

Aluminosilicate Species in the Hydrogel Phase Formed during the Aging Process for the Crystallization of FAU Zeolite

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Faujasite zeolite is synthesized hydrothermally after an aging process under various conditions. Hydrogel is formed during the aging, and the amount increases with increasing the duration. Aluminosilicate species included in the hydrogel phase during the aging is investigated for the changes in Si/Al ratios and Q units during the aging and the crystallizing processes by means of ^{29}Si magic-angle spinning NMR spectroscopy. Aging for more than 1 day is necessary to obtain faujasite with high crystallinity. The distribution in Q^4 units in the hydrogel is gradually changed, and the aluminosilicate species having mainly a $\text{Q}^4(4\text{Al})$ unit is obtained after 7 days of aging, while 2 days of aging results in remanent silicate species derived from the starting silica source. The former gives faujasite crystallites with higher crystallinity, sharper particle size distribution, and a lower Si/Al ratio. On the basis of these findings, the crystallization mechanism is discussed.

Introduction

Considerable interest has been focused on designing and synthesizing novel porous crystals, especially zeolites. However, because zeolite nucleation and growth is not well understood at a molecular level, most of the zeolite syntheses have evolved according to empirical fashions.^{1,2} The technological importance of these materials as adsorbents, ion exchangers, and catalysts³ has resulted in extensive studies on the influence of composition, temperature, and environment on the zeolitization process. A basic understanding of the crystallization process at a molecular level coupled with this enormous body of existing empirical knowledge will provide opportunities for syntheses of novel zeolite frameworks.⁴

As described above, thermodynamic variables in the syntheses of zeolites are the temperature, pressure, and overall chemical composition of the reactant mixtures. These variables do not necessarily determine the products obtained in hydrothermal reactions because the reactant mixtures may be heterogeneous and because nucleation appears to be kinetically, rather than thermodynamically, determined and controlled. When competing species appear, the tendency is for the least stable phase to crystallize first and then to be replaced by a more stable form, and so on, until the final, most stable product results, that is, Ostwald's step rule of successive transformations. This, however, is still only

a partial description because a number of nonthermodynamic factors may decisively influence the kinetic stage of nucleation and so the compounds that form. These include the treatment of reactants prior to crystallization, that is, a pre-nucleation stage, sensitive to their chemical and physical natures and the influence of mineralizers, templating cations, and other additives.

The chemical precursors to zeolite formation such as dissolved silicate, aluminato, aluminosilicate species, and their hydrogels^{1,2,5} are complicated, providing difficulty in understanding their nature. From the viewpoint of zeolite synthesis, dissolved aluminosilicate precursors to nucleation are of particular interest. High-resolution ^{29}Si NMR spectroscopy has been very successful in elucidating the structures of siliceous species present in solutions. Recently, the high resolution obtained in solutions has been extensively obtained in crystalline solids using high-speed magic-angle spinning with high-power proton decoupling and polarization transfer. The ^{29}Si atoms give chemical shifts that differ according to the position of this atom in the structure. Thus, the shifts fall into subdivisions with well-separated ranges for monosilicates (Q^0), disilicates or chain end groups (Q^1), middle groups in chains (Q^2), chain-branching positions (Q^3), and three-dimensional cross-linked framework positions (Q^4); in no case was there overlap between the shifts.⁶ Results obtained with solid aluminosilicates may serve as a guide because it has been found that there is a strong paramagnetic influence of four-coordinated Al substituting for Si in the second-coordination sphere of Si. Different extents of substitution of Si by Al in the aluminosilicates give

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(1) Barrer, R. M. *The Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982.

(2) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

(3) Williams, B. A.; Babitz, S. M.; Miller, J. T.; Snurr, R. Q.; Kung, H. H. *Appl. Chem.* **1999**, A177, 161, and the references therein.

(4) Martens, J. A.; Jacobs, P. A. *Adv. Funct. Mater.* **2001**, 11, 337.

(5) Kasahara, S.; Itabashi, K.; Igawa, K. *Stud. Surf. Sci. Catal.* **1986**, 28, 185.

(6) Engelhardt, G.; Zeigan, D.; Jancke, H.; Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1975**, 418, 17.

rise to nonequivalent Q⁴ units of different degrees of Al substitution with different chemical shifts.

When silicate is mixed with aluminate, a hydrogel is formed, which must initially be more heterogeneous than hydrogels made from well-stirred mixtures of solutions of soluble silicates and aluminates. The syntheses of zeolite faujasite (FAU), often from the hydrogels derived from colloidal silica, require room-temperature aging of the hydrogel prior to heating to induce crystallization.^{1,2} Aging is a well-known process performed prior to the crystallization of zeolites, and aging suppresses the formation of zeolitic phase other than the objective zeolite and enables reduction to be made in the amounts of excess silica and base required to crystallize. On the other hand, the structural information of hydrogel species formed prior to zeolite crystallization has been less than that of precursors for high-silica zeolites, where clear solution systems were examined using various organic structure-directing agents. Some structural rearrangements might occur during aging that lead to the formation of zeolite FAU nuclei.¹ The rate of crystallization and the composition of the crystalline products depend strongly on the quantity and composition of an amorphous aluminosilicate solid produced during aging⁷ because the aluminosilicate precipitate formed during aging serves as the precursors for nuclei that induce the crystallization of FAU.⁸

In this study, we focus on the hydrogel species formed during aging. FAU is adopted as a model zeolite because the purity of this zeolitic phase is strongly affected by its crystallizing procedures and conditions such as aging, agitation, H₂O concentration, and coexisting alkali cations. Here, the hydrogel involving aluminosilicate species was investigated by use of ²⁹Si MAS NMR, useful for clarifying the local structure and composition of aluminosilicate compounds.

Experimental Section

Synthesis of FAU Zeolites. FAU was synthesized hydrothermally at 90 °C for 1.5 to 24 h without the addition of organic compounds for structure-directing. The composition of the hydrogel was 10:1:50:4000 SiO₂:Al₂O₃:Na₂O:H₂O, where the yield of the Na-P-type zeolite (GIS) was minimized.⁹

The starting materials were colloidal silica (Aldrich, Ludox HS-40; SiO₂, 40 wt %; Na₂O, 0.43 wt %), sodium aluminate (Wako Chemicals), and sodium hydroxide (Wako Chemicals). In a typical synthesis, 1.25 g of colloidal silica was added to a mixture composed of 0.137 g of NaAlO₂ and 3.27 g of NaOH granules dissolved in 60 mL of distilled water, with vigorous stirring in a 100-mL polypropylene bottle. After mixing, the solution was aged at room temperature while stirring for a proper period of 7 days at maximum, followed by crystallization at 90 °C in the bottle without agitation.

Characterization of Products. The precipitated hydrogel or product was filtered immediately, rinsed with distilled water, and analyzed by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and ²⁹Si magic-angle spinning NMR.

Products before and during crystallization were characterized by a powder X-ray diffraction method (M03X HF22, MAC

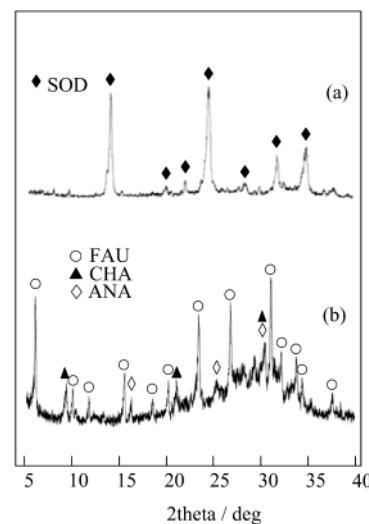


Figure 1. XRD patterns of the products obtained by (a) 24 h of crystallization without aging; (b) 48 h of crystallization with 1 h of aging.

Science), with a Cu K α line at 40 kV and 40 mA at a scanning rate of 4°/min by a step of 0.02°.

Observation by SEM (S2400, Hitachi) was carried out to observe the crystallinity and particle sizes. The accelerating voltage was set at 20 kV.

²⁹Si MAS NMR was performed to determine the distribution of Al in the framework, some branched units of silicate, and Si/Al ratios of the products. Spectra were recorded on a JEOL CMX 300 (300 MHz for proton), at a ²⁹Si frequency of 59.7 MHz, a spinning rate of 3 kHz with a 90° pulse length of 4 μ s, a recycle time of 20 s, and a scanning time of 3000–8000 depending on the sample. Chemical shifts were referenced to a classical external standard of tetramethylsilane at 0 ppm, and polydimethylsilane at –34.16 ppm as the secondary standard.

Results

The XRD patterns for products, which were obtained at each period of crystallization after aging for 0 or 1 h, 2 days, and 7 days, are summarized in Figures 1, 2, and 3, respectively. Less aging resulted in the formation of other phases of sodalite (SOD), chabazite (CHA), and analcime (ANA), well-known as byproducts against FAU. FAU became the main product with increasing of the aging period. It was found that at least 1 day of aging was required to obtain a pure phase of FAU. From the viewpoint of the crystallization period, it was noticed that FAU phase started to be observed after 6 h of crystallization in the case of 2 days of aging, while after 3 h for 7 days of aging. Formation of GIS occurred in further-crystallized products. Therefore, enough aging leads to the rapid formation of a pure phase of FAU, and the shorter crystallization time is preferable to maintain the purity.

Figure 4 shows the typical SEM images of the FAU obtained by crystallization with 2 or 7 days of aging. Very tiny particles were found in the 7-days aging sample; the average particle size was 0.6 μ m in diameter with sharp distribution. In contrast, the sample of 2 days aging consisted of much larger particles, of which the size was 3 μ m, along with smaller ones similar to those observed in the 7-days aging sample, resulting in wider size distribution.

(7) Ginter, D. M.; Bell, A. T.; Radke, C. J. *Zeolites* **1992**, *12*, 742.
(8) Ginter, D. M.; Went, G. T.; Bell, A. T.; Radke, C. J. *Zeolites* **1992**, *12*, 733.

(9) Osada, M.; Sasaki, I.; Nishioka, M.; Sadakata, M.; Okubo, T. *Microporous Mesoporous Mater.* **1998**, *23*, 287.

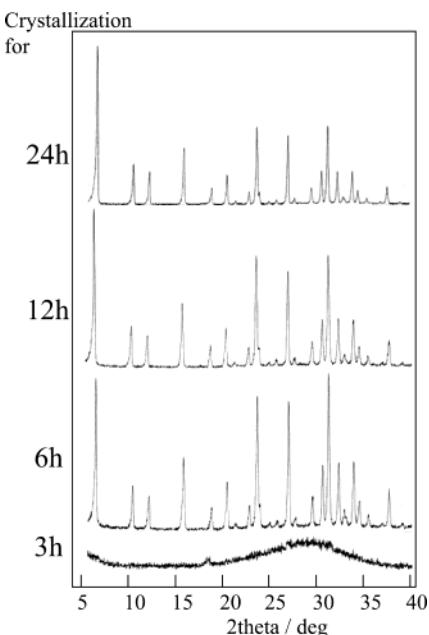


Figure 2. XRD patterns of the products with 2 days of aging prior to the crystallization.

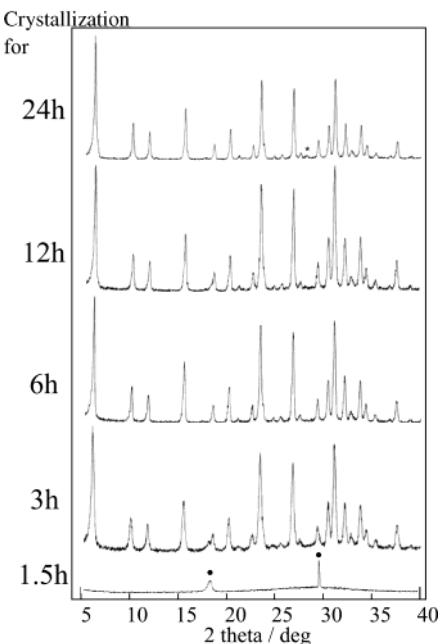


Figure 3. XRD patterns of the products with 7 days of aging prior to the crystallization. Asterisk and ● represent Na-P(GIS) and an unknown phase, respectively.

As generally reported, gelation occurs during the aging period in the system for crystallizing FAU. As can be observed in Figure 5, the hydrogel was formed under the experimental conditions employed in this study, and the quantity of the hydrogel apparently increased with increasing of the aging period. It can be considered that the product selectivity depends strongly on the hydrogel formed during the aging.

Structural changes of the hydrogel occurred, which were clearly confirmed by use of ^{29}Si MAS NMR. The NMR spectra of aluminosilicate species obtained after aging were illustrated in Figure 6. A sharp and intense signal centered at -110 ppm with a shoulder at around

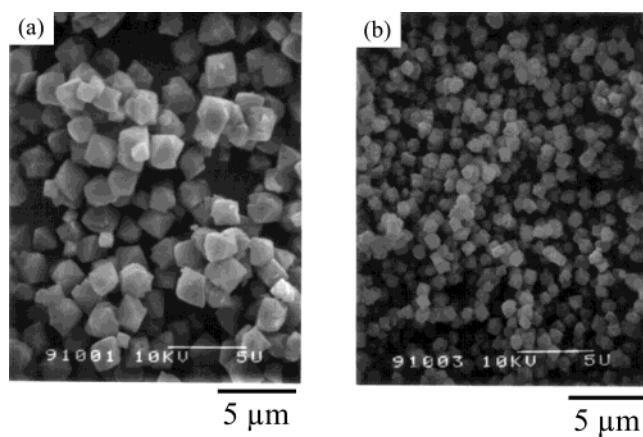


Figure 4. SEM images of FAU crystallized with 2 days of aging (a) and 7 days of aging (b).

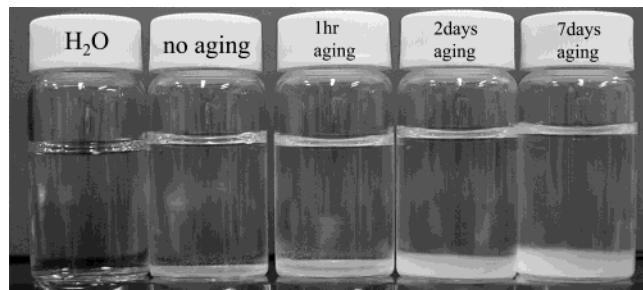


Figure 5. Aluminosilicate species formed during the aging process for each period.

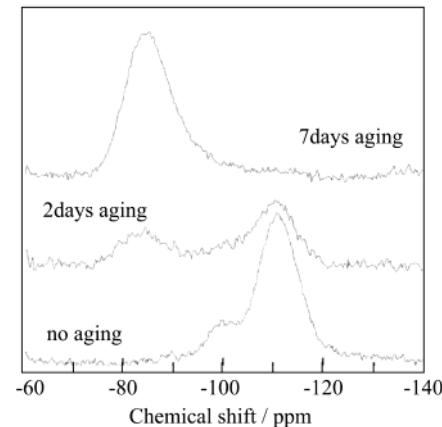


Figure 6. ^{29}Si MAS NMR for aluminosilicate species obtained after the aging process for each period.

-100 ppm was included in the spectrum for no aging. The former peak was assigned to a $\text{Q}^4(0\text{Al})$ unit of silica that remained undissolved in the hydrogel phase and the latter a Q^3 unit of aluminosilicate species. An increase in the aging period led to the decrease in the intensities of these peaks and, in turn, to the appearance of the peak centered at -84 ppm, which is attributed to aluminosilicate having a $\text{Q}^4(4\text{Al})$ unit. This indicates that colloidal silica as a starting material is dissolved during the aging process and that dissolution is a slower step compared to the subsequent formation of aluminosilicate species. One of the important roles of aging in the crystallization of FAU is involved in the acceleration of this dissolving step to enhance the crystallization for FAU. Quantitative analyses in the liquid phase of reactant revealed that prolonged aging

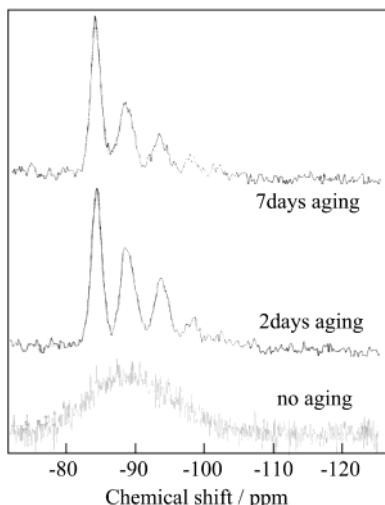


Figure 7. ^{29}Si MAS NMR for the products obtained after the aging process for each period, followed by crystallization.

Table 1. Distribution of Al in the Framework of FAU Obtained by Crystallization after Each Aging Period and the Widths of Each Peak

aging	chemical shift (ppm):	Q ⁴ (nAl)					Si/Al
		n: 4	3	2	1	0	
Composition (%)							
2 days		32.4	30.5	21.8	9.3	6.0	1.46
7 days		49.5	29.3	14.3	4.3	2.6	1.25
Width (Hz)							
2 days		93.9	145	145	145	174	
7 days		88.1	130	120	90.1	106	

resulted in a higher recovery of silicon and aluminum. About 80% of siliceous species remained in the liquid, and in that, aluminum was hardly detected. This indicates that the yield of zeolite is influenced by the amount of aluminum source in the liquid phase when enough siliceous species coexist in the liquid phase, as indicated in the report from the International Zeolite Association (IZA) synthesis committee.¹⁰

Figure 7 demonstrates the NMR spectra of the products after crystallizing of the hydrogel in Figure 6. The product given without aging showed a broad spectrum centered at -89 ppm. On the other hand, the spectra of the products that were purely FAU are composed of five peaks typically observed for low silica FAU. Each peak was assigned to Q⁴(4Al) at -84 ppm, Q⁴(3Al) at -88 ppm, Q⁴(2Al) at -93 ppm, Q⁴(1Al) at -98 ppm, and Q⁴(0Al) in FAU at -102 ppm. It is noted that differences in the relative intensities of these peaks, which contribute to the Si/Al ratio in the crystallite, could be found, as summarized in Table 1, as well as the peak widths. As for intensities, the product after 7 days of aging is mainly composed of the Q⁴(4Al) unit, indicating that Al distribution in the framework is highly occupied by Al-rich phase. On the other hand, the product after 2 days of aging was inclined toward various distribution of Al in the framework, resulting in high Si/Al ratio. It is also noteworthy that the peak widths of the 7-days sample were narrower than those of the 2-days sample. A peak width of the NMR

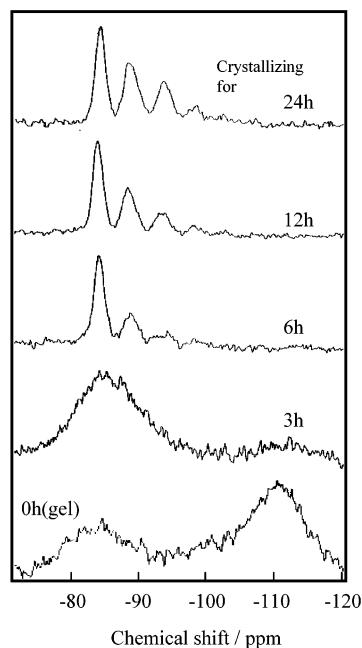


Figure 8. ^{29}Si MAS NMR spectra of the products obtained with 2 days of aging prior to crystallization.

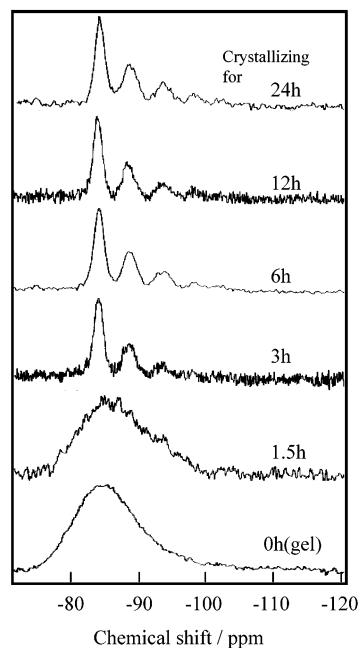


Figure 9. ^{29}Si MAS NMR spectra of the products obtained with 7 days of aging prior to crystallization.

spectrum is dependent on the symmetry of the units in their environment; therefore, the FAU with 7 days of aging possesses higher crystallinity than that with 2 days.

As for the differences in Si/Al ratios, different modes of building to FAU were revealed by the NMR spectra for the products in the course of crystallization, as shown in Figures 8 and 9 for the products with 2 and 7 days of aging, respectively. The peak of silicate observed in the hydrogel with 2 days of aging became diminished with a prolonged crystallizing period, indicating that the residual silica is dissolved during crystallization. The appearance of the broad peak centered at -84 ppm was separated into some sharp peaks at the time when FAU phase was formed, and after that the peaks, particularly

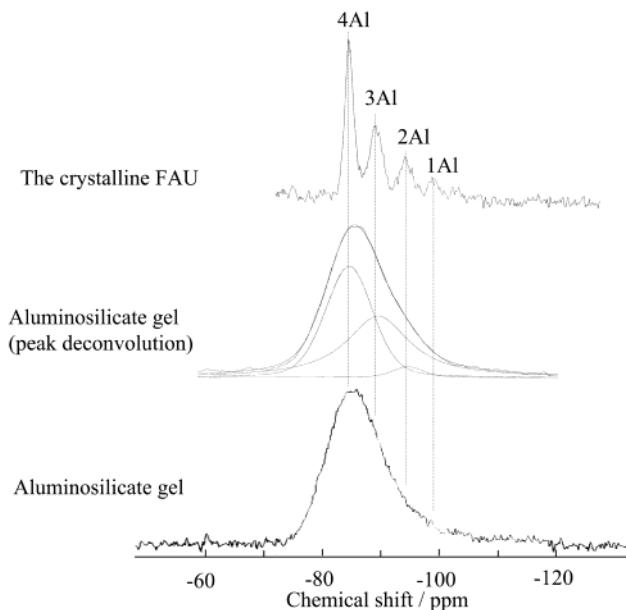


Figure 10. ^{29}Si MAS NMR spectra of the products obtained with 7 days of aging.

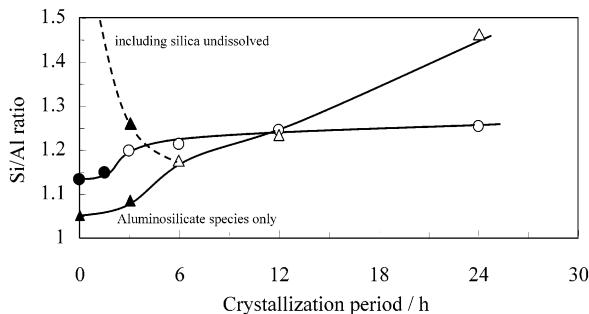


Figure 11. Si/Al ratios of the products obtained at each crystallization period. \triangle , \blacktriangle : 2 days of aging; \circ , \bullet : 7 days of aging; solid symbol: before the formation of FAU phase detected by XRD; open symbol: FAU phase was observed.

of the $\text{Q}^4(3\text{Al})$ unit, gradually developed. In contrast, the relative intensities of the peaks in the products with 7 days of aging were hardly changed after the formation of FAU.

Before the formation of FAU, the top of the peak appears to be stable at -84 ppm from the point of chemical shift; therefore, the broad peaks obtained before crystallization to FAU were deconvoluted in the manner represented in Figure 10. As a result, the units of $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(2\text{Al})$ were found to be already involved in the hydrogel before crystallization at relative peak areas to $\text{Q}^4(4\text{Al})$ of 37% and 18%, respectively.

The Si/Al ratios of the products, including the hydrogel, were calculated on the basis of NMR spectra, as displayed in Figure 11. After formation of FAU phase, Si/Al ratio of the zeolite with 7 days of aging was hardly changed, while increasing with increasing crystallization period, up to almost 1.5, in the zeolites with 2 days of aging. Before the formation of zeolitic phase, that is, hydrogel, the Si/Al ratios of the products with 2 days of aging increased upon the extension of the line in the range of zeolitic phase formation without consideration of the remanent silicate species. The increase in Si/Al ratio was also observed in the hydrogel with 7 days of aging, although the differential was much narrower than that in the case of 2 days of aging.

Discussion

Promotional Effect of Aging and the Role of Hydrogel Phase. As mentioned in the Results section, the dissolution of colloidal silica is a slow step under the experimental conditions used in this study. Aging plays an important role in this stage; the prolonged aging resulted in the formation of aluminosilicate species at the aging stage and the rapid formation of FAU at the subsequent crystallizing stage. Compared with the dissolution of colloidal silica, the formation of aluminosilicate is rather fast because Q^3 or some branched species could not be detected by cross-polarized ^{29}Si MAS NMR during crystallization and because the yield of FAU is determined by the amount of Al. In contrast to siliceous species, sodium aluminate was considered to behave as a fully dissociated salt of Na^+ and $\text{Al}(\text{OH})_4^-$ or a mixture of $\text{Al}(\text{OH})_4^-$ and AlO_2^- under the conditions utilized.^{1,11} Barrer¹ has also supported these reactions at the aging stage: the compositions of both solid and liquid were evolving over 7 days of aging, yielding a liquid much enriched in dissolved silica but with little dissolved aluminum species, free of aluminosilicate species, and a hydrogel much enriched in aluminum.

The aluminosilicate species obtained at the aging stage is not zeolitic but some structural information is included so that the centered peak was not changed in the chemical shift. Further siliceous species must be required to crystallize FAU at last; at the crystallizing stage, the siliceous species seems to be incorporated within the aluminosilicate species just before the formation of FAU, resulting in a higher Si/Al ratio.

After the formation of FAU, the Si/Al ratio increased in the case that silica remained in the hydrogel phase. However, as shown in Figure 11, the Si/Al ratio, with consideration of the silica, is much higher than the formed FAU, and the amorphous silica species was not observed in the products; therefore, consideration of a direct transformation of hydrogel into zeolite can be omitted. Siliceous species is supposed to be incorporated into the zeolitic framework via a liquid phase.

The formation of large-size particles, and the change in the Si/Al ratio in the course of crystallization, leads us to deduce that there exists Al distribution inside one particle, Al-rich zeolite inside and Si-rich zeolite outside of the particle. At last, FAU with a Si/Al ratio of 1.5 was obtained in the case of 2 days of aging. Such FAU could be obtained only in the seeded synthesis.¹² This also supports the deduction that Al distributes inside the particle and that the formation of high-silica FAU is enhanced by the initially formed Al-rich FAU. On the size distribution of the particles as well as the Si/Al ratio, the alkalinity of the hydrogel composition is critical for enhancing the Si/Al ratio and the size of Na-X-type zeolite when lowering aging temperatures and less alkaline hydrogel composition was used.¹³ Crystallization temperature and agitation also show a dependency on controlling the crystal size of Na-X-type zeolite.¹⁴

(11) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Krieger Publishing: Malabar, FL, 1976.

(12) Kacirek, H.; Lechert, H. *J. Phys. Chem.* **1975**, *79*, 1589.

(13) Korglu, H. J.; Sarioglu, A.; Tather, M.; Erdem-Senatalar, A.; Savasci, O. T. *J. Cryst. Growth* **2002**, *241*, 481.

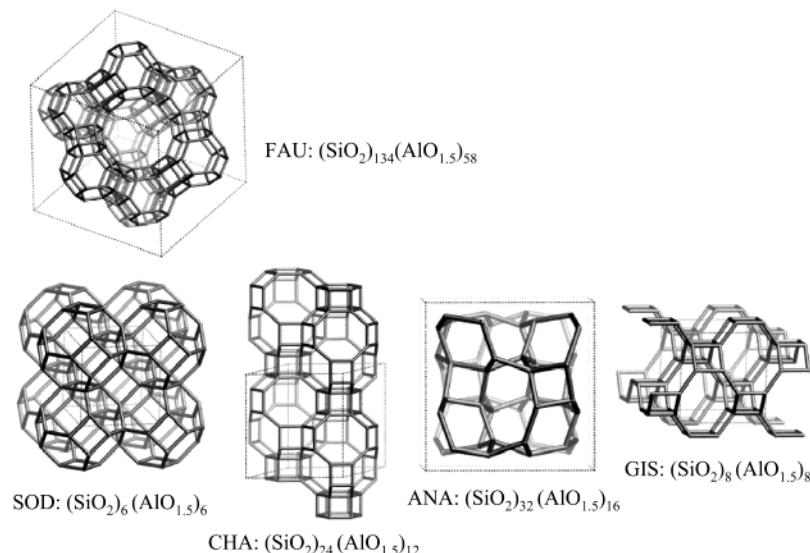


Figure 12. Framework diagrams of the zeolites¹⁰ obtained in this study.

Prolonged aging accelerates the formation of hydrogel phase, so the amount of hydrogel phase increased with increasing aging period. Along with the results of NMR, the hydrogel phase is considered to be mainly composed of aluminosilicate species. Once hydrogel is formed, a pure phase of FAU is formed, confirmed by the syntheses of FAU even with agitation, which is generally accepted to facilitate the formation of other phases such as LTA and GIS. These results suggest that the formation of hydrogel phase, that is, the aluminosilicate, is important for obtaining FAU.

Formation Mechanism of FAU. The aluminosilicate formed during the aging stage was not changed in the sense of the peak top of the Q⁴(4Al) unit in their structure. The peak centered at -84 ppm was not changed even in the course of crystallization when pure FAU was crystallized. On the other hand, the hydrogel for SOD or other impurities is composed of apparently different aluminosilicate species; the Q⁴(4Al) unit was observed at -89 ppm. In the NMR studies, Si/Al ratios of the aluminosilicate species without the consideration of the remanent silica were confirmed to be close to 1. The dependency of chemical shift in ²⁹Si MAS NMR is strongly due to Si/T atomic ratio, but the angle of Si—O—T contributes to the shift. The aluminosilicate for FAU is totally different in the structure from that for SOD or other phases.

The Si/Al ratio of the products increased in the early stage of crystallization, and FAU with a higher Si/Al ratio was formed along with the crystallization. Let us consider the byproducts: SOD, CHA, ANA, and GIS. The secondary building units of these zeolites are mainly a four-membered ring (4R) and a six-membered ring (6R): SOD is composed of 4R, 6R, and 6R+2, CHA is 4R, 6R, and double-6R (D6R), ANA is 6R and 4R, and GIS is 4R and 8R, according to the data from IZA,¹⁰ as shown in Figure 12. The secondary building units of FAU are D6R, 6R+2, 6R, and 4R. The literature^{1,15,16}

has suggested that silicate species in the liquid phase is limited, and 6R and larger membered rings cannot be detected, when no organic compounds as structure-directing agents are added to the reactant solution. The Si/Al ratio of SOD is 1 so the 4R consists of 2Si2Al and that of FAU is above 1 so the 6R includes less 3Al, a Si-rich structure, of which the configurations must be in good accordance with the rules of Löwenstein¹⁷ and Dempsey.¹⁸ The increase in the amount of aluminosilicate species, less impurity after gelation, and the composition of the ring structure of the zeolites observed in this study lead one to speculate that the more hydrophilic 4R is formed in the liquid phase and a little hydrophobic 6R can be seen only in the hydrogel phase. It can be speculated that less aging is preferred for developing zeolites that are constructed by 4R such as SOD and prolonged aging facilitates the formation of zeolites mainly composed of 6R such as CHA, ANA, and at last FAU.

Taking into account the formation of GIS, 4R might be formed from 6R inside the hydrogel phase. Osada et al. reported that a lesser amount of H₂O in the hydrogel and prolonged crystallization result in the formation of GIS.⁹ The latter situation was generally observed also in this study, as shown in Figure 3. The lack of Al in the liquid phase at the later stage of crystallization negates the speculation that 4R is newly formed in the liquid phase.

The formation mechanism of FAU and other zeolitic phases and the occurrences of their precursors during the aging process are illustrated in Figure 13. First, the dissolution of colloidal silica is necessarily involved because of the possibility to successively form the Q⁴(4Al) unit. Under highly alkaline conditions, the colloidal silica can react further with alkali to bring silica into solution to help homogenize the hydrogel. In Barrer's description,¹ GIS, ANA, and hydrated SOD appear at 100 °C from clear sodium aluminosilicate solution. In the clear solution, cyclic tetramer and

(14) Zhan, B. Z.; White, M. A.; Lumsden, M.; Mueller-Neuhaus, J.; Robertson, K. N.; Cameron, T. S.; Gharghouri, M. *Chem. Mater.* **2002**, *14*, 3636.

(15) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Zeolites and Related Systems*; John Wiley and Sons: London, 1987.

(16) Knight, C. T. G.; Kinrade, S. D. *J. Phys. Chem.* **2002**, *B106*, 3329.

(17) Löwenstein, W. *Am. Mineral.* **1954**, *39*, 92.

(18) Dempsey, E. *J. Phys. Chem.* **1969**, *73*, 3660.

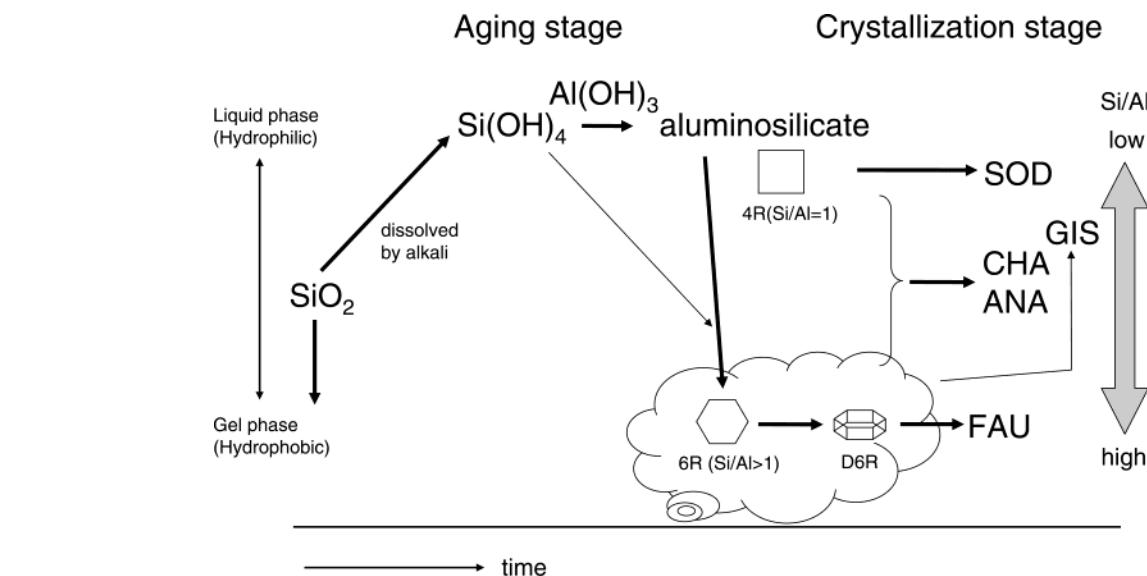


Figure 13. Illustration of the proposed formation mechanism and the promotional effect of aging on the zeolites crystallization.

hexamer species could be found in the liquid phase to generate sodalite cages.¹⁹ These accounts mean that these zeolites are nucleated homogeneously in the liquid phase and grown without intervention of hydrogel. During the nucleation period, the solid amorphous phase consists of predominantly six-membered aluminosilicate rings, investigated with Raman spectroscopy.²⁰ The 6R has a role in the structure-directing for FAU, with a lesser amount of GIS.²¹ The speculation illustrated in Figure 13 is also conceivable and noncontradictory to the mechanism claimed by Mintova et al.²² Lechert suggested that the formation of FAU occurs via a 4R,²³ investigated by the linear growth observation. The rate of formation of this species is similar to the Langmuir–Hinshelwood equation of a bimolecular catalytic reaction assuming that the reaction step is rate-determining, starting with monomeric silicate and aluminate in the solution phase, which is bound to the surface and forms then the mentioned ring structures and by further reorganization the structural elements of the growing zeolite. These steps seem to be rate-determining. Melchior et al. claimed by use of ²⁹Si MAS NMR to identify Al distributions in the framework that the immediate precursor to the FAU lattice is the hexagonal prism tertiary building unit and that the secondary unit is the single 4R.²⁴ In the liquid phase, such specific aluminosilicate species could not be detected under the conditions used, actually because of their low concentration in the aqueous solution. Further investigation into the aluminosilicate species included in the hydrogel is highly necessary to elucidate the crystallization mechanism, which will be reported elsewhere in the near future.

(19) Thangaraj, A.; Kumar, R. *Zeolites* **1990**, *10*, 117.
 (20) Dutta, P. K.; Shieh, D. C.; Puri, M. *J. Phys. Chem.* **1987**, *91*, 2332.
 (21) Twu, J.; Dutta, P. K.; Kresge, C. T. *Zeolites* **1991**, *11*, 672.
 (22) Mintova, S.; Olson, N. H.; Bein, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3201.
 (23) Lechert, H. *Zeolites* **1996**, *17*, 473.
 (24) Melchior, M. T.; Vaughan, D. E. W.; Pictroski, C. F. *J. Phys. Chem.* **1995**, *99*, 6128.

Conclusions

Solid-state NMR of ²⁹Si is useful for determining the structures of silicate and aluminosilicate species formed in the aging process prior to the crystallization of FAU zeolite. Gelation occurred during the aging, and the amount of hydrogel increased with increasing aging period. Along with the duration, the formation of the aluminosilicate species, having mainly a Q⁴(4Al) unit, took place instead of dissolution of the silicate species, which remained in the hydrogel phase, without forming some branched (alumino)silicate species such as a Q³ unit and so on. Without aging or lesser aging resulted in the formation of SOD, ANA, or CHA. With, at least, 1 day of aging, a pure phase of FAU was crystallized, although prolonged crystallization led to the formation of GIS. Under the experimental conditions employed in this study, the dissolution of colloidal silica is a slow step relative to the successive formation of the aluminosilicate. The aluminosilicate species involved in the hydrogel prior to crystallization has an important role in nucleating FAU. The remanent silicate species was fabricated into the pre-nucleated FAU as a growing unit to obtain larger particles and a higher Si/Al ratio. On the basis of the results obtained, it can be concluded that a higher concentration of aluminosilicate species in the hydrogel phase results in the formation of FAU crystallites at an earlier stage with higher crystallinity and sharper size distribution.

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