NAG8-[illegible]
IN-76-CR

WORCESTER POLYTECHNIC INSTITUTE

"Growth of Large Zeolite Crystals in Space"

A. Sacco, Jr., A. Dixon, R. Thompson, G. Scott and J. D'Itr

Introduction

An increase in the average crystal size of the product is observed when triethanolamine (TEA) is added to zeolite Na-A synthesis gels. Work in this laboratory (1) and several studies by other authors (2-5) have attempted to establish more precisely the role of TEA in the system.

In order to quantify its effects, a systematic study was carried out in this laboratory on the addition of TEA to zeolite Na-A synthesis gels over a large concentration range (6). A gel composition of $Al_2O_3\ 0.84SiO_2\ 1.94Na_2O\ qTEA\ 194H_2O$ where q was varied from 0-30 was chosen for the study. A q was increased from 1-10 the average size of the zeolite Na-A crystals produced increased from 2 - 50µm, with a corresponding increase in crystallization time from 4 hours - 6 days. Zeolite Na-X began to form in increasing amounts for $q > 10$, and was the predominant product formed above 20 parts TEA. The average size of the zeolite Na-X crystals obtained was around 30µm. All syntheses were carried out at 368±1K under static conditions.

In an analogous set of experiments where the relative Al_2O_3 content of the gel was reduced from 1 to 0.7, it was found that zeolite Na-X formation occurred at a lower TEA concentration. For a TEA/Al_2O_3 ratio of 10 the final product distribution was 50% Na-A; 50% Na-X, compared to 100% Na-A for the corresponding TEA concentration in the previous experiment. These experiments suggest that the effect of TEA is dependent on the absolute amount of aluminum in the synthesis gel. It was concluded from these results that the amine must interact with aluminum during the crystallization.

The aim of the present work was to confirm the existence of an aluminum/TEA complex, and to determine its binding mechanism. ^{13}C nuclear magnetic resonance (NMR) measurements on the zeolite synthesis media, and crystallization experiments in the presence of close analogs of TEA were used to accomplish this.

Synthesis of Zeolite Na-A in the Presence of TEA Analogs

Synthesis experiments to date have provided strong evidence to suggest that TEA reduces the active concentration of aluminum during zeolite Na-A crystallization. However neither the oxidation state of the trapped aluminum nor the nature of the complex has yet been ascertained. A study was therefore carried out on substances closely related to TEA in order to determine the relative importance of molecular shape and electronic configuration on the aluminum complex forming abilities of the amine.

(NASA-CR-183262) GROWTH OF LARGE ZEOLITE CRYSTALS IN SPACE (Worcester Polytechnic Inst.) 5 p CSCL 20L
N89-14100
Unclas
G3/76 0167498

Experimental Procedure

The experimental procedure and product characterization for these syntheses was as described in a precious report (6) but with the substitution of the desired amine for TEA. The amines used were obtained from Aldrich and were of >98% purity. Each product was characterized using X-ray powder diffraction (Cu, Kα , G.E. XRD-Z80) for phase determinatio and degree of crystallinity. Size analyses were by visual observation using optical microscopy (Olympus BH-2). Differential scanning calorimetry (Mettler DSC 20; 323-873K @ 10K min^{-1}) was used to determine the extent of occluded amine in the material.

Results and Discussion

A series of amines with a similar structure to TEA was chosen for the initial study. These were: triethylamine, N,N-diethylethanolamine, and N-ethylethanolamine. Although the number of hydroxyl moieties is different for each substance, they are all examples of tertiary amines with three ethyl substituents.

Identical syntheses to those carried out in the presence of TEA were made with all of the above mentioned amines using 10 molar equivalents of the amine. The nature of the products obtained is shown in Table 1. The products crystallized in the presence of the three TEA analogs were identical to that of the standard amine-free system. These amines appear to have little effect on the gel chemistry. Addition of TEA in the same concentration yields crystals of 40 to 50 microns.

Given the strong similarities between these amines and TEA, the results suggest that all three hydroxyl groups present in TEA are necessary in order to successfully complex aluminum. On this basis, one can postulate a cage-like chelate structure where each hydroxyl group (or oxygen ion if dissociation is complete) interacts with the aluminum or aluminate species.

Because this data suggests that all three hydroxyl groups are necessary for complexation, further aditives were chosen to ascertain the relative importance of the amine group. Unfortunately, the carbon substituted analog of TEA could not be obtained. As an alternative, two compounds closely related to TEA which were available in both amino and carbon forms were chosen for the study. The results obtained for the addition of 10 molar equivalents of 1,1,1 tris (hydroxymethyl) ethane and its amine counterpart 1,1,1 tris (hydroxymethyl) aminoethane to zeolite Na-A synthesis gels are shown in Table 2. The structures of these materials are included in the table.

The enhancement in crystal size obtained using the amino compound, and the absence of any effect for its carbon analog suggest that an amino group is necessary for successful aluminum complexation. Tris (hydroxymethyl) aminoethance was less successful than TEA in terms of crystal size enhancement which suggests a less than optimal arrangement of the functional groups necessary for complexation.

These experiments have illustrated the importance of both the structural and electronic aspects of TEA in terms of its effect on zeolite Na-A crystallization.

Nuclear Magnetic Resonance Studies on TEA Solutions

^{13}C Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for determining the chemical environment of carbon atoms in organic compounds. Solution phase ^{13}C NMR was used in this study to examine the effect of aluminate and silicate species on the spectrum obtained for TEA. It was hoped that the existence of a complex between TEA, and either of these two species, would be revealed through a change in the spectrum.

Experimental Procedure

Nuclear magnetic resonance experiments were carried out using a Bruker AC-E 200 superconducting Fourier Transform nuclear magnetic resonance spectrometer. Sample solutions were prepared using deuterium oxide (Aldrich, 99.8 atom%) and included 1% acetonitrile as an internal reference. The complete composition of each sample analyzed is shown in Table 3.

Results and Discussion

A representative ^{13}C NMR spectrum of TEA in sodium hydroxide solution (for exact composition, see Table 3) is shown in Figure 1. There are two peaks in the spectrum corresponding to the two carbon environments associated with the amine. There are three identical carbon atoms in TEA attached to the amine group and three hydroxyl bonded carbon atoms. These are designated C^1 and C^2 respectively on Figure 1. Peak assignments were made based on well established chemical shift data for similar carbon environments. The two peaks observed are closely spaced (δ C^1, 56.1 ppm: δC^2, 59.8 ppm) and of similar intensity. The peaks in the spectrum at around 0 and 120 ppm correspond to those for acetonitrile which was used as an internal reference material.

Having established a standard spectrum for TEA it was now possible to determine the effect of aluminate ions on the chemical environment of the amine. A solution was prepared with an aluminum/TEA ratio typical of a zeolite Na-A synthesis mixture (5 parts TEA, Composition 1). The spectrum obtained is shown in Figure 2. The original peaks corresponding to unbound TEA are still present but there are two additional peaks which have been assigned to aluminum-bound TEA. A second peak, shifted down-field from its original position, was observed for both carbons (δC^1, 52.3 ppm; δC^2, 56.3 ppm). This is strong evidence to suggest that aluminum is indeed complexing with a portion of the TEA present in the solution.

A shift in the peak position for each carbon type shows that both the nitrogen and the hydroxyl groups take part in the aluminum complexing mechanism. This was suggested by the analog experiments previously described, and further evidence is given by the NMR technique. It is interesting to note that the carbon associated with the amine group, C^1, is shifted to a greater extent than the C^2 carbon. This suggests that the amine group is more strongly bound to the aluminate species than the dydroxyl groups.

Given that aluminate species are indeed complexed by TEA in alkaline solutions, it was necessary to establish whether or not silicate species, also present in zeolite synthesis gels, led to a similar interaction. A TEA solution was prepared with a silica content exactly comparable to the previous aluminum experiment (see Table 3). The spectrum obtained is shown in Figure 3, and reveals identical peak positions to those found for standard TEA in the absence of additives (δC^1, 56.2 ppm; δC^2, 59.8 ppm). This clearly shows that TEA has no complexing abilities with respect to silica in this environment.

^{13}C nuclear magnetic resonance spectroscopy has provided an elegant method for *in-situ* investigation of the behavior of TEA in zeolite syntheses. Further work will be carried out using this technique to probe the effect of organic additives on the solution chemistry of zeolite synthesis gels.

Conclusions and Further Work

Synthesis studies carried out using close analogs of TEA have shown that all three hydroxyl groups and the amine group in this molecule are necessary to provide nucleation suppression. Studies using ^{13}C NMR revealed that the hydroxyl ions and the amine group are involved in the formation of an aluminum complex. It was also shown that silicate species do not interact in this way with TEA in alkaline solution. These results suggest that successful aluminum complexation leads to nucleation suppression in zeolite-A crystallization.

Having established ^{13}C NMR as a powerful technique for mechanistic studies in this system, there is much scope for further work. A study of the ratio between bound and unbound aluminum as a function of TEA concentration could be carried out in order to explain the behavior of the system at high TEA additions. This technique also provides a method to look at the labile nature of the complex. The relative concentration of bound and unbound TEA will be determined as a function of crystallization time.

This technique will also aid in the design of further nucleation suppressants because it provides a convenient method for determining their aluminum complexing ability.

These experiments will help define the mechanism of nucleation suppression by organic amines in zeolite crystallization. This is vitally important for the successful design of second generation hardware for microgravity processing.

REFERENCES

1. Sand, L.B., Sacco, A., Jr., Thompson, R.W. and Dixon, A.G., Zeolites, 1988, **7**, 387.

2. Charnell, J.F., J. Crystal Growth, 1971, **3**, 291.

3. Neels, H. Schmitz, W., Berger, E-M. and Lutz, D., Kristall und Technik, 1987, **13**, 1345.

4. Gutze, A., Kornatowski, J., Neels, H., Schmitz, W. and Finger, G., Crystal Res. Tech., 1985, **20**, 151.

5. Schmitz, W., Kornatowski, J., and Finger, G., Crystal Res. Tech., 1987, **22**, 35.

6. November 1987 Progress Report to Clarkson NASA Center.

(SEE TABLES AND FIGURES ATTACHED.)