8-1993

Formation of Bimodal Zeolite Crystal Populations from Clear Synthesis Solutions

Aimee A. Brock

Gregory N. Link

Peter S. Poitras

Robert W. Thompson
Worcester Polytechnic Institute, rwt@wpi.edu

Formation of Bimodal Zeolite Crystal Populations from Clear Synthesis Solutions

Aimee A. Brock, Gregory N. Link, Peter S. Poitras and Robert W. Thompson*
Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA

Several recent reports on molecular-sieve zeolite synthesis from clear aluminosilicate solutions have indicated that bimodal crystal-size distributions were produced. This curious result was attributed to agitation or heterogeneous nucleation in one case. It is suggested by results presented here that bimodal crystal-size distributions may be the result of ageing the clear solutions at room temperature.

Molecular-sieve zeolites are crystalline aluminosilicates having very regular pore structures of molecular dimensions, which are used extensively for catalysis, ion exchange, drying, and adsorption separations. As many as 150 different natural and synthetic molecular-sieve zeolites are known. Most commercial zeolites are synthesized in basic media by mixing appropriate amounts of aluminates, silicates, water, and other additives. NaOH is commonly used to provide the basicity and the solvating environment for the solution-mediated transformation process.

Most frequently, an amorphous aluminosilicate gel is formed immediately upon mixing the reagents. However, it is of some fundamental interest that several syntheses can be carried out in the absence of the amorphous gel phase, i.e. in solutions sufficiently dilute that all of the aluminosilicates dissolve initially. Such systems permit one to observe nucleation and growth rates without interference from the turbid (or opaque) gel phase, and to separate gel dissolution from the other kinetic aspects of the process. In principle, in such systems crystals should nucleate and begin to grow, and the process should terminate as the supersaturation is relieved by the consumption of the dissolved reagents onto the growing crystal surfaces. At 'equilibrium' the crystal population should remain intact, barring any Ostwald ripening or transformation to other more stable phases.

Recently, two reports of the synthesis of bimodal crystal populations from clear aluminosilicate solutions have appeared.[1,2] The curious aspect of these experimental results is that after nucleation and crystal growth had commenced a second population of crystals was nucleated at some later time. One must question what driving force precipitated the formation of the second population, and, if there was sufficient driving force to precipitate a second population, why the first nucleation event ceased. In one report it was suggested that either secondary nucleation catalysed by agitation of the first population of crystals or the late release of hetero-nuclei caused the second burst of nuclei to form.[1]

While these explanations are plausible, it will be suggested here that the simple effect of ageing the solution prior to hydrothermal treatment is sufficient to produce a bimodal crystal population in some instances.

Several syntheses of the zeolite, analcime, were carried out according to the hydrothermal conditions used by Di Renzo et al.[2] The batch composition used was given by the following molar oxide ratios: $SiO_2{:}Al_2O_3 = 84$; $Na_2O{:}Al_2O_3 = 87$; $H_2O{:}Al_2O_3 = 2560$. In these experiments, NaOH was dissolved in the deionized water, followed by addition of $NaAlO_2$, and finally the silica source, Cab-O-Sil (fumed silica, Cebot). Solutions were stirred at room temperature until clear, ca.

4 h. The syntheses were carried out without stirring in Teflon-lined sealed autoclaves (8 cm³ total volume) placed in ovens at 150 °C. Autoclaves were removed after 65 h of heating, and quenched. The crystalline product was isolated by filtration, washed with deionized water, and oven dried at 80 °C overnight. Syntheses were carried out using fresh solutions, the same solutions aged at room temperature for 10 days (as for Di Renzo's procedure, due to launch protocols), and the same solutions aged for 20 days.

The crystalline phase was determined to be analcime by powder X-ray diffraction. No other crystalline phases were detected by X-ray diffraction. The character of the particulate product and the nature of the crystal size distribution were observed by scanning electron microscopy.

Fig. 1(a) and (b) show samples from duplicate syntheses conducted as noted without ageing of the solutions. Analcime was observed to be the dominant crystalline material in photographs of all samples in this study. The acicular material seen in Fig. 1(b) was observed only in some areas of sample 13, and was present in sufficiently small mass, relative to the population of large analcime crystals, that it was not detected by XRD. The analcime crystals were ca. 55–60 μm in dimension, and it is observed that all crystals were about the same size, suggesting that one nucleation event occurred. The formation of a monodisperse crystal size distribution would be expected from a clear solution synthesis in the absence of secondary nucleation caused by stirring, i.e. consistent with these results, since stirring was not employed.

Fig. 2 and 3, show SEM photomicrographs of samples synthesized after 10 and 20 days ageing at room temperature, from the same solution as that used in experiment 11 without ageing. It is observed that a bimodal crystal size distribution was produced in both cases, suggesting that two nucleation events occurred in the syntheses after ageing the solution at room temperature. The particle dimensions of the two crystal populations after 10 days ageing were ca. 6–8 and 25–30 μm. After 20 days ageing the two populations were ca. 4 and 8 μm. The formation of a bimodal size distribution is consistent with the results of Di Renzo et al.[2]

The reason for the apparent agglomeration of the two distinct populations shown in Fig. 2 is uncertain at this time, but these results do suggest that the two populations settled as ensembles of particles, but at different times. This observation suggests that the crystal populations were formed at different times. The same phenomenon was observed from a solution which had been aged for 2 months prior to heating at 150 °C, but not from the solution aged for 20 days.

The question of why the bimodal crystal size distribution formed must be addressed. First, no agitation was employed

(a)

⊢—⊣ 10 μm

(b)

⊢————⊣ 100 μm
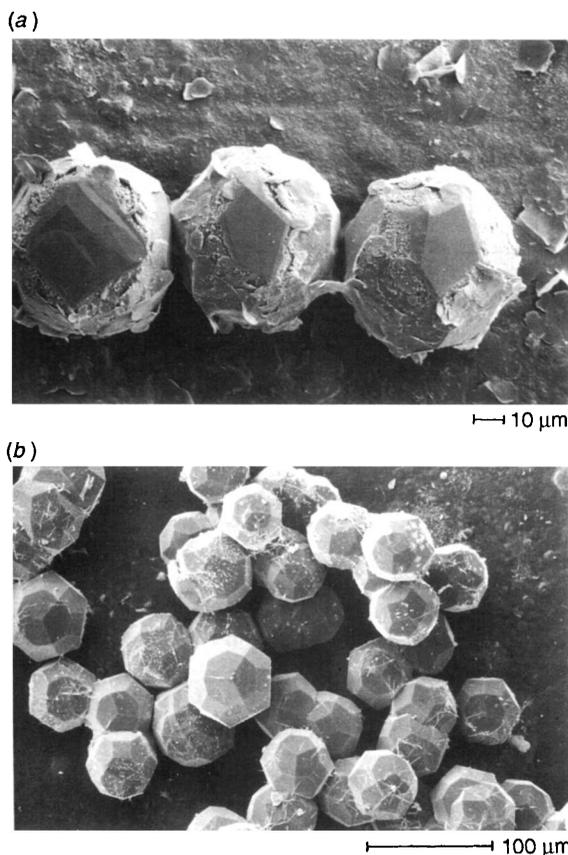
Fig. 1 (a) SEM photomicrograph of analcime crystals from experiment number 11. Synthesis solution mixed for 4 h at room temperature until clear, then heated immediately at 150 °C for 65 h. (b) SEM photomicrographs of analcime crystals from experiment 13, a duplicate of experiment 11. Synthesis solution unaged, as in experiment 11.

⊢——⊣ 10 μm
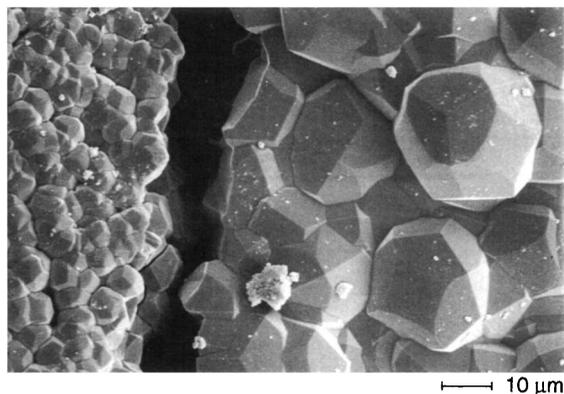
Fig. 2 SEM photomicrograph of analcime crystals from experiment 11, but heated at 150 °C for 65 h after clear synthesis solution aged at room temperature for 10 days

⊢——⊣ 10 μm
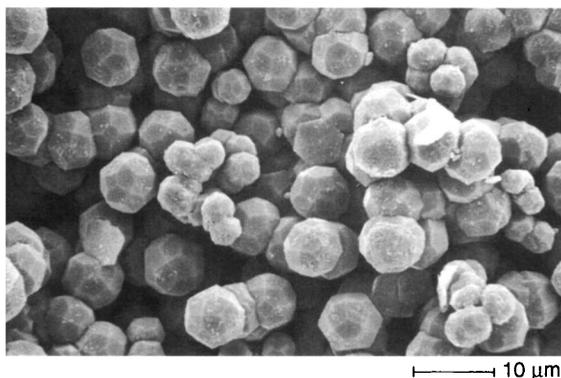
Fig. 3 SEM photomicrographs of analcime crystals from experiment 11, but heated at 150 °C for 65 h after clear synthesis solution aged at room temperature for 20 days

in these experiments, and, therefore, secondary nucleation due to mechanical forces and microattrition can be ruled out. Secondly, if the second population had resulted from a heterogeneous nucleation mechanism, occurring at reaction temperature, the unaged solution should have formed a bimodal crystal size distribution also, since the same solution was used in all three syntheses. This suggests that the bimodal size distribution due to heterogeneous nucleation also must be ruled out. Formation of a population of nuclei during the ageing step itself appears to be the most logical explanation for these results, since that was the only variable examined in these experiments.

It was demonstrated previously that nucleation and crystal growth of zeolite NaA to essentially complete conversion occurred at room temperature over ca. 30 days.[3] Thus, it is not unreasonable to suggest that some nucleation and growth occurs in zeolite systems at lower temperatures over shorter time periods. It also was noted previously by Bronic et al.,[4] that a bimodal crystal size distribution formed when zeolite NaA gel mixtures were aged for various periods of time (see their Fig. 4). It is noted as well that the bimodal crystal size distributions of silicalite were formed from solutions aged at room temperature for 7 days.[1]

The ageing step prior to zeolite crystallization at elevated temperatures also is noted to result in smaller final crystal sizes.[4] This effect previously has been asserted to be due to nuclei formation during the ageing step. The results shown here are consistent with that hypothesis, since the final size of analcime crystals formed after ageing has been shown to be smaller than those formed without ageing.

The results of this investigation suggest that some nuclei formed at room temperature during the ageing of the prepared solutions. Nucleation of a second population of crystals occurred at elevated temperature, while those nucleated at room temperature had already commenced growing, even during the heat-up phase. Thus a bimodal population forms when solutions are aged, but not when the synthesis is carried out with freshly prepared (unaged) solutions.

While the results noted here do not prove that bimodal crystal size distributions are formed as a result of the ageing step, the evidence points toward the ageing step as being a common factor in those experiments cited in which bimodal size distributions formed.

It also is noted that Di Renzo et al. synthesized analcime, mordenite, gismondine and zeolite-β aboard the CASIMIR-1 flight, and that only the analcime synthesis resulted in a bimodal size distribution. Undoubtedly, the relative magnitudes of the temperature-dependent nucleation and growth steps must be just right for this effect to be manifested. For this reason, ageing of zeolite synthesis solutions cannot always be expected to produce bimodal crystal size distributions.

References

1 C. S. Cundy, B. M. Lowe and D. S. Sinclair, *J. Cryst. Growth*, 1990, **100**, 189.
2 F. Di Renzo, R. Dutartre, P. Espiau, F. Fajula, and M-A. Nicolle, *Crystallization of Zeolites in the Microgravity Environment of Space*, Eighth European Symposium on Materials and Fluid Sciences in Space, Brussels, April, 12–16, 1992, ESA SP-33, pp. 691–695.
3 L. B. Sand, A. Sacco Jr., R. W. Thompson and A. G. Dixon, *Zeolites*, 1987, **7**, 387.
4 J. Bronic, B. Subotic I. Smit, and L. J. A. Despotovic, in *Innovation in Zeolite Materials Science*, ed. P. J. Grobet, W. J. Mortier, E. F. Vansant and G. Schulz-Ekloff, Elsevier, Amsterdam, 1987, vol. 37, p. 107.