Synthetic Zeolites: Growth of Larger Single Crystals

Abstract. *Synthetic zeolites 4A, P, and X were grown in acrylic gel to a size suitable for study of single crystals by x-ray diffraction.*

Crystallographic studies of synthetic zeolites have been impeded by the lack of sufficiently large crystals. When the zeolites are prepared by the usual methods, they normally grow to 5 to 10 μ in size. For single-crystal x-ray diffraction work, a size of at least 50 to 100 μ is required. We have grown synthetic zeolites of such size by a method described by Henisch, Dennis, and Hanoka (*1*); it is illustrated by the following example.

A gel was formed by dissolving, in a Waring blendor, 5 g of Carbopol 934 (*2*) in 100 cm^3 of 1N sodium hydroxide solution. A portion of the gel was poured into a ½-inch (12.5-mm) diameter Tygon tube bent to an O-shape (Fig. 1). Aqueous slurries of sodium disilicate nonahydrate and sodium aluminate were poured into opposite ends of the tube, leaving a 30-cm long interdiffusion path through the Carbopol gel. The tube was pinched at both ends by means of hose clamps, sealed with a soldering iron, and placed in a water bath kept at 80° to 90°C. After about 2 weeks, the tube was cut into sections and their contents were washed into a 2-liter beaker; water was added to make the total volume about 1.5 liters. The slurry was stirred for from 30 minutes to 1 hour and allowed to settle before the supernatant was decanted. The procedure was repeated two or three times until only crystalline aluminosilicate was left.

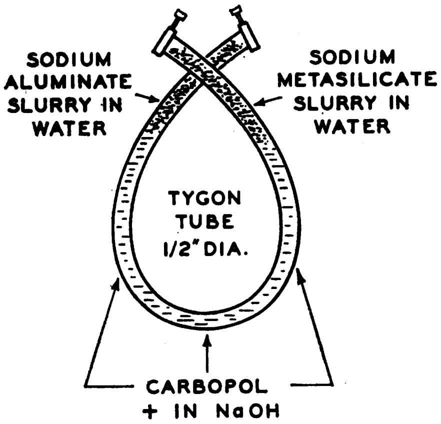

Fig. 1. Gel tube used for preparation of zeolitic crystals.

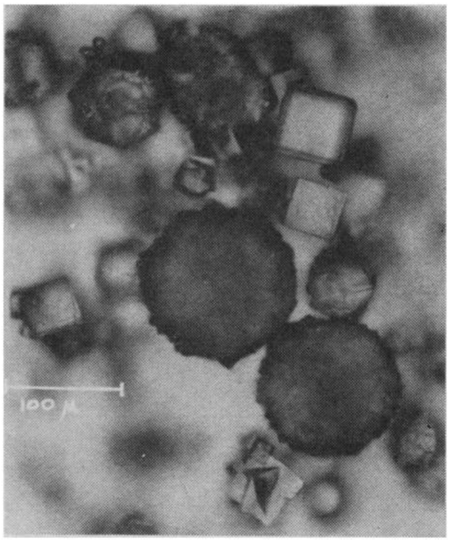

Fig. 2. Barrer species P spherulites and Linde-4A cubes grown in Carbopol gel.

The crystals were examined by optical microscope and by x-ray diffraction methods. Figure 2 shows 110-μ spherulites of Barrer species P and 60-μ cubes of Linde-4A molecular sieve. Hexagonal prisms of gibbsite, 250 μ in diameter and smaller, were also observed in the same batch but do not appear. The largest single 4A crystal that we have yet obtained was 75 μ in size. X-ray diffraction, single-crystal, rotation patterns show sharp reflections characteristic of an excellent single crystal. Acrylamide gel was tried without success, probably because the gel decomposed in the caustic medium.

Other crystallizations were carried out in Carbopol gel, with pyrex glass used instead of Tygon tubes. Three definite zones were identified, each of which contained the zeolitic species expected from the local composition. The 4A crystals in the aluminate-rich zone were numerous and small, probably because of the reaction between solution and glass silica. Faujasite crystals in the middle zone were well-formed octahedra up to 40 μ in size. Polyhedra of Barrer species P up to 150 μ in size were found in the silica-rich zone, but one could not determine whether they were single or twinned crystals.

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References and Notes

1. H. K. Henisch, J. Dennis, J. I. Hanoka, *J. Phys. Chem. Solids* **26**, 493 (1965).
2. Soluble acrylic acid polymer; B. F. Goodrich Chemicals Co.
3. Obtained by D. Olson, Central Research Division, Mobil Oil Corp.

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Clathrate Hydrates of Some Amines

Abstract. *A crystallographic study of some alkylamine hydrates establishes that these are polyhedral clathrate hydrates. While the simpler alkylamines form hydrates with water structures related to those of the gas hydrates or the alkylonium salt hydrates, the diethylamine and* tert-*butylamine hydrates have water frameworks forming cages which have not previously been observed in the clathrate hydrates.*

The simpler alkylamines form crystalline hydrates which melt between +5° and −35°C (*1*). The stoichiometry of some of these has led to the suggestion (*2*) that they are clathrate hydrates with water framework structures based on or derived from those found in the gas hydrates or alkylonium salt hydrates. In order to obtain structural evidence concerning the nature of interactions between the amine and water, we have examined the x-ray diffraction data of nine of these hydrates and have carried out complete crystal-structure determinations on two of them. Our results support the inclusion of these compounds in the general class of polyhedral clathrate hydrates and reveal novel geometrical features of water frameworks not previously observed.

The hydrates of ethylamine and dimethylamine (m.p. −7.5° and −16.9°C, respectively) have cubic lattices of dimensions and symmetry which are characteristic of the 12-Å cubic gas hydrates such as $6Cl_2 \cdot 46H_2O$ (*3*). The trimethylamine, *n*-propylamine, and isopropylamine hydrates (m.p. 5.3°, −13.5°, and −4.2°C, respectively) crystallize in hexagonal structures similar in dimensions and symmetry to that of the pseudohexagonal alkylonium salt hydrate $(iso\text{-}C_5H_{11})_4N^+ \cdot F^- \cdot 38H_2O$ (*4*). In these hydrates, the amine molecules appear to enter the water frameworks of the gas hydrates without disrupting their basic structural patterns. Other amine hydrates examined include two hydrates of diethylamine (m.p. −6.6° and −7.0°C), one of *tert*-butylamine (m.p. −1°C), and a second hydrate of *n*-propylamine (incongruently melting). Since these have crystal lattices which are basically dissimilar to those of the clathrate hydrates generally known, complete structure analyses have been carried out on two of them, namely $(C_2H_5)_2NH \cdot 8.67H_2O$ which is orthorhombic, and $(CH_3)_3CNH_2 \cdot 9.75H_2O$ which is cubic. Both these structures are polyhedral clathrate hy-