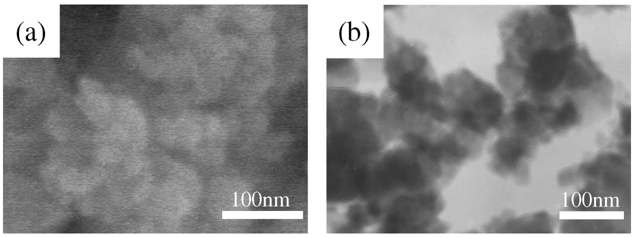

Figure 2. (a) FE-SEM (Hitachi S-4000) and (b) TEM (JEOL JEM2000FX, operating voltage: 120 kV) images of NZ.

Table 1. Results for the nanosized A-type zeolites

Run	Inhibitor	Conc /%[a]	Time /min[b]	Composition[c] x	y	z	Primary particle size d$_s$/nm[d]	V/%[e]	d$_x$/nm[f]
1	C12E6	19	60	1.1	2.0	3.7	32	16	40 ± 10
2	PEG	14	60	1.1	2.0	3.7	33	23	40 ± 10
3	C12	31	5	1.0	2.0	3.8	270	25	

[a]Concentration of the crystallization inhibitor in the synthesis solution. [b]Aging time at 80°C. [c]Zeolite composition; xNa$_2$O:ySiO$_2$:Al$_2$O$_3$:zH$_2$O. [d]Mean diameter of the primary particles determined by SEM. [e]Variation coefficient of the primary particle size determined by SEM. [f]Mean diameter of the primary particles determined by XRD.

The existence of more silanolates means that the reaction of the silanolates of the zeolite precursors and the zeolites was suppressed in the crystallization process of NZ. The controlled reaction should arise from the interaction between the silanolates and the co-existing C12E6 molecules. In order to clarify the interaction, we attempted to synthesize nanosized A-type zeolites in the presence of various crystallization inhibitors (Table 1). As well as C12E6 (Run 1), PEG afforded nanosized A-type zeolite with the primary particle size of 33 nm (Run 2), while submicron-sized (270 nm) A-type zeolite was obtained by using dodecane (Run 3, C12). These results indicate that ethylene oxide segments of C12E6 and PEG, but not alkyl chains of C12E6, should play a decisive role in the interaction to inhibit the growth and the phase transition of the zeolite crystallites.[17]

In conclusion, nanosized A-type zeolites (primary particle size: 30–40 nm), which exhibit higher cationic exchange rate than commercially available A-type zeolites (primary particle size: 2 μm), were successfully synthesized in the high concentration range (Al$_2$O$_3$/H$_2$O = 0.042) from the sodium silicates and the sodium aluminates by using the crystallization inhibitor such as the nonionic surfactant and polyethylene glycol. The present simple method might be applicable to various functional zeolite syntheses with different crystal structures. Further investigations are currently underway to clarify the formation mechanism of the nanosized A-type zeolites and their properties.

References and Notes

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9 Chemical analysis (X-ray fluorescence analysis) yields: 1.1 Na$_2$O:2.0 SiO$_2$:1 Al$_2$O$_3$:3.7 H$_2$O. Inductively coupled plasma (ICP) analysis exhibited that a solution filtrated from the aqueous slurry of zeolite particles contained 0.0042% Si and 0.022% Al, indicating almost 100% reactivity of the starting materials, the silicates and the aluminates, in the present synthesis solution. In FT-IR spectrum of NZ no peak was observed in the range of 1400–1500 cm^{-1} and 2800–3000 cm^{-1} which are assignable to alkyl chains of C12E6, which indicates that almost of C12E6 could be removed from NZ by the processes of filtration and wash with deionized water.
10 The primary particle size of the amorphous aluminosilicates was 30 nm (variation coefficient: 20%) by the FE-SEM observation.
11 Based on the density of 12.9 (Si, Al)/nm^3 of A-type zeolite,[18] a spherical particle (1.1 Na$_2$O:2.0 SiO$_2$:1 Al$_2$O$_3$:3.7 H$_2$O) with the size of 30 nm and a cubic (1.1 Na$_2$O:2.0 SiO$_2$:1 Al$_2$O$_3$:4.0 H$_2$O) with the size of 1.8 μm can be calculated to have external surface area of 7 m^2/g and 0.1 m^2/g, respectively. The larger experimental values than the calculated ones may be due to the rough surface and shape (not perfect) of the zeolite particles.
12 ^{29}Si and ^{27}Al magic-angle spinning solid-state NMR spectra were recorded using a Varian INOVA UNITY 300 spectrometer (spinning rate: 5 kHz). Tetramethylsilane and 1 M AlCl$_3$ aqueous solution were used as the external standard for ^{29}Si and ^{27}Al NMR, respectively.
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17 The co-existence of C12E6 or PEG in the present synthesis systems should lead to a local increase in the alkaline concentration, which may also contribute to the reduction in the primary size of A-type zeolites.[19]
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