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Study of the crystallization of zeolite NaA by quasi-elastic light-scattering spectroscopy and electron microscopy

Leszek Gora, Kiril Streletsky, Robert W. Thompson, and George D.J. Phillies

INTRODUCTION

All aspects of the molecular sieve zeolite NaA have been studied for over 35 years, including its synthesis, crystal structure, ion exchange properties, and properties as a desiccant material. However, despite the vast literature on zeolite NaA, and even though zeolite NaA is perhaps the most tolerant of zeolites insofar as its synthesis conditions are concerned, there are still uncertainties regarding the mechanisms of synthesis of zeolite NaA. It should be possible to synthesize extremely small or extremely large zeolite NaA crystals if the details of its hydrothermal synthesis were completely understood, but these feats still elude scientists.

Although typical zeolite syntheses are carried out in concentrated aluminosilicate solutions that contain amorphous gel phases, it also is possible to synthesize several zeolites in dilute aluminosilicate systems in which the amorphous phase is not present. The first such clear solution system that produced zeolite NaA was reported at the International Zeolite Association (IZA) meeting in Tokyo.¹ The batch composition in Ref. 1 formed the starting point of the present work.

The clear solution environment permits the use of *in situ* observations using light scattering techniques, because the solution is not clouded by the amorphous

phase. Both static light-scattering and dynamic light-scattering techniques have been used to study syntheses of zeolites NaA and NaY,² hydroxysodalite,³ and the ZSM-5 and silicalite family of zeolites.⁴⁻⁷ These reports have generally concluded that both nucleation and crystal growth occur within the solution phase, that fewer crystals are nucleated at higher temperatures, and that surface integration kinetics, rather than diffusional limitations, govern the rate of zeolite crystal growth. Certainly similar conclusions have been reached in studies of turbid systems, but the clear solution environment has the advantage of eliminating the gel dissolution step, thus isolating the events pertaining to the crystalline phase. Furthermore, noninvasive observations can be made *in situ*.

Recent evidence⁸⁻¹⁰ has suggested that zeolite nucleation does not occur strictly in the solution phase as one might imagine from classical nucleation concepts, but that some physical rearrangements occur within amorphous aluminosilicate particles. These reports, based on simultaneous SAXS/WAXS observations, and the determination of the fractal dimensions of the particles in various stages of development, concluded that amorphous particles form, even in "clear" aluminosilicate solutions, and that restructuring to form crystalline material, the "nuclei," occurs inside these amorphous particles. Refs. 8-10 concluded that zeolite crystal growth from the solution follows the formation of crystalline material from amorphous particles.

Use of the term "induction time" in this work refers to the time at which particles were first observed by

laser light scattering. This induction time is much shorter than the "induction time" normally reported from mass observations, e.g., powder X-ray diffraction, because we begin with no particles and look for the first appearance of particles, and light-scattering spectroscopy is much more sensitive than other standard techniques to the presence, in a clear solution, of small numbers of small particles. In fact, induction times reported by mass measurement techniques are somewhat misleading, inasmuch as ultrafine crystalline material is undoubtedly present long before mass measurement techniques observe its presence, due to the rather large domains necessary to overcome most detection limits.

EXPERIMENTAL

Syntheses

All syntheses of zeolite NaA were accomplished using the "clear solution system" composition of Wenqin et al.¹: $x \text{ Na}_2\text{O} : y \text{ Al}_2\text{O}_3 : 1 \text{ SiO}_2 : 200 \text{ H}_2\text{O}$ where x ranged from 5 to 13 and y ranged from 0.1 to 0.2. The synthesis experiments were performed at 60°C or 80°C, whereas all aging, whenever done, was carried out at 25°C. Syntheses were carried out in 60-ml Teflon flasks.

Two separate solutions were prepared. Solution A was obtained by dissolving half of the necessary sodium hydroxide in deionized water. Aluminum wire was added to the sodium hydroxide solution and heated until all the Al wire was dissolved. Solution B was prepared by adding the SiO_2 (Cab-O-Sil) to the hydroxide dissolved in deionized water. Both solutions were filtered through a 0.2- μm disposable SUPOR 200 filter, then mixed together. Syntheses were carried out at the predetermined reaction temperature without stirring.

In order to investigate the evolution of the synthesis over a period of time reaction vessels were removed from the oven at various times. The reaction mixture was transparent until the formation of crystals occurred throughout the vessel (after about 1 h). Products of crystallization were filtered, washed, dried, and prepared for analysis.

QELSS characterization

Starting solutions having composition $10 \text{ Na}_2\text{O} : 0.2 \text{ Al}_2\text{O}_3 : 1 \text{ SiO}_2 : 200 \text{ H}_2\text{O}$, which will henceforth be known as the standard batch composition, were prepared using reagents of analytical grade purity and deionized water essentially free from impurities that scatter light. The solvent used in this study was deionized water obtained from Barnstead 4-cartridge NANO-pure II unit at resistivity $>17.0 \text{ MW}$. This composition gave a clear solution, so this system was ideally suited for study by means of quasi-elastic light-scattering spectroscopy (QELSS), which was used to observe the appearance of zeolite nuclei and to monitor their subsequent growth. Before use, the solutions were filtered directly into clean glass scattering cells through SUPOR-200 filters (0.2 μm). The scattering cell with the reaction mixture was placed in its thermostated holder (25°C, 60°C, or 80°C), and the QELSS data were acquired continuously for the time during which par-

ticle growth occurred, which generally was a few hours.

In cases where solid particles (seeds of zeolite NaA, quartz, or TiO_2) were added to the reaction mixture, the following synthesis procedure was applied. The required amounts of ground solid particles were placed in Teflon flasks (seeds, 0.02 g; quartz, 0.04 g; and TiO_2 , 0.04 g), and about 2.05 g of silica solution (solution B) was added to this solid. After 1 minute (from addition of the SiO_2 solution) about 1.98 g of alumina solution was added, mixed, stirred vigorously, and filtered directly through SUPOR-200 filters (0.2 μm) into clean glass-scattering cells. Finally, after 2 min (from addition of Al solution) the scattering cell with the reaction mixture was placed in its thermostated holder (25°C, 60°C, or 80°C), and the laser light-scattering data were acquired continuously for the time during which the growth of particles occurred. Using this procedure only particles smaller than 200 nm should be present in solution at the beginning of the experiments.

QELSS analyses were performed with a 1.2-W argon-ion laser (Spectraphysics Series 2000), having a polarized beam with wavelength 514.5 nm. Scattered light was monitored by a photomultiplier tube set at 90°C to the incident beam. A 270-channel Brookhaven Instruments model 2030 AT Digital Correlator was used to compute the intensity-intensity autocorrelation function

$$C(\tau) = \int_0^T I(q, t) I(q, t + \tau) dt$$

of the scattered light.

In this work, the field correlation function obtained from $C(\tau)$ was analyzed by applying Koppel's method of cumulants.¹¹

$$g^{(1)}(\tau) = \sum_{n=0}^N K_n(-\tau)^n / n!$$

Here K_n is the n th cumulant, and N is the truncation limit. An N of 2 or 3 was adequate for our data. K_1 gives the light-scattering-intensity-weighted average diffusion coefficient. K_2 gives the width of the diffusion coefficient distribution, expressed as the variance, computed as $V = 100 (K_2)^{1/2} / K_1$. K_1 is usually dominated by the largest major species in the system. QELSS is relatively insensitive to species that are much smaller in size than the dominant scattering species.

For nearly spherical, dilute particles D follows the Stokes-Einstein equation

$$D = k_B T / (6 \pi \mu r)$$

where k_B is Boltzmann's constant, T is the absolute temperature, μ is the solution viscosity, and r is the effective hydrodynamic radius.

Transmission electron microscopy

In order to investigate the crystallinity within the zeolite synthesized in the experiments, transmission electron micrographs and electron diffraction were measured. For this study a JEOL, JEM-100 C transmission electron microscope was used. The specimen was prepared by depositing a small amount of the material on

a TEM copper grid, coated by a carbon film. The deposition of the synthesized particles from QELSS cell onto the TEM grid was done in the following way. First, the sample (from light-scattering experiments) was filtered and washed through a 0.1- μm polysulfone membrane (SUPOR-200). The TEM grid was carefully laid on the membrane with the collected particles. On top of the TEM grid a second 0.1- μm membrane was laid. Next, this sample, with the TEM grid between the two membranes, was turned upside down and water was filtered through the stack, passing from top to bottom. By using this sample preparation technique, some particles from the polysulfone membrane stayed on the surface of the carbon film covering the TEM grid. The magnification factor for the microscope was found based on an electron diffraction pattern of a gold specimen.

RESULTS AND DISCUSSION

A better understanding of the fundamentals of zeolite nucleation and crystal growth may be obtained by observing the particle formation and the growth of the monodispersed crystals, i.e., by monitoring the change of the particle size distribution as the crystallization proceeds. The chemical changes in a reaction mixture can be examined by n.m.r. spectroscopy, where changes in the chemical environment of nuclei are reflected in the observed chemical shifts. Some information also can be obtained from chemical analysis of both the liquid and solid phases. In this study, the physical changes occurring during crystallization were monitored over the synthesis time by dynamic light scattering, by continuously monitoring the thermostatted reaction mixture with QELSS. The standard batch composition was used for these experiments.

Before the onset of crystallization, the reaction mixture scattered very little light, but it was possible with QELSS to detect small species, about 1 nm in size. These species were found to exist in the mother liquor throughout the reaction at all temperatures studied. Two possibilities were considered about the nature of the 1-nm particles. The first was that they formed shortly after mixing both components, and the second was that they already existed in one of the components. To test these possibilities, the silicate solution and aluminate solution were each investigated with QELSS. This study showed that the silicate solution contained small species, whose particles were about 1 nm in diameter. This species did not dissolve, even when the temperature was elevated up to 60°C. (Similar results were reported by Schoemen and Regev after this manuscript had been accepted, see Ref. 24.)

Because of their small size, it was impossible to study the nature of these particles by other techniques. It is known that high temperatures, lower SiO_2 concentrations, or an increase in pH favor the monomer and small oligomers in silicate solution.¹²⁻¹⁵ In this case, the pH was about 13.8 and the concentration of silica in solution was so low that nothing more complicated than monomers and dimers were likely to have formed. Therefore, these 1-nm species could have been sodium cations surrounded by silicate anions. Gaskell et al.¹⁶

using neutron scattering with isotopic substitution of Ca^{2+} in a calcium silicate glass, revealed a high degree of ordering in the immediate environment of Ca^{2+} over distances approaching 1 nm. In order to study the chemical structure of the reaction mixture ^{29}Si n.m.r. was applied. Unfortunately, this did not give any information, because the concentration of silica species in the reaction mixture was too low. Nothing but background noise was observed.

Some information about liquid species was obtained from an ^{27}Al n.m.r. study of the solutions used in these experiments. In alkaline solution (pH ~ 13.8 the most abundant Al- containing anion is the tetrahedral $\text{Al}(\text{OH})_4^-$ species.¹⁷⁻¹⁹ ^{27}Al n.m.r. spectra are presented in Figure 1. In the absence of dissolved silica, a single narrow peak was observed at 79.34 ppm, characteristic of $\text{Al}(\text{OH})_4^-$ in basic aqueous solutions. After mixing the aluminate solution with the silicate solution, the position of the aluminate peak shifted upfield to 77.5 ppm and did not change position during synthesis. The addition of the silicate solution to the aluminate solution resulted in broadening of the spectra and decreasing the intensity of the signal. It is known from Kinrade and Swaddle^{12,13} that ^{27}Al peaks at 75, 70, and 66 ppm correspond to Al centers connected to one, two, and three Si units, respectively. The peak found in this study was broad, and it is possible that some of the area corresponds to Al bound to one Si atom through an oxygen bridge. It also is possible that the intensity of the n.m.r. signal decreased because $\text{Al}(\text{OH})_4^-$ was incorporated into the 1-nm species from the silica solution. Regev et al.²⁰ found that the NaA zeolite formed by means of nucleation via 1-nm globular particles, but they did not discuss the possible origin of these particles.

Aging at 25°C

During the first five hours of crystallization (or aging) at 25°C, the small species mentioned above were present. Larger particles were first detected at 5 h, and had a diameter of about 170 nm (Figure 2). This was the first time for which it was possible to obtain light-scattering spectra for the intensity decay; the spectra could be fitted well with two or three cumulants. According to QELSS the size of the product did not change during next 30 h of crystallization. Cumulant analysis showed that during this time (up to 35 h) the particle size was about 180 nm, and the signal to noise ratio (S/N) increased with time, indicating that the number of particles had increased. The distribution of particles sizes during this time period was wide. The distributions were relative values, corresponding to the variance of the light-scattering spectrum calculated using the cumulant fit, and was about 50–60%. When crystallization was carried out for a longer time, the variance increased at 74 h up to ~500. Such huge values correspond to systems containing a very wide range of particle sizes. Figure 3 shows a TEM photomicrograph of the product obtained at 25°C after 44.5 h of crystallization. The sample crystallized for 44.5 h contained particles ~400 nm in diameter surrounded by much

Figure 1 ^{27}Al NMR spectra for the reaction mixture.

smaller species. The product obtained after 73.5 h of crystallization contained a wide spectrum of particle sizes (consistent with the QELSS observation). The smallest particles were about 20 nm in diameter. All other particles, which had sizes up to 1.1 μm , looked like agglomerates of the smaller ones.

For samples synthesized for 44.5 h at 25°C , the electron diffraction pattern showed the presence of one very broad and weak circle. This type of pattern may be evidence for the presence of some crystalline material, but it was not possible to determine where this crystalline material was present. Some scientists believe that semi-crystalline particles form when aluminosilicate gels precipitate during the aging process.

Based on the results it is difficult to give a clear picture of all the processes taking place during the aging period (crystallization at 25°C), but the aluminosilicate particles that formed during the aging process may be precursors of crystal nuclei. This is further suggested by the observation that the solution that was aged 38.5 h was shown to be very effective as an initiator of nucleation.²¹ Addition of even 2.7% of this solution to a reaction mixture increased the nucleation rate considerably. Therefore, it is reasonable to assume that the particles present in an aged solution are aluminosilicate flocs that form with heating of the solution at the reaction temperature or a source of semi-crystalline particles covered by aluminosilicate gel.

Synthesis at 60°C

The next phase of the study was conducted at 60°C . The same reaction mixture used previously ($10 \text{ Na}_2\text{O} : 0.2 \text{ Al}_2\text{O}_3 : 1 \text{ SiO}_2 : 200 \text{ H}_2\text{O}$) was filtered into a thermally controlled glass cell and continuously monitored with QELSS over a period of several hours. Before the onset of crystallization, the reaction mixture scattered very little light. After 65 min of crystallization it was possible to obtain light-scattering spectra for the

Figure 2 Increase in diameter of product from the standard composition measured by QELSS at 25°C .

Figure 3 TEM photograph of product obtained at 25°C after 44.5 h of crystallization.

intensity decay. A single exponential fit to the data was good. Delay times (sample times) were chosen to permit examination of a reasonable portion of the spectral decay and ranged from 5 to 30 ms. The best fits were obtained by using cumulants analysis. All spectra were fitted well with two or three cumulants, the use of additional cumulants having little effect on a fit's statistical merit. The distribution of particle sizes obtained at synthesis times up to 85 min was wide, but decreased with increasing synthesis time. The variance changed from 73% after 68 min to 15% after 117 min.

Figure 4 shows experimental results for a typical run in the series, in which QELSS was used to measure the size of the product as a function of time. The diameters found by light scattering were in good agreement with those found by electron microscopy. The first reasonable spectra were obtained from data collected after about 1 h of crystallization. The average size of particles was observed to increase linearly with time; the growth rate was determined directly from the slope of the plot.

Figure 4 QELSS determination of the particle size of zeolite NaA seeds crystallized at 60°C from clear solution. Composition of the initial mixture 10 Na₂O : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O. (□), unaged; (■), aged for 1 min.

Figure 5 Increase in diameter of product from the standard composition measured by QELSS at 80°C (■) and 60°C (□).

Based on this slope the particles of zeolite NaA in an unaged clear solution of the standard composition grew at a rate of 4.63 nm/min. These results were difficult to reproduce, because the reaction mixture was very sensitive to the time of aging. If the time interval between mixing the two components (aluminate solution and silicate solution) and putting the reaction mixture into a thermostated cell was increased by as little as 1 min, the zeolite started to form sooner, as shown in Figure 4.

The induction time was obtained by extrapolating the growth curve to zero particle size. The induction period for crystallization of zeolite NaA from the unaged clear solution in this study was 42 min. Extrapolation of the curve for the solution aged for 60 s was less reliable, but the induction time was reduced to on the order of 25 min. Twomey et al.⁷ proposed that during this time the initial germ, or nonviable nuclei, were being generated from aluminosilicate species in solution and had not yet reached the critical size necessary for further growth to occur spontaneously. It seems more likely from these data that a small amount of growth occurred either during aging or while the solution was being heated to 60°C.

Synthesis at 80°C

Increasing the temperature of reaction to 80°C accelerated the crystallization process, increasing the crystal growth rate from 4.63 nm/min to 36.67 nm/min when the temperature was raised from 60°C to 80°C, as measured by the slopes of the lines in Figure 5. With the increase in temperature, the length of the induction time also decreased significantly, from about 42 min at 60°C to 10 min at 80°C.

Figure 6 shows an SEM photograph of zeolite NaA particles formed at 80°C and 60°C. When 80°C was used a bimodal population of crystals formed. The second population was much less concentrated than the population of larger particles. In order to study a system with a bimodal population, the concentration of each component (large and small particles) would have to be adequate to be detected. Therefore, the data presented in Figure 5, for the experiment run at 80°C, rep-

Figure 6 (A) SEM photograph of zeolite NaA crystallized from clear solution at 80°C after 44 min (QELSS exp.). (B) SEM photograph of zeolite NaA crystallized from clear solution at 60°C after 120 min (QELSS exp.).

resents an approximation of the real situation, as only the population of larger crystals is reported. The growth rate of those crystals was constant.

Study of aging on the micro-scale

The processes occurring during aging are unclear, one possibility being that during this period chemical rearrangements occur giving rise to crystal nuclei. Such nuclei are believed to be of the order of a few unit cells across and to be present in insufficient concentration for detection by standard X-ray or electron diffraction. Several series of experiments were carried out on clear solution systems in which the solution was subjected to aging at room temperature and in which the effects on the lengths of the induction time and the rate of crystal growth were monitored.

The reproducibility of these experiments was studied using a crystallization from a solution aged for 10 h. Crystals grew from the aged mixture, as in previous experiments, with a constant rate of increase in diameter. The results did not change when the difference in aging time was 5 min (i.e., 10 h + 5 min aging time).

Figure 7 QELSS determination of particles size of zeolite NaA crystallized at 60°C from a clear solution aged for 10 h.

Figure 7 shows experimental results for two runs (essentially the same experiment repeated) with good agreement between the results.

Solutions having the standard batch composition were aged at 25°C for 7 h, 10 h, 1, 2, and 6 days. The effects of aging the solution at 25°C on subsequent crystallization kinetics at 60°C is illustrated in Figure 8, with the corresponding parameters listed in Table 1. After aging, reaction mixtures were filtered through 0.20- μm polysulfone membranes directly into glass-scattering cells. In Figure 8, the rate of growth of zeolite NaA particles in aged clear solutions was taken from the slope of each plot; the induction time was taken as the x -intercept (Table 1).

The growth rate of the crystallites was strongly influenced by the aging procedure, for aging times beyond approximately 7 h, increasing from 4.63 nm/min for unaged samples to about 11.13 nm/min after 10 h of aging. Aging longer than 10 h did not change the growth rate of the crystals. The growth rate for particles crystallized from solution aged for 1, 2, or 6 days was approximately 11 nm/min. Unlike the growth rate, the induction time changed for all aging times, and for

Figure 8 Effects of aging the standard solution at 25°C on subsequent crystallization kinetics at 60°C. (■), nonaged; (○), aged for 7 h; (□), aged for 10 h; (●), aged for 1 day; (◇), aged for 2 days; (◆), aged for 6 days.

Table 1 Effects of aging the standard solution at 25°C on the growth rate and induction time

Aging time (h)	0	7	10	24	48	144	With 162 nm seeds
Growth rate (nm/min)	4.63	5.8	11.1	9.9	11.5	10.8	11.27
Induction time (min)	43.3	8.9	8.14	2.3	2.65	0	0

synthesis from a solution aged for 6 days it was close to 0 min. Induction times for solutions aged beyond a certain period may be due solely to the heating time.

Electron photomicrographs for two of the samples in those experiments (particles obtained from solution aged for 7 h and 6 days) are shown in *Figure 9, a* and *b*. The diameters found by light scattering were in good agreement with those found by electron microscopy. It is evident in *Figure 9b* that particles obtained from the solution aged for 6 days at room temperature were agglomerates. This observation confirmed the previous suggestion based on macro-scale experiments,²² that twin growth and formation of an intergrown mass of zeolite can be explained by agglomeration of nuclei at very early times in their existence. Agglomeration of nuclei during aging also could explain the apparent accelerated growth rates observed here and by Twomey et al.,⁷ because polycrystalline particles have a higher surface area per particle, and, therefore, would be expected to assimilate material faster than single crystals with regular planar surfaces. In this study particles larger than 200 nm were removed by initial filtration of the aged solutions, but we believe that the remaining particles formed during aging were responsible for the faster apparent activation of nuclei from solution with longer aging.

Study of aging on the macro-scale

It is known that during aging, solutions of active aluminosilicate solute species are created, which then form nuclei and are consumed by growth of these nuclei. The longer the solution is aged the more active solute species form and more nuclei are created in consequence.

Products of zeolite A crystallized at 80°C from aged solution had a uniform size distribution in this study. Particles crystallized from reaction mixtures aged for different times had a different appearance. *Figures 10–13* show a comparison of the progress of the reaction over time between samples with different aging periods (with Cab-O-Sil used as the silica source). Crystals obtained from a solution aged for 10–30 min were noted to be either single or twinned. However, crystals obtained from solutions aged for 3–38.5 h were clumped together in polycrystalline formations. *Figure 10 a–d*, show crystals after 1 h of crystallization (the first collectable sample); those from a solution aged for 10–30 minutes were smaller than those from solution aged for 3–38.5 h (a definite difference can be seen between the size of the zeolite crystals obtained from the reaction mixture aged for 10 min and that aged for 38.5 h). After 1.5 h of crystallization (*Figure 11, a–d*), particles from solutions aged for different times had a similar size, but those from mixtures aged for 3 h or longer had sharp edges and formed intergrowths. *Figure 12, a–d*, shows the product after 1.75 h of crystallization. Particles from the solution aged for 10–30 min were 1.5 times larger than particles from the reaction mixture aged for 3–38.5 h. And, after 2.25 h (*Figure 13, a–d*) the size of particles from solutions aged for 10–30 min were twice as large. The mass of zeolite that forms from reaction mixtures aged for a longer time (3–38.5 h) was much greater (*Figure 14*).

The effects of aging a clear solution can now be summarized. The longer the solution was aged the more “active” the solution appeared, inasmuch as the crystal growth rates seem to increase. However, it seems that two effects occurred during aging: activation of increased numbers of nuclei, and agglomeration of some

Figure 9 (A) SEM photograph of particles obtained after 75 min of crystallization from solution aged for 7 h. (B) SEM photograph of particles obtained after 34 min of crystallization from solution aged for 6 days.

Figure 10 SEM photographs of zeolite A obtained after 1 h of crystallization at 80°C, aged at room temperature.

of the nuclei given sufficient aging time. Superimposed on these processes involving activation and agglomeration of nuclei, there also must be very small levels of growth of these crystallites even at room temperature and during the heating time. Thus, the induction time was reduced for aging times up to some level due to increased numbers of activated nuclei that began growing sooner than without aging. The growth rate increased after sufficient agglomeration of nuclei had occurred due to increased surface area, but this effect became less important with increased aging due to limits on the number of nuclei activated and the limited extent to which particles could become agglomerated. This additional growth potential is reflected in the mass growth curves in *Figure 14*.

Figure 11, a–d, shows that particles obtained after 1 h of crystallization from a solution aged longer were larger than from less aged solutions due to agglomeration with longer aging times. Finally, after longer crystallization times, individual crystals in a solution aged for 10–30 min grew larger than particles from a reaction mixture aged for 38.5 h (*Figure 11*), because competition for the active solute was higher in crystallization from the solution aged a longer time. Fewer nutrients were available per nucleus in a solution aged longer after more than 1 h of crystallization. With the production of so many nuclei and growing of these nuclei the solution became depleted of nutrients, thus

causing the growth period to be shorter. This happened after 1.75 h, i.e., the crystals obtained from the solution aged for 3–38.5 h essentially stopped growing. It also is noteworthy that from very early on the samples from the longer aged solutions (3 and 38.5 h) showed evidence of agglomeration, whereas the samples from the shorter aged solutions (10 and 30 min) did not. This observation supports the notion that agglomeration of the smallest crystallites (or nuclei) occurred very early in the longer aged samples.

In the final stages, *Figure 13, a–d*, shows that all the samples formed a highly intergrown mass. Because the solutions aged for 10 and 30 min previously contained single crystals, agglomeration undoubtedly occurred after settling, as noted previously.²² The fact that crystals grew into one another at relatively early times in the solutions aged for 3 and 38.5 h is evidence that crystals do not necessarily form twins from a single crystal on the vessel bottom; they may grow as twins or multicrystals from the beginning of crystallization if sufficient nuclei are present. It seems unlikely that several crystals formed from one nucleus. A more reasonable explanation of twin growth of crystals is that nuclei agglomerated soon after their creation. This conclusion is supported by the fact that some degree of twinning was noted at very early times, that the extent of twinning increased with aging time (more nuclei were present having a longer time to agglomerate), that the twinned

Figure 11 SEM photographs of zeolite A obtained after 1.5 h of crystallization at 80°C, aged at room temperature.

crystals were approximately the same size, suggesting that they grew for about the same period of time, and that their apparent centers overlapped rather than being separate, suggesting that their respective centers were close to one another.

The longer the solution is aged, the more nuclei are created. Increased concentration of nuclei due to aging promotes intergrowth of the product crystals. Based on experimental data (size of particles and mass of product) the number of particles growing in an aged reaction mixture were calculated. The number of particles increased 10-fold during the first 10 min of aging (from 3.25×10^6 without aging to 3.25×10^7 particles per gram of solution). In a solution aged for 3 h or more the concentration of particles increased another ten times, up to 3.5×10^8 particles per gram of solution. Aging of the synthesis solution thus produces a significant increase in the number density of growing crystallites (see Table 2). Twomey et al.⁷ noted that the number of nuclei increased with aging up to 25 days but decreased with an aging time of 100 days, suggesting the possibility of a reduction of growth centers due to agglomeration of the nuclei.

Study of the reaction limit

The last column in Table 1 shows the growth rate for seeded experiments carried out in the standard non-

aged clear solution, obtained from Figure 15. The seeds used in this experiment were fully crystalline zeolite NaA material. The seeds were ground using a mortar and pestle, added to the reaction mixture, and the whole solution was filtered through a 0.2-μm membrane. In a control experiment using the same procedure of sample preparation, but using water as the solution medium, QELSS indicated that the particles were about 162 nm in dimension. Therefore, the first measured point on Figure 15 is 162 nm. However, SEM analysis revealed that the 162-nm particles were probably made up of agglomerates of smaller particles approximately 50 nm in dimension. Thus, the fundamental particle in the seed sample was something smaller than 162 nm and was closer to 50 nm.

As in all experiments where particles were studied in the cell at 60°C or higher temperature, it was not possible to record any “useful signal” from QELSS at the beginning, because convection flow in the reaction mixture was disturbing measurements of diffusion-scattering species. After 6 min it was possible to get the first experimental data for this experiment. The reason why particles monitored after 6 min of crystallization were smaller than those measured in water before the beginning of reaction was speculated to be the breakup of the 162-nm particles in the hot caustic solution. Extrapolation of the data reported in Figure 15 would suggest that the starting size was about 50 nm, the same

a. 10 minutes

b. 30 minutes

c. 3 hours

d. 38.5 hours

Figure 12 SEM photographs of zeolite A obtained after 1.75 h of crystallization at 80°C aged at room temperature.

a. 10 minutes

b. 30 minutes

c. 3 hours

d. 38.5 hours

Figure 13 SEM photographs of zeolite A obtained after 2.25 h of crystallization at 80°C, aged at room temperature.

Figure 14 Influence of solution aging (at room temperature) on zeolite NaA crystallization. (○), nonaged, (□), aged for 10 min; (■), aged for 30 min; (◇), aged for 3 h; (◆), aged for 38.5 h.

size as the particles making up the 162-nm agglomerates observed by SEM.

In this experiment the seeds grew from a nonaged solution. The growth rate was about 11.27 nm/min, the same as the growth rate of particles grown from solutions aged for 10 h or more. These results show that seed particles assimilate species necessary for growth faster than particles nucleated from a nonaged solution assimilate the same species. Three explanations can be postulated for this observation: surface kinetic limitations to growth, different structures of new nuclei and crushed crystalline fragments, and enhanced growth rates of fragmented seeds due to a surface area effect.

The first explanation is that diffusion of aluminosilicate species in the reaction mixture is a fast process compared to the reaction kinetics between these species and the surface of nuclei or particles nucleated from solution. This conclusion is consistent with the results of Schoeman et al.,²⁻⁶ Twomey et al.,⁷ and Wijnen et al.⁸ Schoeman et al.⁵ used a chronomal analysis to demonstrate that the zeolite crystal growth process was surface kinetics limited rather than diffusion limited, and that the surface growth step was represented by a first-order mechanism. Twomey et al.,⁷ based on activation energies of the nucleation and growth of silicalite, concluded that it was not diffusion of crystal-building units, but rather chemical interaction of the silicate species that is the limiting step for both pro-

cesses. Wijnen et al.,⁸ studying the formation of silica gel from aqueous silicate solution, showed that diffusion of growth species in the silicate solution was fast compared to the reaction kinetics between two aggregating particles. However, this explanation does not address the issue of why the surface integration kinetics would increase with aging time or why seed crystals inherently grow faster than newly nucleated crystals.

As a second explanation, the results presented here could imply that particles nucleated from solution have a different bulk structure than seeds. One must remember that the seeds used in this experiment were perfect crystalline zeolite NaA (ground) and were synthesized from the same standard solution as that from which the particles were growing. Therefore, the results can be interpreted in the following manner: After mixing both components of the reaction mixture, reactive species form momentarily, and then form nuclei after some time at temperature. Particles that grew from these nuclei did not have perfect crystalline order at least at their outer surfaces. It is possible that as soon as nuclei formed (but were not present in sufficient concentration for detection by X-ray or electron diffraction) they were covered by silicate species and that these particles, which were mostly amorphous, were the precursors of nucleation. Presence of these precursors in the aged solution enhanced crystallization when the aged solution was added to the reaction mixture.

It is not clear how these precursors finally can transform into fully crystalline zeolite NaA. It was reported in the literature that the transformation of gel into silicalite (zeolite) was recorded by SAXS-WAXS technique.^{9,10} When an ionic material such as a salt is rapidly precipitated from a highly supersaturated solution, it may initially be amorphous, but it rapidly rearranges to the ordered crystalline state. Iler²³ suggested that such rearrangement can occur in silica, but only at elevated temperature or in the presence of a solvent such as water under hydrothermal conditions. Recently, Wijnen et al.⁸⁻¹⁰ proposed a model for structure transformation in silica gel.

Figure 16 shows that the product obtained using 162-nm seeds in clear solution formed agglomerates, the same as those crystallized from solution aged for a few days. From these observations, the third explanation that can be suggested is that agglomeration occurs during aging, producing polycrystalline aggregates that

Table 2 Crystal number obtained from aged reaction mixtures

Aging time	Crystallization time			
	1 h		1.5 h ^b	
	Size (nm)	Number of particles (particles/g sol) ^a	Size (nm)	Number of particles (particles/g sol) ^a
10 min	1.22	3.22×10^7	2.34	3.30×10^7
30 min	1.33	3.88×10^7	2.5	3.55×10^7
3 h	1.67	3.08×10^8	1.67	3.76×10^8
38.5 h	1.67	3.76×10^8	1.67	3.55×10^8

^a Number of crystals in solution determined by using the relation $N = V/ru$.

^b After longer time the product agglomerated.

Figure 15 QELSS size determination of zeolite NaA seeds (162 nm) growing in clear solution at 60°C (■); (□), without seeds. Composition of reaction mixture 10 Na₂O : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O.

grow at a faster rate than single crystals due to their increased surface area. Seed fragments that also have irregular areas may be imagined to grow at faster rates as well due to their larger surface areas per unit volume, due to surface roughness on the molecular level.

CONCLUSIONS

Molecular sieve zeolite NaA synthesis was studied using QELSS and electron microscopy. We found that crystal growth rates were constant over the course of experiments conducted at elevated temperatures, regardless of the aging time. Increasing the synthesis temperature from 60°C to 80°C was shown to increase the crystal growth rate from 4.63 nm/min to 36.67 nm/min, almost an order of magnitude.

Crystal growth during aging at 25°C was not uniform. Aging of the reaction mixture for even as little as 1 min before elevating the temperature was shown to have the effect of reducing the induction time. Aging the synthesis solution was shown to result in the ultimate for-

mation of more zeolite crystals, most likely due to nucleation at room temperature during aging. Prolonged aging of the prepared solution, between about 7 and 12 h, was shown to increase the crystal growth rate, however, the induction time continued to decrease for all aging times up to 6 days. It was demonstrated also that prolonged aging of the synthesis solution resulted in increased levels of polycrystalline particle formation, probably due to agglomeration of the nuclei during the aging period. That is, with increased aging time, more nuclei formed, and they had more time to agglomerate before growth. The increases in the growth rates with aging time were probably an indication that nuclei had agglomerated, and the growth rate measured by QELSS was the apparent rate of growth of the agglomerate, which was higher because of the increased surface area. This phenomenon probably does not occur in gel systems because the amorphous gel suspends and isolates the crystallites until very near the end of the process when settling of macroscopic single crystals occurs.

The addition of crushed seed crystals to the synthesis solution, of about 162 nm in size, was shown essentially to eliminate the induction time and result in slightly faster growth rate, i.e., 11.27 nm/min with the seeds compared to 4.63 nm/min in the same solution without seeds. Samples grown from the seeded systems also were shown to be polycrystalline aggregates or highly twinned, resembling the samples from aged systems. This observation suggested either that the seeds had agglomerated early in the synthesis, or that their multifaceted texture, due to crushing, had not healed during growth.

Small particulates were observed in the silicate solution before preparing the aluminosilicate synthesis solution. These particulates, ca. 1 nm in dimension, persisted throughout the synthesis, at least in the early stages. Although they may have been the same particles observed by Doktor et al.^{9,10} and Schoeman and Regev,²⁴ we could not determine whether they partici-

Figure 16 (Top) SEM photograph of a product obtained using 162-nm seeds from clear solution at 60°C after 1.75 h. (Bottom) SEM photograph of a product obtained using 162-nm seeds from clear solution at 60°C after 42 min (QELSS exp.).

pated in the synthesis in this study. However, we did observe that the particulates were present in our silicate solutions and not the aluminate solutions.

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