Effect of Steam on the Steam-Assisted Crystallization of *BEA-Type Zeolite

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We have studied the effect of steam in the steam-assisted crystallization (SAC) of *BEA-type zeolite. It was found that after an aluminosilicate dry gel with $SiO_2/Al_2O_3 = 100$ was treated with steam in an autoclave at 130 °C and autogenous pressure, the thermal treatment of a resulting product at 130 °C in an autoclave without the addition of water gave *BEA nanoparticles with a high crystallinity. It was presumed that pseudo-*BEA structures as intermediates were formed during the SAC treatment, and the dehydration of silanols in the pseudo-*BEA solids during the thermal treatment in the presence of a minimum amount of water possibly promoted the transformation of the pseudo-*BEA phase into *BEA crystalline phase with a periodicity in long-range order.

Aluminosilicate zeolite β (framework type code as *BEA) possessing a 3-dimensional 12-membered ring micropore system has been found to be a promising catalyst for the cracking of paraffin,[1] isomerization of hexane[2] or heptane,[3] and the disproportionation and transalkylation of toluene and C9 aromatics,[4] and recently commercialized as an acid catalyst for ethylbenzene[5] and cumene[6] production via the alkylation of benzene with ethylene and propene, respectively, due to its large micropore size and mild acidity. The development of *BEA nanoparticle synthesis is an attractive issue for the enhancement of its catalytic properties, avoiding the diffusion limitation of large reactant/product molecules. Since Camblor et al.[7] first reported the synthesis of *BEA nanocrystals, several hydrothermally synthetic approaches of *BEA nanocrystals with particle sizes smaller than 100 nm have been investigated.[7–13] Moreover, *BEA nanocrystals obtained using confined space synthesis, in which zeolite nanocrystals were formed in the pores of active carbon as a matrix, showed high catalytic activity in the acetylation of anisole with acetic anhydride in comparison with micron-sized *BEA crystals.[13]

Although zeolite crystals are generally synthesized in the presence of excess water in the synthetic media, Bibby and Dale[14] first reported the synthesis of SOD zeolite in an ethylene glycol media, indicating that the presence of water in direct contact with the aluminosilicates in the synthetic media is not essential to crystallize a zeolitic phase. We have developed an alternative technique of zeolite crystallization called dry gel conversion (DGC), where a silicate or aluminosilicate hydrogel is dried and the resulting dry gel is converted to zeolite crystals in vapor. The DGC method is classified as two separate methods, (1) a vapor-phase transport method in which a dry gel is crystallized in the vapor of water and structure-directing agent (SDA) like ethylenediamine, and (2) a steam-assisted crystallization (SAC) method in which a dry gel containing non-volatile SDA molecules like tetraethylammonium (TEA^+) salts is crystallized in steam. Kim et al.[15] and our previous studies[16,17] confirmed that VPT method can be applied to synthesis of various zeolites such as ANA, FER, MFI, MOR, and MWW. While *BEA zeolites are generally crystallized under hydrothermal conditions using TEA^+ cations as an SDA, we have found that *BEA zeolite can be obtained by SAC,[18] in which an aluminosilicate dry gel containing TEA^+ cations is crystallized in steam at 100–170 °C under autogenous pressure. In comparison with the conventional hydrothermal synthetic method, SAC enables rapid production of highly crystalline *BEA zeolite from dry gels with a wide range of SiO_2/Al_2O_3 ratios from 7 to infinity.[18–20] We have investigated the crystallization mechanism of *BEA zeolite under SAC conditions on the basis of the results of XRD, high-energy XRD, ^{29}Si NMR, Raman spectroscopy, and electron microscopy.[19–23] It was found that the crystallization of *BEA zeolite by SAC occurs from a dry gel via nanoparticle intermediates.[20] We have recently proposed that the SAC of a *BEA phase requires the existence of double 3-membered rings (3-MR) or "4–2"-type secondary building units (SBUs) in the dry gel containing TEA^+,[21,22] and proceeds through the formation of a pseudo-*BEA structure comprised of the linear connection of "4–2"-type SBUs, giving a crankshaft structure.[23] Recently, Chen and Huang have reported unique ^{17}O NMR studies of the involvement of steam in the SAC of $AlPO_4$-11 (AEL).[24] Their ^{17}O NMR observations suggest that some building units such as 4- and 6-MR are common in both layered intermediate and $AlPO_4$-11, resulting from the selective incorporation of ^{17}O atoms supplied from ^{17}O-enriched water vapor into the P(2)

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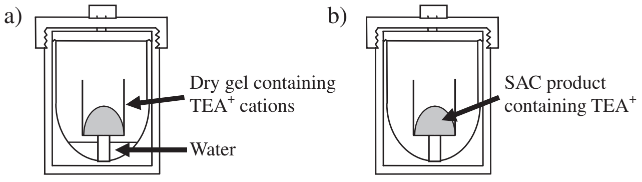

Figure 1. Diagram of autoclaves for the crystallization of zeolites by (a) steam-assisted crystallization and (b) steam-assisted crystallization under the steam-lean conditions.

and P(3) sites in the AEL framework. These studies strongly imply that the presence of water vapor during the SAC is essential to the partial hydrolysis/dehydration of the silicate network causing the transformation from an intermediate to a zeolitic structure. In contrast, a kind of layered aluminosilicate precursor, PLS-1, can be transformed into a zeolitic structure, CDS-1, via the dehydration of corresponding silanols during thermal treatment in the absence of water.[25] In this study, we have found that highly crystallized *BEA nanoparticles with a diameter of ca. 30 nm were obtained by partial crystallization under the SAC conditions followed by thermal treatment in an autoclave without the addition of water, and studied the effect of water vapor in the steam-assisted crystallization of *BEA zeolite. In this report, thermal treatment in an autoclave without the addition of water is referred to as steam-assisted crystallization under steam-lean conditions.

Experimental

Synthetic Procedure for Zeolite *β*. Synthesis of *BEA zeolite was performed following a steam-assisted crystallization method reported elsewhere.[18–23] A parent gel was prepared by mixing colloidal silica (Snowtex-S, SiO_2, 30 wt %; Na_2O, 0.6 wt %, Nissan Chem.), NaOH (>99.0%, Kanto Chem.), anhydrous $Al_2(SO_4)_3$ (>99%, Kanto Chem.) and TEAOH (20% in water, Aldrich). The mixture was heated to 80 °C after stirring at 20 °C for 2 h and then dried while stirring. Dry gel powder was obtained by crushing the dried solid in an alumina mortar. Composition of the dry gel was $SiO_2:Al_2O_3:Na_2O:TEAOH = 1.0:0.010:0.030:0.37$. Dry gel weighing 1.5 g was placed in a Teflon cup, and the cup was set in a 50 cm^3 Teflon®-lined stainless autoclave in which 0.50 cm^3 of distilled water was poured at the bottom as a source of steam, as shown in Figure 1a. The SAC was carried out under autogenous pressure at 130 °C for 1–24 h. After the crystallization, a solid product was recovered without filtration and rinsing, and dried in a vacuum desiccator at room temperature. The dried product obtained by the steam-assisted crystallization is referred to as SAC product. The dried SAC product was treated at 130 °C for 12 h in the autoclave without the addition of water, as shown in Figure 1b. The products obtained after the SAC under the steam-lean conditions was also kept in a vacuum desiccator at room temperature. Additionally, the SAC product was treated at 130 °C for 10 h in a beaker without a cap.

Characterizations. The solid products were characterized by using an X-ray diffractometer (XRD, Miniflex, Rigaku) at 30 kV and 15 mA. The morphologies of the products were observed using field emission scanning electron microscopy (FE-SEM, S-4500S, Hitachi) at 15 kV of ACC voltage. The content of water in the products was determined in flowing air using thermal gravimetry (TG, DTG-50H, Shimadzu) with a heating rate of 10 °C min^{-1}. The ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) measurements of the products were carried out by using an EX270 (JEOL) at a magnification field of 6.3 T. ^{29}Si MAS NMR spectra for the products were recorded at 53.6 MHz with a pulse width of 3.0 s, a pulse interval of 60 s and a spinning rate of about 5 kHz.

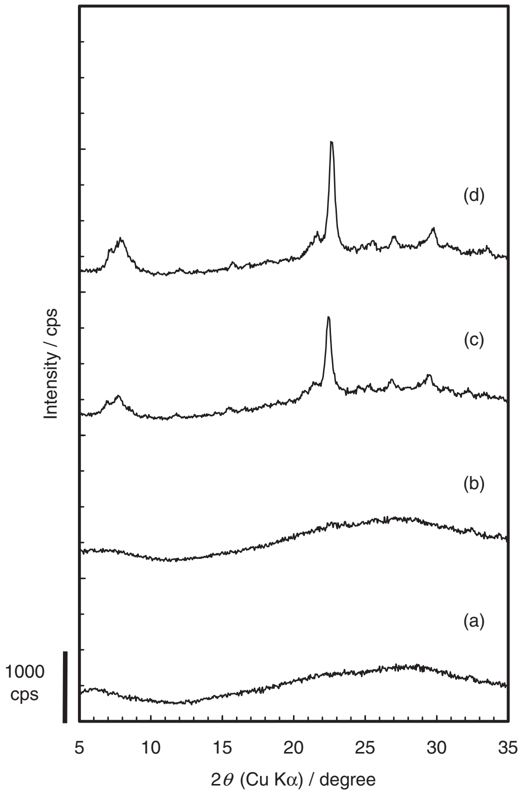

Figure 2. XRD patterns for (a) the dry gel and (b–d) the as-made products obtained after SAC treatment at 130 °C for (b) 3, (c) 4, and (d) 24 h.

Results and Discussion

Figure 2 shows the XRD patterns of the dry gel and the products obtained after SAC at 130 °C, and Figure 3 shows the XRD patterns of the products obtained after SAC at 130 °C for various periods and the following steam-lean crystallization at 130 °C for 12 h. While the product obtained for 3 h of SAC was still amorphous (Figure 2b), 4 h of crystallization gave a *BEA phase (Figure 2c). Crystallization prolonged up to 24 h however to give highly crystallized *BEA product with difficulty (Figure 2d). On the other hand, Figure 3b indicates that the steam-lean crystallization of an amorphous product obtained by SAC for 1 h caused the appearance of a *BEA phase even without the addition of water in the autoclave. It is noteworthy that highly crystallized *BEA was formed from the amorphous product obtained after 3 h of SAC through the following SAC under the steam-lean conditions (Figure 3c), and its relative crystallinity (100%) was much higher in comparison with the SAC product for 24 h (65%, Figure 2d). Moreover, poorly crystallized *BEA obtained by SAC for 4 and 24 h also transformed into highly crystalline *BEA zeolite during SAC under steam-lean conditions (Figures 3d and 3e). On the other hand, Figure 3a shows that the steam-lean crystallization of the

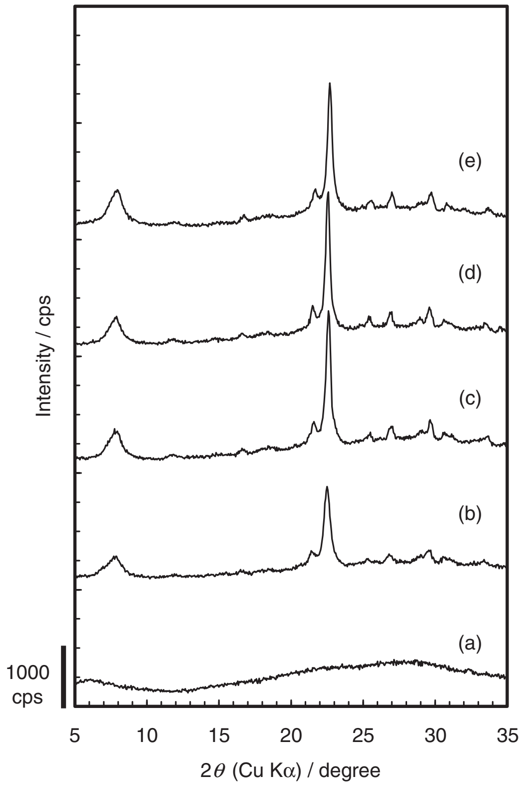

Figure 3. XRD patterns for the products obtained by the SAC at 130 °C for various periods and following SAC under the steam-lean conditions at 130 °C for 12 h. (a) The product was obtained by only the steam-lean crystallization of the dry gel at 130 °C for 12 h. The periods of SAC treatment were (b) 1, (c) 3, (d) 4, and (e) 24 h.

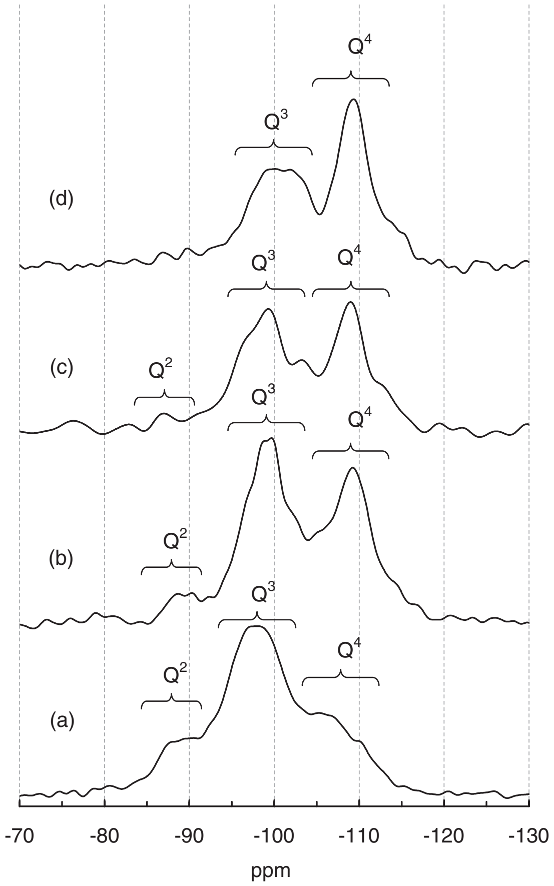

Figure 4. ^{29}Si MAS NMR spectra for (a) the dry gel and (b–d) as-made products obtained by the SAC treatment for (b) 3, and (c) 24 h, and (d) the SAC treatment for 3 h and the following steam-lean crystallization for 12 h.

dry gel hardly gave any crystal phases. We have investigated the crystallization scheme of *BEA crystals from a dry gel in SAC,[19–23] and suggested the existence of a pseudo-*BEA structure, which would contain crankshaft structures consisting of the linear connection of "4–2"-type SBUs, in the amorphous silicate solid exposed to SAC conditions. Combined with our previous study, the XRD results in this study imply that the unordered aluminosilicate network in the dry gel is transformed into the pseudo-*BEA structure with the aid of water molecules supplied from a vapor phase. That is, steam is essential to rearrange an amorphous aluminosilicate network to the intermediate through a series of hydrolysis/dehydration of aluminosilicates.

Figure 4 shows the ^{29}Si MAS NMR spectra of the dry gel, the SAC products and the products obtained by the SAC and the following steam-lean crystallization and Table 1 lists the relative crystallinities and the fractions of Q^n species ($n = 2$, 3, and 4) of their solid products. The NMR spectrum of the dry gel in Figure 4a gave three broad peaks at around −88, −98, and −108 ppm, corresponding to Q^2, Q^3, and Q^4 species, of which the fractions were 16, 52, and 32%, respectively. In our previous study,[23] the appearance of Q^2 peak in the ^{29}Si NMR spectra of the dry gel indicated the existence of "4–2"-type SBUs in the dry gel. When SAC of the dry gel was performed, although Q^2 peak decreased and Q^3 and Q^4 peaks increased with the formation of a *BEA crystalline phase after 4 h of crystallization (Figure 4b), the prolonged 24 h SAC however hardly changed the fraction of Q^n species (Figure 4c) and improved crystallinity. On the other hand, SAC for 3 h and the following steam-lean crystallization for 12 h caused the dehydration of silanols in the solid, as evidenced by an increase of Q^3 and Q^4 peaks at the expense of Q^2 peak (Figure 4d). The drastic improvement of the crystallinity of a *BEA phase occurred during the steam-lean crystallization of the SAC product. We therefore infer that the formation of highly crystallized *BEA zeolite in the SAC requires the dehydration of silanols in the SAC product.

We herein investigated the time-course behavior of *BEA crystallization from the amorphous SAC product during SAC under steam-lean conditions. Figure 5 shows typical XRD patterns of the product obtained by SAC for 3 h and the following steam-lean crystallization for various periods. While the product after 4 h of SAC under the steam-lean conditions was still amorphous (Figure 5b), 6 h of SAC under steam-lean crystallization gave a *BEA phase (Figure 5c), and 12 h steam-lean crystallization yielded highly crystallized *BEA zeolite (Figure 5d). Figures 6a and 6b exhibit the time courses of relative crystallinity and the content of water in the solids obtained by only SAC treatment, and the steam-lean crystallization of the amorphous product after 3 h of SAC. The relative crystallinity of the product obtained by SAC for 3 h and

Table 1. Relative Crystallinity of a *BEA Phase and Fraction of Q^n for the Products Crystallized by the SAC and the Following Steam-Lean Crystallization

Period/h		Crystallinity of β/% (XRD)	Fraction of Q^n/% (^{29}Si MAS NMR)		
SAC treatment	SAC under steam-lean conditions		Q^2	Q^3	Q^4
—	—	0	16.2	52.2	31.6
4	—	48	6.7	50.4	43.0
24	—	65	6.4	52.4	41.2
3	12	100	0.0	49.0	51.0

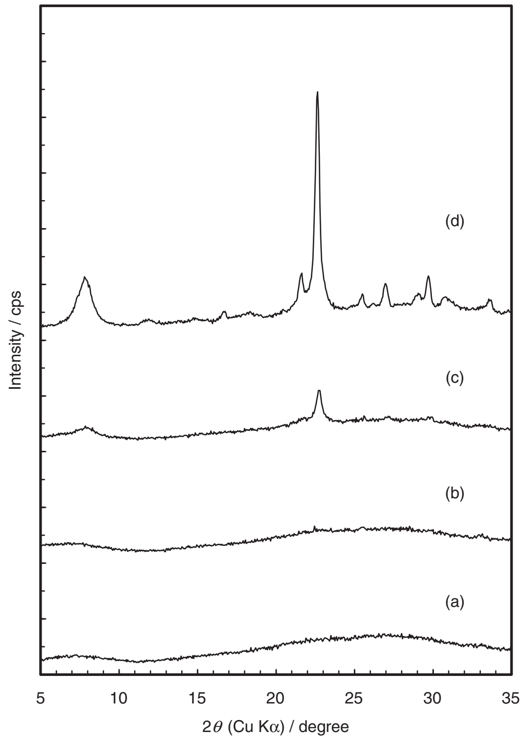

Figure 5. XRD patterns for the products obtained by the SAC treatment at 130 °C for 3 h and the following SAC under the steam-lean conditions at 130 °C for various periods. (a) Only the steaming treatment at 130 °C for 3 h was performed. The periods of SAC under the steam-lean conditions were (b) 4, (c) 6, and (d) 12 h.

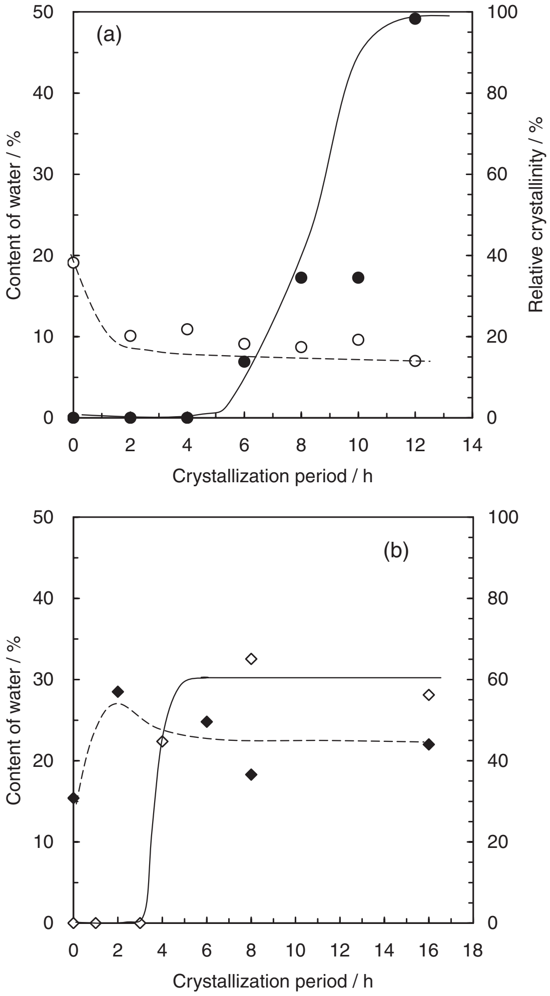

Figure 6. (a) The time courses of content of water (○) and relative crystallinity (●) for as-made products obtained by the SAC treatment at 130 °C for 3 h and the following SAC under the steam-lean conditions at 130 °C. (b) The time courses of content of water (◇) and relative crystallinity (◆) for the dry gel and as-made products obtained by only the SAC treatment at 130 °C.

the successive steam-lean crystallization for 12 h reached at almost 100%, whereas only SAC treatment at 130 °C for 16 h gave a lower relative crystallinity of about 60%. When the dry gel, containing 16 wt % water, was exposed to SAC conditions, the content of water rapidly increased to 28 wt % after 3 h of SAC and then slightly decreased and remained at about 22 wt % until 16 h of SAC. On the other hand, the content of water in the solids reached a plateau at around 8 wt % after 2 h of SAC under steam-lean conditions, as the partial removal of water contained in the SAC product rapidly occurred during the steam-lean crystallization. Consistent with the ^{29}Si NMR data as mentioned above, the removal of water occluded in the SAC product caused the formation of highly crystallized *BEA crystals due to the promotion of the dehydration of silanols in the pseudo-*BEA structure. On the other hand, the existence of a high content of water in the solid probably obstructs the dehydration of silanols in the solids, resulting in the retardation of the crystallization of a *BEA phase. We observed however that thermal drying of SAC product after 3 h of SAC in an open beaker gave no crystal phases (See Supporting Information 1), implying that the formation of highly crystallized *BEA

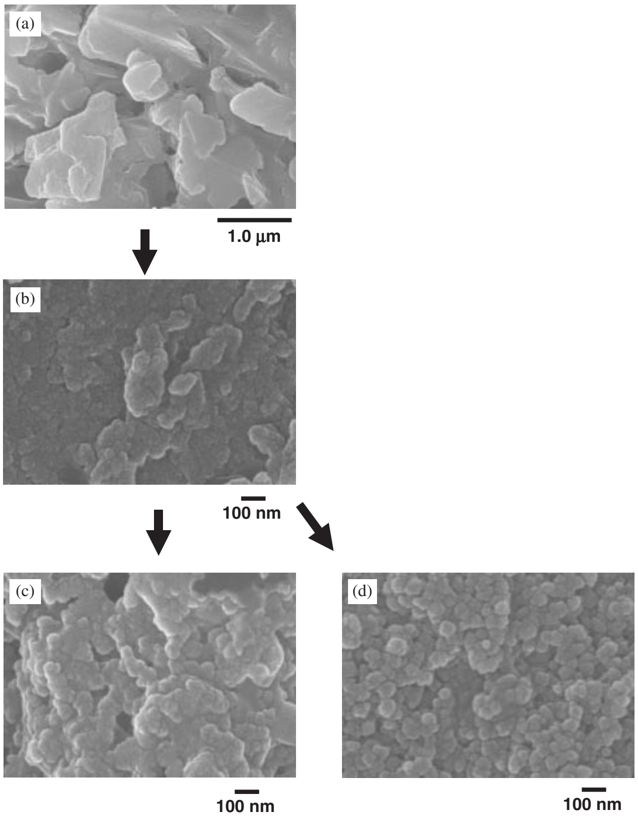

Figure 7. Typical FE-SEM images for (a) the dry gel and (b–d) as-made products obtained by SAC for (b) 3 h and (c) 8 h, and (d) SAC for 3 h and the following SAC under the steam-lean conditions for 12 h.

crystals probably requires the presence of water vapor, though the pressure of steam may be extremely much lower than saturated.

Figure 7 shows typical SEM images of the dry gel and crystallized products. Figure 7b indicates that the product for 3 h of the SAC was composed of 30–50 nm nanoparticles, whereas Figure 7a shows that the particle size of the dry gel was ca. 1.0 µm. We have previously reported that the dry gel particles with micron-order sizes were transformed into *BEA zeolite crystals via the formation of nanoparticles as intermediates, probably containing the pseudo-*BEA structure.[20,23] We have previously termed the unique transformation from nanoparticles intermediates to large zeolitic particles during the SAC as "fusion."[20] Figure 7c indicates that SAC up to 8 h caused the "fusion" of nanoparticle intermediates to form large 100–300 nm particles.[20] On the other hand, Figure 7d clearly shows that the SAC for 3 h and the following steam-lean crystallization for 12 h gave isolated *BEA nanoparticles with a diameter of ca. 30 nm. We believe that although the formation of nanoparticle intermediates requires a sufficient amount of water supplied from the vapor phase into the solid, the dehydration of silanols on the external surface of the nanoparticles predominantly occurred under SAC conditions, resulting in the "fusion" of nanoparticles. The steam-lean crystallization of the nanoparticle intermediates however caused the transformation of highly ordered *BEA nanocrystals without "fusion" of the nanoparticles, due to the rapid removal of water from the solid phase during thermal treatment in the absence of the minimum amount of steam in the autoclave.

Conclusion

Highly crystallized *BEA nanocrystals with a diameter of around 30 nm can be obtained by short SAC followed by steam-lean crystallization of aluminosilicate dry gel containing TEA^+ cations. We have found that the formation of a pseudo-*BEA structure requires an exposure of the dry gel to steam for a few hours, and nanoparticle intermediates containing a pseudo-*BEA structure can be transformed into highly ordered *BEA zeolite due to the dehydration of silanols within a solid phase during the steam-lean crystallization. On the other hand, prolonged SAC of the dry gel at 130 °C gave poorly crystallized *BEA products, accompanied by the "fusion" of nanoparticles. Additionally, the steam-lean crystallization of poorly crystallized *BEA also gave *BEA zeolite with high crystallinity.

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Supporting Information

In the XRD measurement, thermal drying of SAC product after 3 h of SAC in an open beaker gave no crystal phases. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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