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Study of the effects of initial-bred nuclei on zeolite NaA crystallization by quasi-elastic light scattering spectroscopy and electron microscopy

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

INTRODUCTION

It is common practice to add seed crystals to a molecular sieve zeolite synthesis solution to promote the rate of crystallization and to favor the synthesis of a desired crystalline phase. The mechanism by which seed crystal addition enhances the rate of crystallization has been the subject of several previous reports.^{1–6} In the prior work it has been demonstrated that seed crystal growth alone is not sufficient to rationalize the rate enhancement caused by the addition of seed crystals, but that seed crystals carry with them much smaller entities, which also grow to become macroscopic crystals. These have been labeled “initial-bred nuclei,” have been shown to reside on the surfaces of seed crystals,¹ have been shown to be easily washed off the seed crystal surface,⁴ and have been shown to grow quite separately of the seed crystals in the synthesis solution.⁵

One of the hypotheses regarding the origin of the initial-bred nuclei that were found on the seeds and in the washing solution from these seeds was that these small particles were nonreacted aluminosilicate gel left from syntheses of seeds. It was shown previously^{6,7} that these small spheres form from residual aluminosilicate material, that they can grow, and finally that they form crystals of zeolite NaA; however, this mechanism was developed based on the appearance of the first sample, which was collected after 45 min of crystallization. During this first 45 min of crystallization many events could

have taken place. For example, during the first few minutes gel particles could have dissolved completely, followed by the nucleation of crystals from solution. When the first sample was collected after 45 min, it is possible that the crystallites were larger than the gel spheres added at the beginning of the experiment, making it appear that crystallites had formed from the gel spheres. It also is possible that the aluminosilicate gel spheres contained microcrystalline regions within them, which themselves were the initial-bred nuclei. Therefore, new experiments were conducted with seeding, and this time samples were taken every 5 min during crystallization. It was possible to observe what happened with the aluminosilicate spheres added to the reaction mixture with more frequent sampling.

Light scattering has been demonstrated to be a useful technique for studying the behavior of submicron particles in liquid systems.^{8,10–16} Therefore, quasi-elastic light scattering spectroscopy (QELSS) was used in the study of the behavior of gel particles collected from seeds. It was believed that, using this technique, information about how initial-bred nuclei changed size during crystallization could be obtained. There are a number of ways in which the initial breeding of nuclei can influence the crystallization kinetics. First, the initial-bred nuclei could simply increase in size by consuming solute species, accompanied by gel phase dissolution, and finally zeolite formation. Another possibility is that the gel spheres could contain crystalline material on the order of a few unit cells—insufficient repeat units for detection by electron diffraction—covered by an amorphous layer. When the amorphous layer dissolves, the nuclei then exposed to the mother liquor could grow. It was believed that information about how initial-bred nuclei change size

during crystallization (obtained from QELSS observations) would help to distinguish between these alternatives.

EXPERIMENTAL

Synthesis

Starting materials having the composition $10 \text{ Na}_2\text{O} : 0.2 \text{ Al}_2\text{O}_3 : 1 \text{ SiO}_2 : 200 \text{ H}_2\text{O}$ were prepared from a sodium silicate solution and a sodium aluminate solution, as described elsewhere.⁸ The mixed solution was filtered through SUPOR-200 polysulfone membrane filters having pore dimensions of $0.2 \mu\text{m}$, thus producing a "clear solution," transparent to laser light. After the initial combined solution was prepared, a measured number of seeds was added to 36.7 g of the reaction mixture and was stirred vigorously in 60-ml Teflon flasks, which were used as the reaction vessels. The reaction vessels were heated in the oven at 80°C without further agitation. The precursor seed material was prepared from a gel with an initial batch composition of $0.84 \text{ SiO}_2 : 1.94 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 194 \text{ H}_2\text{O} : 5.5 \text{ TEA}$, which was then heated at 90°C for 1 or 2 days as in Ref. 6. This seed material was X-ray amorphous after one day, but contained about 11% crystalline material in the solid sample after 2 days at temperature.

To investigate the evolution of synthesis over a period of time, reaction vessels were removed from the oven at various times and were quenched immediately. The product of crystallization was filtered, washed, dried, weighed, and prepared for analysis. All samples were analyzed by X-ray diffraction to determine the zeolite phase(s) present.

In cases where gel particles, or seeds of zeolite NaA, were added to the reaction mixture for QELSS experiments, the following synthesis procedure was applied: 0.02 g of solid particles (seeds or gel particles) was placed in Teflon flasks, and 2.05 g of the silicate solution was added to this solid. After 1 min from the addition of the silicate solution, 1.98 g of the aluminate solution was added, mixed, stirred vigorously, and filtered directly into clean glass light-scattering cells through a SUPOR-200 filter ($0.2 \mu\text{m}$). Finally, after 2 min from the addition of the aluminate solution, the scattering cell with the reaction mixture was placed in a thermostated holder (25 , 60 , or 80°C), and 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 the solution at the beginning of the experiments.

Transmission electron microscopy

To investigate the crystallinity within the zeolite synthesized in the light-scattering cell, transmission electron micrographs were made and electron diffraction was measured. For this study a JEOL, JEM-100 C transmission microscope was used. The specimen was prepared by depositing a small amount of the material on a TEM copper grid, which was coated by a carbon film. The deposition of the synthesized particles from the QELSS cell onto the TEM grid was done in the follow-

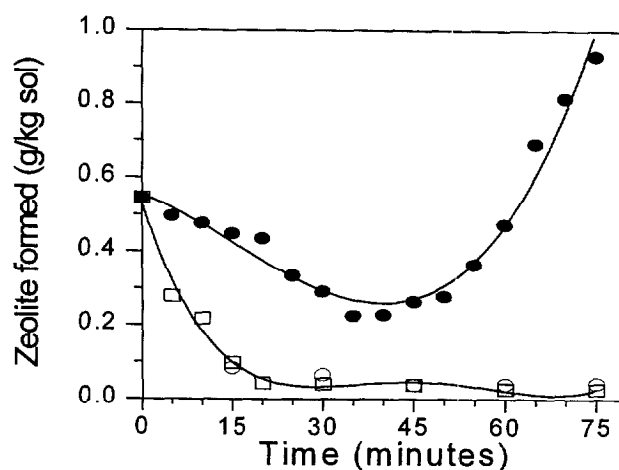


Figure 1 Crystallization of zeolite NaA from clear solution with 0.02 g of seeds synthesized for 1 day (●) at 80°C (sample taken every 5 min); (□), 1-day seeds in NaOH solution at 80°C ; and (○), experiment without seeds.

ing way. First, the sample from the QELSS experiment was filtered and washed through a SUPOR-200 polysulfone membrane with pore openings of $0.1 \mu\text{m}$. The TEM grid was carefully laid on the membrane with the collected particles. A second $0.1\text{-}\mu\text{m}$ membrane was laid on top of the TEM grid. Next, this sample, with the TEM grid between the two membranes, was turned upside down and water was filtered through everything. By using this sample preparation technique, some particles from the polysulfone membrane stayed on the surface of the carbon film covering the TEM grid. Based on an electron diffraction pattern of a gold specimen, the magnification factor for the microscope was found. This factor was necessary for analyzing data.

Infrared transmission spectroscopy

The infrared spectrum in the region of 200 to $1,300 \text{ cm}^{-1}$ is a sensitive tool, indicating structural features of zeolite frameworks. More intense bands in the spectra of zeolite A, around $1,100\text{--}995 \text{ cm}^{-1}$ are assigned to internal tetrahedra vibrations and asymmetric Si-O-T (T = Si or Al) stretching modes. The band around 466 cm^{-1} is attributed to Si-O-T bending modes. Stretching modes involving motions primarily associated with the T atoms, alternately described as symmetric stretching modes, are assigned to a peak at 670 cm^{-1} . The external linkage frequencies occur in two regions of the zeolite A spectrum, 557 and 378 cm^{-1} . These bands are attributed to double-four rings (557 cm^{-1}) and pore opening (378 cm^{-1}).¹⁷

The infrared transmission spectra were obtained using the KBr wafer technique. All samples studied using FT i.r. were dry. A small amount of sample was mixed with potassium bromide and was ground using a mortar and pestle. This mixture was used for making the wafers in a press. A typical wafer concentration was 0.5 mg of zeolite in 500 mg of KBr. Spectra were determined with a Perkin Elmer PE 1600 FT i.r.

QELSS characterization

The behavior of initial-bred nuclei in the reaction mixture was studied using quasi-elastic light scattering

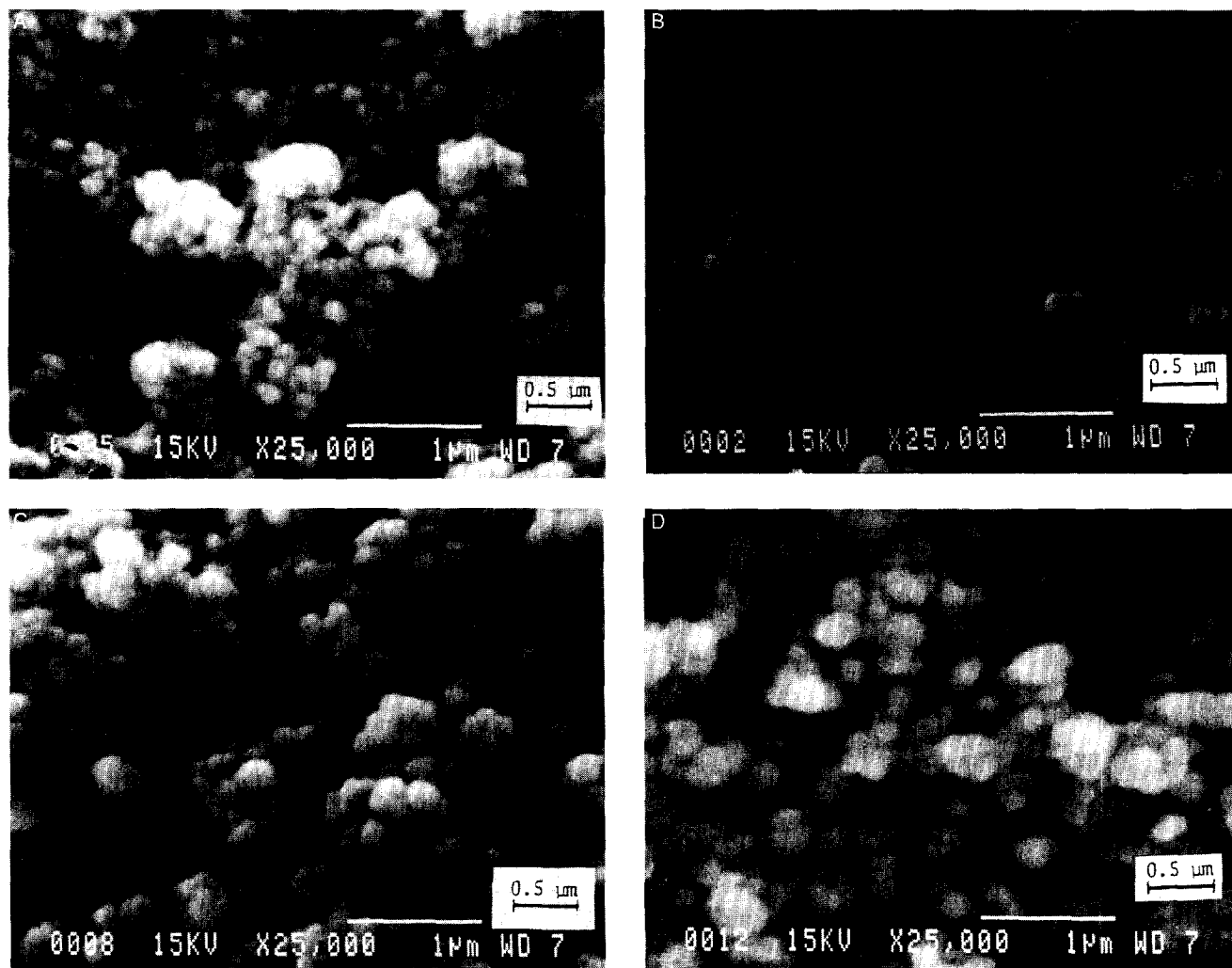


Figure 2 (Continued on facing page)

spectroscopy. QELSS analyses were performed with a 1.2-W argon-ion laser (Physics Series 2000), having a polarized beam with a wavelength of 514.5 nm. Scattered light was monitored by a photomultiplier tube set at 90° to the incident beam. Time-varying signals (photon counts) were analyzed with a 270-channel Brookhaven Instruments model 2030 AT Digital Correlator. Using this technique, information about how initial-bred nuclei change size during crystallization could be obtained. More details of the technique were reported previously.⁸

RESULTS AND DISCUSSION

In *Figure 1* the amount of zeolite A formed with 0.02 g of "1-day" seeds is plotted as a function of time (data was collected every 5 min up to 75 min). *Figure 1* shows that initially the amount of solid material decreased and then increased after 40 min of crystallization. The phenomena taking place in the reaction mixture with the presence of gel spheres were easier to understand when photographs of the solid samples were taken. The sequences of photographs *Figure 2* show that particles changed size during this process. At the same time the number of these spheres decreased (*Figure 1*). These

data clearly show that within the first 40 min some gel material dissolved and that the smallest particles dissolved faster than larger ones. The reason why particles in successive photographs appear larger may be that while the smallest particles were dissolving, the larger ones were growing by an Ostwald ripening mechanism.

One reasonable explanation for the growth of the large particles can be the precipitation of aluminosilicate on the surface of the gel particles. However, the photographs in *Figure 2* also show that the particles formed agglomerates. It was reported previously that in unstable aqueous colloidal dispersions, the large interfacial free energy associated with small particles is a driving force to reduce the total precipitate surface area by a secondary growth process called ripening.^{18,19} Ripening can occur by the dissolution of smaller particles and the growth of large ones (Ostwald ripening¹⁹) or by coagulation or aggregation combined with crystallization.²⁰ The same initial-bred nuclei (the 1- or 2-day-old seeds) added to an NaOH solution, having the same NaOH concentration as the batch composition of the synthesis solution, dissolved completely at 80°C within 15 min. Complete dissolution also occurred within 15 min when initial-bred nuclei were added to an aluminate-free silicate or a silicate-free

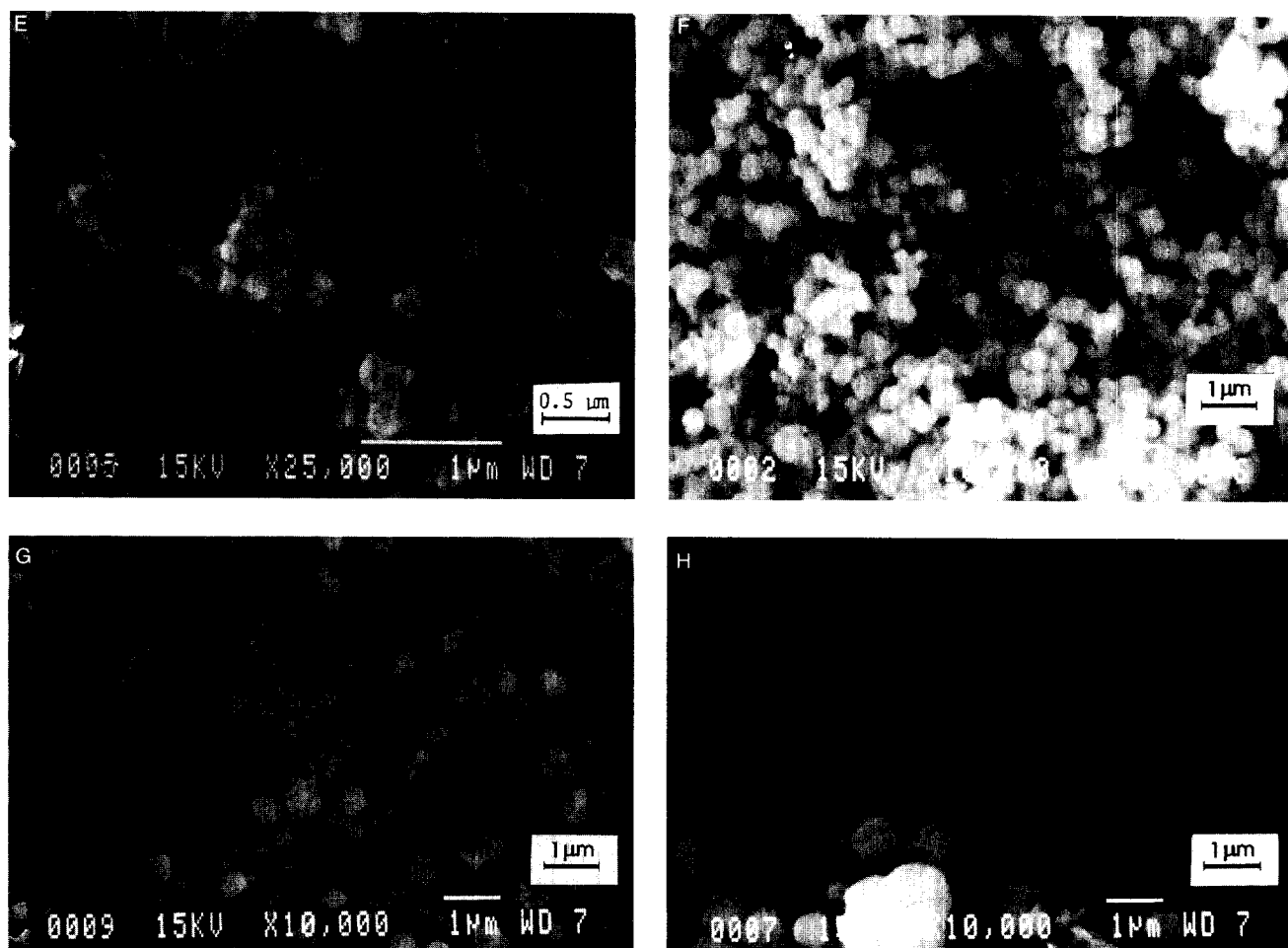


Figure 2 SEM photographs of product obtained using 0.02 g of 1-day seeds. (A) 5 min; (B) 10 min; (C) 15 min; (D) 30 min; (E) 35 min; (F) 40 min; (G) 45 min; and (H) 55 min.

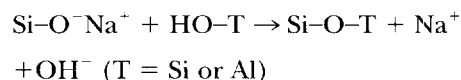
aluminate solution having the same concentration (including the NaOH) as the reaction mixture. These data show that the gel particles (initial-bred nuclei) were more stable in the reaction mixture, because crystal growth occurred in the complete synthesis solution, whereas dissolution occurred in any of the parts of the synthesis solution. Thus, aluminosilicate anions were required for growth, whereas the aluminate or silicate anions separately did not prevent the rapid dissolution of these particles.

The solid samples collected every 5 min also were investigated by infrared spectroscopy. Figure 3 shows *FT* i.r. spectra of the solid product obtained using 0.02 g of "1-day seeds." The last spectra on Figure 3 present data collected from a zeolite NaA standard. The *FT* i.r. spectrum of standard of zeolite NaA does not show the pore-opening band, because it was beyond the spectrophotometer's operating range. The *FT* i.r. spectra of the solids obtained up to 40 min of crystallization do not show features characteristic of zeolite NaA.

The peak positions at about $1,000\text{ cm}^{-1}$ (asymmetric stretching) show little shift. The shift in the symmetric stretching is larger between 1-day seeds (before addition to the reaction mixture) and the sample collected after 5 min of crystallization. After 15 min of crystallization, the position of the peak essentially did not

change. It is well known that stretching frequencies increase with a decrease in the amount of structural aluminum.¹⁷ Therefore, the aluminum from solution was incorporated into the solid phase quickly after pouring the gel material into the reaction mixture.

This observation agrees with the observations of Ginter et al.^{21,22} They reported that the dissolved aluminum immediately adsorbs onto the surface of the solid silica particles. A broad Si-O-T bending ($T = \text{Si or Al}$) can be observed at 450 cm^{-1} in addition to a broad band at 720 cm^{-1} . As the reaction proceeded from 0 to 50 min the band at 450 cm^{-1} narrowed and shifted to about 466 cm^{-1} (Si-O-T bending modes). The band at 720 cm^{-1} disappeared, and a peak at 670 cm^{-1} appeared (Si-O-T symmetric stretching). After 40 min of crystallization, the band associated with the four-membered ring appeared (557 cm^{-1}). The absorption band near 870 cm^{-1} is assigned to an Si-OH bending vibration, which decreased as the crystallization of NaA proceeded. Disappearance of the OH group from gel particles can be explained by the condensation reaction¹⁸:



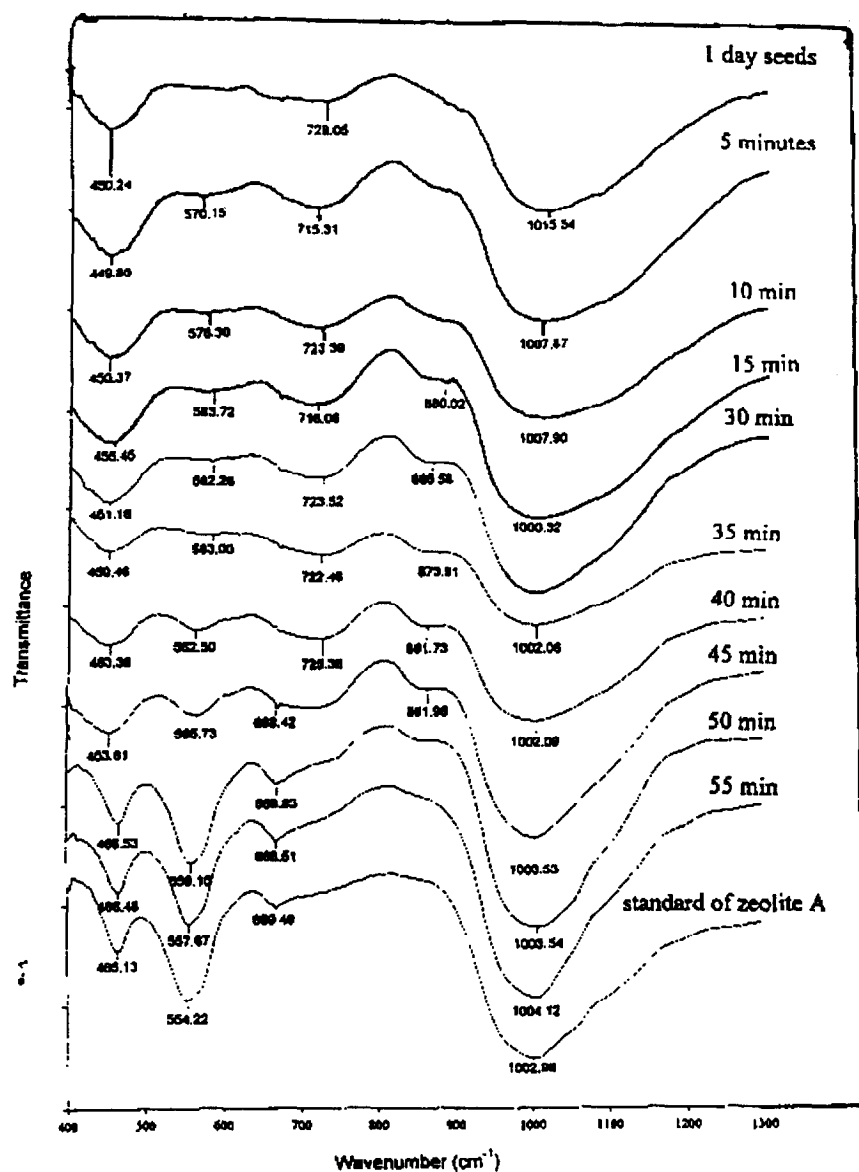


Figure 3 Transmittance FT i.r. spectra of solid phase in zeolite NaA synthesis in the experiment with the addition of 0.02 g of seeds (1-day seeds), in reaction mixture with molar composition 10 Na₂O : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O.

Study of initial-bred nuclei using QELSS

Each sample for these experiments was prepared by mixing 0.02 g of "2-day seeds" with approximately 4 g of the standard reaction mixture, which was then filtered directly into a glass light-scattering cell through a 0.2- μ m membrane. Using the 0.2- μ m membrane allowed only about 0.005 g from the 0.02 g of seeds to pass through to the reaction cell. Assuming that all the gel dissolved, the concentrations of Si and Al would not change much, the concentration of SiO₂ would increase 0.9% (0.2 mg) and the concentration of Al would increase 2.3% (0.2 mg). It seemed unlikely that the increase in the concentration of these components in the reaction mixture would cause the nucleation of new crystals. However, assuming that nuclei are on the order of 10 nm in size, only 1.85×10^{-12} g of Al and 1.03×10^{-11} g of SiO₂ are needed to form them from 4 g of reaction mixture. To check the stability of initial-bred nuclei at the reaction temperature, an experiment was conducted where gel particles were added to water at 80°C and were continuously monitored

with QELSS. Even though only about 0.005 g of gel material was in the reaction mixture, that small mass of initial-bred nuclei was easy to observe by QELSS. During the first 3 min, when the temperature in the cell was not uniform, it was not possible to see these particles because of convection flow in the reaction mixture. However, as soon as the temperature in the cell became uniform, sufficient light was scattered from the initial-bred nuclei in the solution. Gel particles were stable in H₂O at 80°C. Even after 58 h it was still possible to observe these species, but the intensity and signal-to-noise ratio decreased compared to readings collected during first few hours. The size of the gel particles did not change (*Figure 4*), nor did the particles agglomerate. When these particles were put into NaOH solution, silicate solution, or aluminate solution at 80°C, they dissolved immediately. These observations agreed with those from macro-scale experiments, except that the smaller individual particles dissolved more quickly in the cuvette compared to the larger agglomerated particles used previously. When the

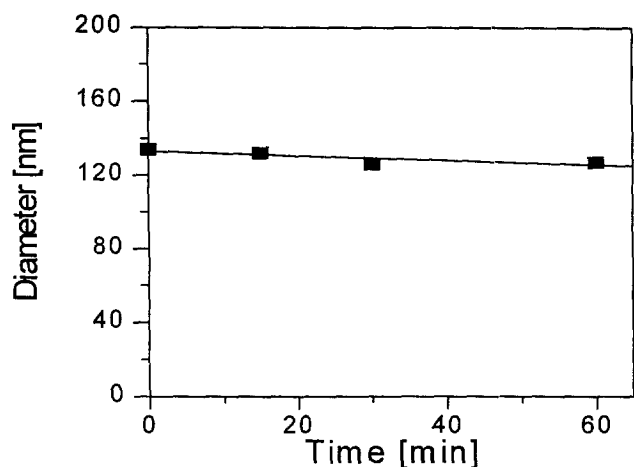


Figure 4 Behavior of gel particles in H₂O at 80°C.

solution was filtered, only individual particles (~130 nm) were present in the solution; these separate particles dissolved more readily than did larger ones. In the next step of the study, initial-bred nuclei from "2-day seeds" were put into the reaction mixture. Experiments were conducted at three different temperatures: 25, 60, and 80°C. As before, when gel particles were studied in hot H₂O after the temperature in the cell became uniform, abundant light was scattered from the reaction mixture containing the initial-bred nuclei. It was easy to fit the spectra well, with two or three cumulants.

Figure 5 illustrates the effect of addition of the initial-bred nuclei on the kinetics of crystallization. There was a noticeable difference in the behavior of the system with the addition of gel particles and without. According to QELSS, the size of the product was considerably enhanced by an addition of gel particles. The product obtained using gel particles after 44 h of crystallization contained a wide spectrum of particle sizes, as shown in Figure 6. The smallest particles in the picture are about

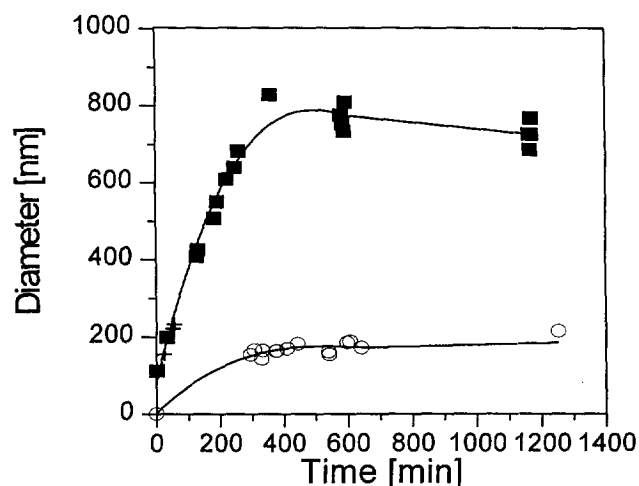


Figure 5 QELSS size determination of product obtained from clear solution at 25°C with the initial addition of gel particles (125 nm). Composition of the reaction mixture Na₂O : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O. (■, +), with addition gel particles; (○), without addition.

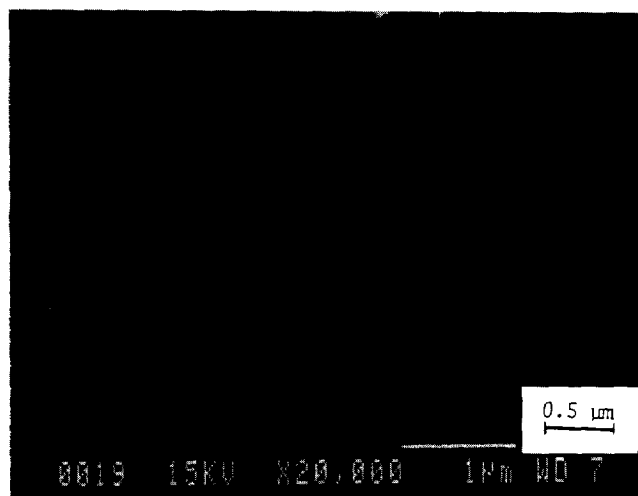


Figure 6 SEM photograph of product obtained using 125-nm gel particles, from clear solution at 25°C after 44 h of crystallization.

150 nm. The largest particles have a size of about 1 μm in diameter and look like agglomerates of small particles. During the first 5 h of the process, the size of the particles increased linearly. The first measured point, 130 nm, corresponds to the size of gel particles added at the beginning of the process to the reaction mixture. This linear increase in the size of particles present in the system indicated that gel particles did not dissolve in the reaction mixture but, rather, did the opposite: they grew. This growth, as reported previously,⁸ was due to agglomeration and a build-up of aluminosilicate species on their surface. Harvey and Glasser,²³ based on a study of the gelation behavior of aluminosilicate solutions, concluded that in a solution containing a mixture of silicate species, aluminum preferentially complexed with larger species almost immediately. An increase in the pH of such solutions resulted in the cleavage of Si–O–Si bonds, whereas

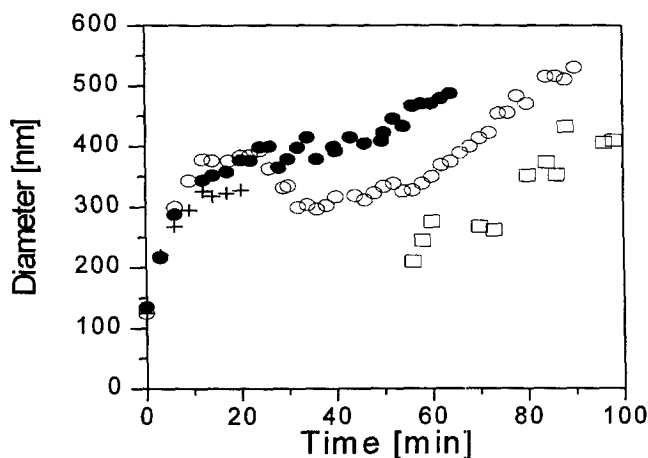


Figure 7 QELSS size determination of zeolite NaA growing in clear solution at 60°C with an initial addition of gel particles (125 nm). Composition of reaction mixture 10 Na₂O : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O. (□), without addition of gel particles; (●, ○, +), with addition of gel particles (experiments 1, 2, and 3).

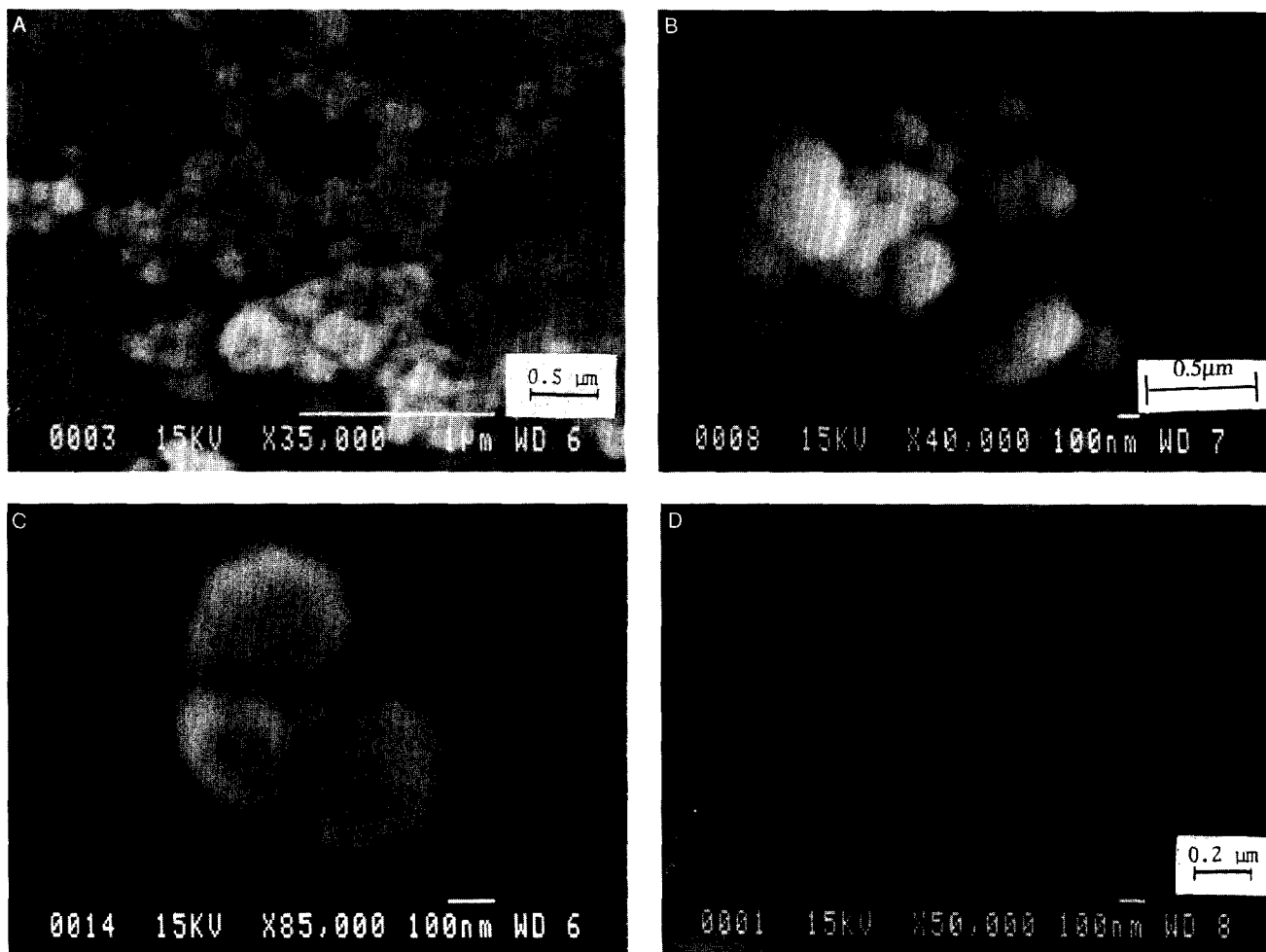


Figure 8 SEM photographs of product obtained using 125-nm gel particles, from clear solution at 60°C. (A) 20 min (QELSS exp.); (B) 30 min (QELSS exp.); (C) 42 min (QELSS exp.); and (D) 64 min (QELSS exp.).

Si-O-Al bonds are resistant to cleavage under alkaline conditions and so, once formed, are stable. After the initial binding of silicate species with aluminum, gel particles grew slowly by the addition of silicate species from

solution. It was concluded that aluminum acted as a cross-linking agent in the condensation of poly-alumino-silicates.²³ Iler¹⁸ lists several examples where the addition of even very small amounts of aluminum reduces the

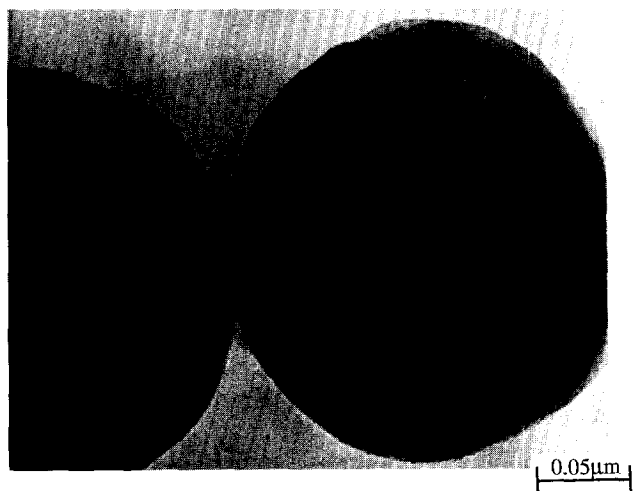


Figure 9 TEM photograph of product obtained using 125-nm gel particles, from clear solution at 60°C after 64 min of crystallization.

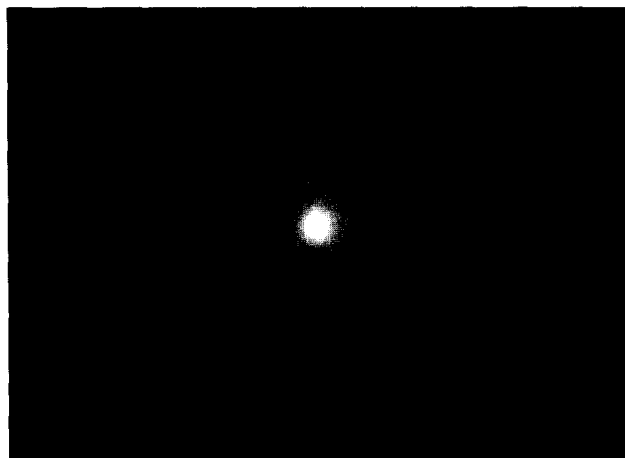


Figure 10 Electron diffraction pattern of product obtained using 125-nm gel particles, from clear solution at 60°C after 64 min of crystallization (see figure 9).

Table 1 Electron diffraction data for the synthesized zeolite NaA, compared to literature X-ray powder diffraction data. Sample from an experiment with gel particles, and 64-min crystallization time

h k l	Experiment with addition of gel particles to reaction mixture d(Å)	Breck ²⁴ d(Å)
410, 322	3.064	2.987
420	2.758	2.754
332	2.627	2.626
441	2.121	2.144

dissolution of silica considerably, consistent with effects arising from surface modification of the silica particles.

The electron diffraction pattern (for a sample synthesized for 44.5 h at 25°C) shows the presence of one very broad and weak circle. When a temperature of 60°C was applied, periods of different growth rates were observed, as shown in *Figure 7*. Up to 30 min of crystallization the size changed relatively rapidly, whereas beyond 30 min the size increased more slowly. This behavior was consistent with two processes, which can occur simultaneously, namely, the dissolution of small particles and the growth of large particles. The variance (second cumulant) of the spectrum was quite small, consistently at about 30, indicating that scattering was dominated by particles in a single size range (namely, the group of particles that were the largest, although still accounting for a substantial part of the zeolite mass), that these particles grew rapidly at first and slower later on, but that all grew at about the same rate.

When the synthesis was carried out without the addition of gel particles, the product started to form later than when gel particles were added. This was the next indication that gel particles enhanced the nucleation process. Scanning electron micrographs for samples collected after 20, 30, 42, and 64 min of crystallization are shown in *Figure 8*, which confirmed the QELSS observation about the behavior of the system. The product ob-

tained at 30 min of crystallization represented aggregates and single particles that were larger than those present in the reaction mixture at 20 min. Particles synthesized at 64 min were almost perfect spheres, having a uniform size of 480 nm. To investigate the crystallinity within the zeolite synthesized in the QELSS cell, the transmission electron micrographs and the electron diffraction were measured (*Figures 9 and 10*). The electron diffraction showed concentric circles, indicating crystallinity. This powder pattern is really a large number of single crystal diffraction patterns, each rotated by a small amount with respect to each other. The *d*-spacing values for four diffraction circles in the diffraction pattern were calculated and were compared with the values from powder X-ray diffraction of zeolite NaA reported in the literature (*Table 1*). The calculated *d*-spacing values are in reasonable agreement with the values from the X-ray diffraction data. It was difficult to prepare samples for TEM from the product obtained at shorter times of crystallization, due to the small amount of sample precipitated at that time. The presence of gel particles at all times during the process (*Figure 7*) suggests that crystallization starts in or on the growing amorphous gel particles. Some of the gel particles added at the beginning dissolved, whereas some increased in size by the aggregation or condensation of aluminosilicate species. Before crystallization began, some kind of reorganization in the remaining gel particles took place. It is plausible that some of the gel particles contained crystalline domains that began to grow after the dissolution of their amorphous cover.

Increasing the reaction temperature to 80°C eliminated the presence of two regions of different crystal growth rates, due to the acceleration of all processes at higher temperatures. The growth rate was constant over the entire synthesis time. However, in this case two populations of crystals formed. *Figure 11* shows two samples obtained at about 44 min of crystallization, and it clearly shows the two crystal populations. Comparing these results to experiments without the initial addition of gel particles, crystals formed with a bimodal size

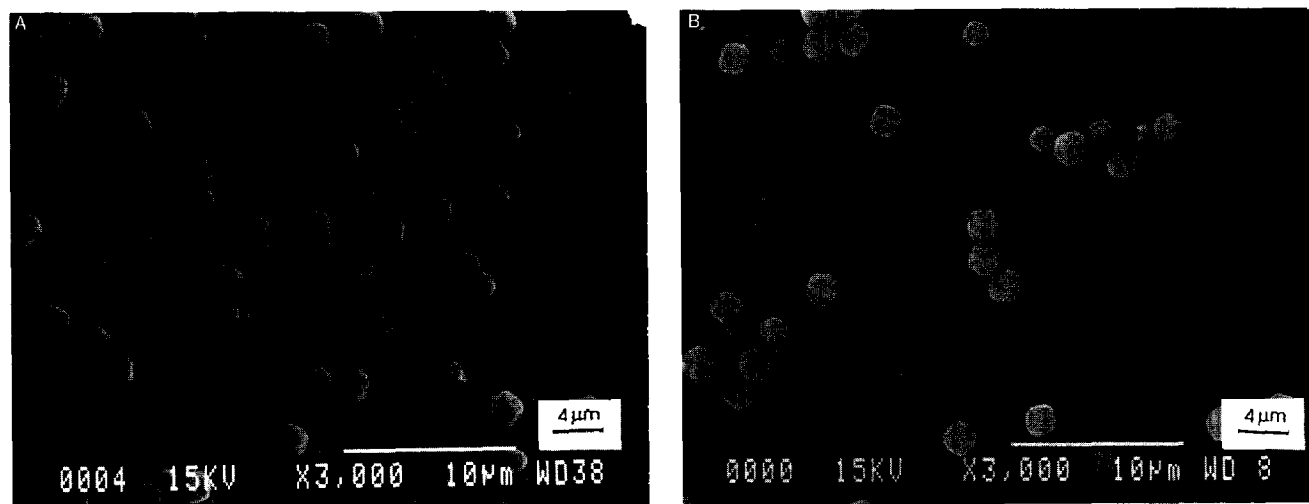


Figure 11 SEM photographs of product obtained using 125-nm gel particles, from clear solution at 80°C. (A) 43 min (QELSS exp.); (B) 44 min (QELSS exp.).

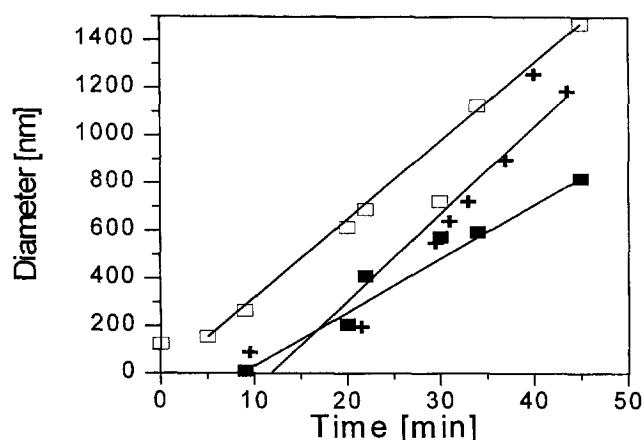


Figure 12 QELSS size determination of zeolite NaA growing in clear solution at 80°C with the initial addition of gel particles (125-nm). Composition of reaction mixture 10 NaO₂ : 0.2 Al₂O₃ : 1 SiO₂ : 200 H₂O. (+), without the addition of gel particles; (□), first population of crystals; and (■), second population of crystals.

distribution when gel particles were added, whereas only one population formed without gel addition. Both crystal populations grew at constant, but slightly different, rates (Figure 12). However, one must be very careful with the type of QELSS data shown in Figure 12, inasmuch as data from a bimodal population can easily be misinterpreted. Much more light was scattered from the sample where gel particles were added at the beginning than from samples without the addition, due to the much higher concentration of particles in the system when gel particles were added. The data in Figure 12 represent an average of all particles present.

CONCLUSIONS

Syntheses were carried out at 25, 60, and 80°C using a clear sodium aluminosilicate solution that precipitated zeolite NaA. Seeds were added to some syntheses in the form of dried aluminosilicate gel particles, which had been reacted separately for 1 or 2 days using another batch composition that formed a gel phase before crystallization. The seed material that had been reacted for 1 or 2 days showed 0 or 11% crystallinity, respectively. Analysis by powder X-ray diffraction showed that zeolite NaA was the only phase present in all of these experiments.

The seed material, largely amorphous particles according to X-ray analysis, were found to dissolve completely within 15 min in an NaOH solution, a silicate solution, and an aluminate solution, each having the same partial composition as that part of the complete synthesis solution. The dissolution was even faster in a QELSS cuvette than in those experiments, because the solution was filtered and the individual particles were smaller than the aggregates in the unfiltered solution.

Despite the filtration of the reaction solutions before synthesis, particulates on the order of 130 nm were observed in the filtrate after gel particles were added. These particulates were initially observed to shrink in size, and then to grow with increased time at reaction tempera-

ture. These particulates contributed to the faster crystallization rate and larger crystal mass precipitated after gel particles were added. The added gel particles made only a small change in the solute concentrations, so it is unlikely that a concentration change caused a burst of nucleation. Rather, it is likely that initial-bred nuclei were associated with the gel particles, either inside the particles or on their surfaces, and that these initial-bred nuclei grew in the sodium aluminosilicate solution after the amorphous part of the gel particles dissolved.

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