

Plenary Paper — Synthesis

ZEOLITE SYNTHESIS AND CRYSTALLIZATION

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ABSTRACT

An evaluation is given of the current problems and opportunities that exist in zeolite synthesis and in crystallization phenomena of both the synthetic and naturally occurring zeolites. Subtopics include the standard variables, $P_{T_{Xt}}$, and the additional parameters of metastability, dissolution of reactants and intermediate species, structural solution chemistry, morphological phenomena, and the inter-facing of the synthetic and natural systems.

INTRODUCTION

Although over a hundred zeolites have been synthesized, including synthetic analogues of those occurring naturally, with the exception of a few like dachiardite, it has been postulated by crystallographers that only ten percent of the possible polymeric configurations have been discovered. If this assumption is true, it follows that in spite of the large number of useful molecular sieve zeolites that have been synthesized, the field is in an early stage of development with many opportunities to create new species. Until a basic understanding is developed of the crystallization mechanisms and controlling factors such as the structure of the solution phases present during initial nucleation and subsequent crystallization, progress will be almost entirely through experimental phase chemistry. Although this also is the case in most of phase chemistry, the difficulty is compounded by the metastable, nonequilibrium nature of the zeolite systems of industrial interest, as well as those natural zeolites that have crystallized on or near the earth's surface. In an even more elementary stage of knowledge and development is an understanding of the silicate species in solution during the various stages of crystallization, the structure of the solutions, the mechanisms of nucleation and crystal growth, and the correlation between solution chemistry and the resulting crystal species.

This paper attempts to put this branch of zeolite research in perspective with the objective of convincing interested scientists and engineers, particularly academic, to regard this area as in an initial stage of development with many opportunities to contribute. The broad base in synthesis and properties established by Professor Barrer and his associates has been extended remarkably by the industrial laboratories. Out of proprietary necessity, much of the data in zeolite synthesis are couched in patent language or remains unpublished. Even so, the volume of information can appear overwhelming; and, coupled with the tedium and expense associated with experimental phase chemistry, might explain the few numbers of academics engaged in this research activity. As a result, even though the creation of useful zeolite species is the prerequisite for other investigations, basic research in synthesis and crystallization phenomena has lagged far behind and needs to be put on a firmer scientific basis.

SYNTHESIS

With the exception of the "silicalite" end member of the isostructural ZSM-5 series, zeolites are synthesized in an oxide system consisting of $H_2O-SiO_2-Al_2O_3$ -(alkali, alkaline earth, organic) generally below $200^\circ C$ at autogenous pressure. Excellent summaries of these have been given by Flanigen [1] and by Breck [2]. The experimental procedures are quite simple and can lead one accustomed to precise measurements as unworthy of attention. However, the chemistry of the reaction system is extremely complex due to the following main factors:

- the formation of an intermediate gel phase in most systems.
- the metastable phase transformations.
- the effect of dissolution rates of the reactants.
- sensitive nucleation phenomena.

Early researchers could not understand, given the same PTXt conditions with presumably the same reactants, that duplication of results were difficult. Although not as serious, it still remains a problem. To illustrate the complexity of some systems, the following simultaneous reactions can occur in one experimental run:

- precipitation of a gel phase.
- dissolution of the gel.
- nucleation of zeolite(s).
- continued crystallization and crystal growth of the zeolite(s).
- dissolution of the initial metastable phase(s).
- nucleation of a more "stable" metastable phase or phases.
- continued crystallization and crystal growth of the new crystalline phase(s) while the initial crystals are dissolving.
- dissolution of the metastable phase(s).
- nucleation of the equilibrium phase(s).
- crystallization and crystal growth of the final crystalline phases.

As a start to reach an understanding of the reactions taking place during the runs in a given system, an approach used by metallurgists for many years, notably in the Fe-C system, was tried in several zeolite systems. This is what the metallurgists call the isothermal metastable phase transformation approach. These are

essentially Xt (composition, time) phase diagrams, and in the zeolite systems, it was found most effective to select a given batch composition and a given temperature, vary the cation ratios, determine the crystallization curves, and then plot these on an isothermal metastable phase transformation diagram [3]. A study of this type also is reported at this conference.

Valid questions often are raised about the value of obtaining activation energies of nucleation and crystallization from crystallization curves using the Arrhenius plot. It is proper to refer to these as "apparent activation energies". These generally are obtained by taking the slope at 50% crystallization at the inflection point in the autocatalytic reaction. There is no question that in-depth studies are needed to quantify these values; at the present time they serve a useful purpose in obtaining approximate values, and in checking the validity of the experimental data.

Morphological studies, i.e., the size and shape of the resulting crystals, have started to receive more attention. The thrust of the industrial efforts has been primarily to obtain the smallest crystals possible within manufacturing limitations in order to minimize the rate-limiting step of intracrystalline diffusion affecting the total process. This assumption might be correct for certain zeolites but not for others. Tentatively, 3-dimensional pore systems, as in zeolite A and in zeolites X and Y, might favor small crystals, whereas 1-dimensional pore systems, as in mordenite, might favor large crystals. One study with one mordenite with one sorbate system at one temperature illustrates the latter which is shown in Figure 1 [4]. At present the question is open and is deserving of much study for the reason that it is desirable in some applications to produce relatively large crystals in the fluid and fixed bed size ranges which have

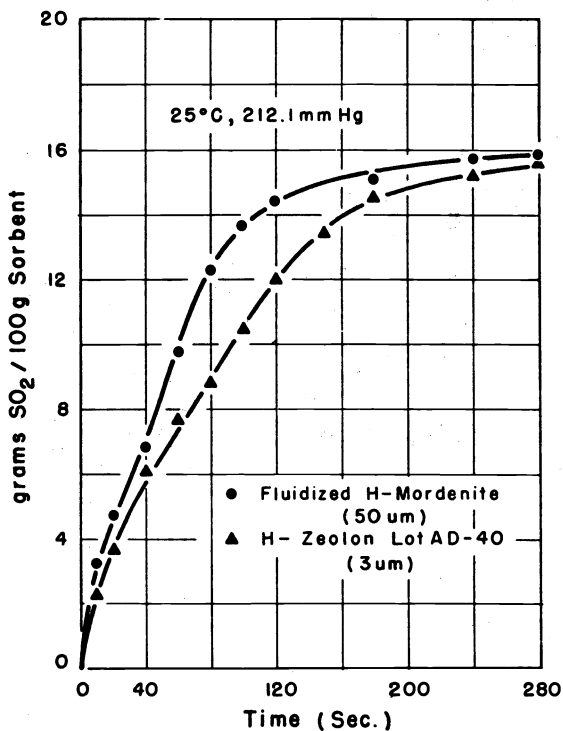


Figure 1. Rates of SO₂ sorption by 50µm mordenite crystals and 3µm mordenite crystals at 25°C and 212 torr.

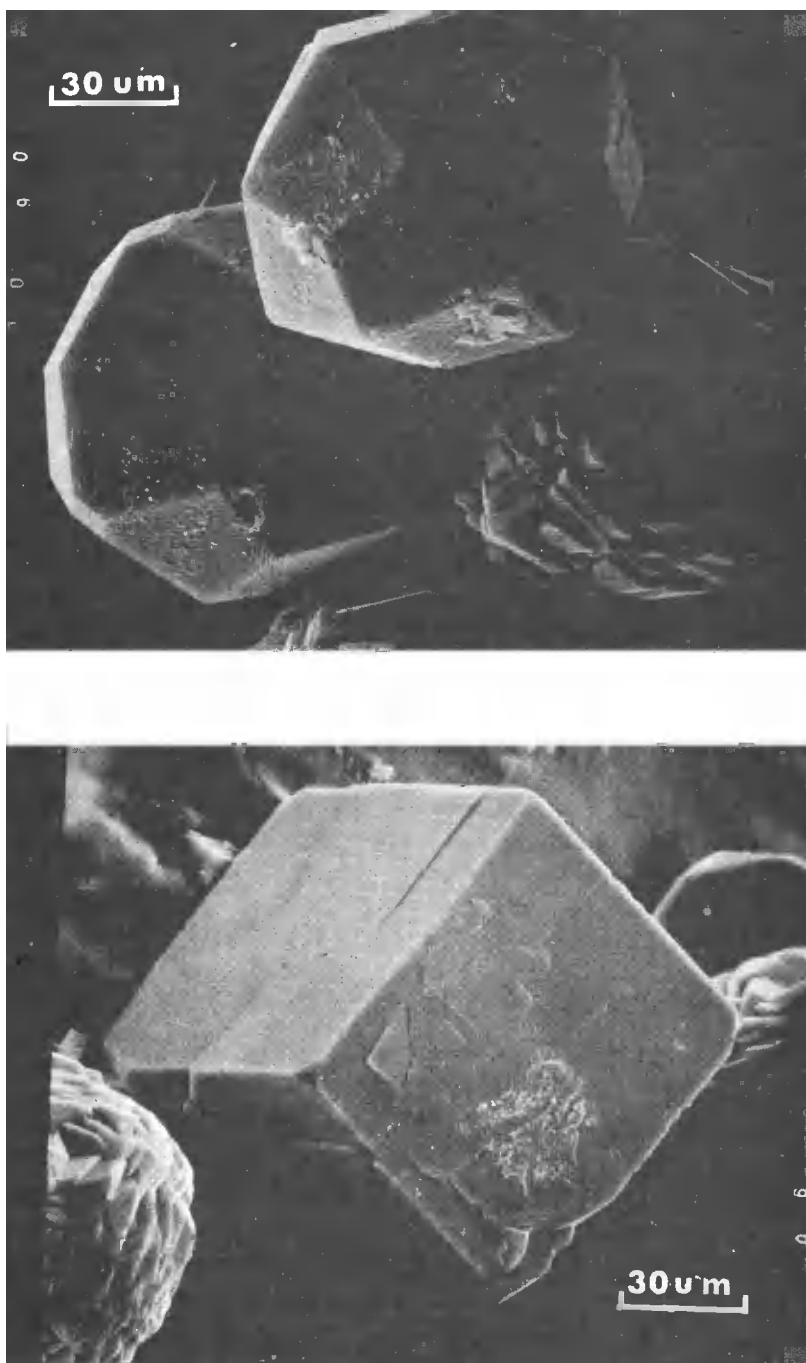


Figure 2. Left. Scanning electron micrograph of synthetic analcime grown in the hydroxide system showing common trapezohedra. Right. SEM of synthetic analcime grown with fluoride addition.

either higher dry crushing strength, attrition resistance, or wet crushing strengths. If one may generalize at this early stage of knowledge, the cation(s) in the synthesis system determines the resulting zeolite species, and the anions added to the system have a pronounced effect on the morphology. An example of this is shown in Figure 2 which shows the effect of anion addition on the resulting

morphology of analcime crystals [5]. Another example is given at this conference in the ZSM-5 system [6]. In this area of research, not only can the morphology be controlled in the production of polycrystalline zeolite powders which subsequently are particulated with binders, but large zeolite crystal aggregates can be produced under certain conditions from powder reactants by mechanisms not yet understood, or by the well known method of in-situ replacement or pseudomorphic conversion of a precursor reactant particle [7].

CRYSTALLIZATION

This section will discuss primarily the current status of crystallization studies in the natural systems. As an aside, it is hoped that this conference will fulfill one of its objectives of promoting interaction between researchers on the synthetic systems and on the natural systems.

As is extensively described in the literature [8], zeolites crystallize in the natural environment in great abundance, as was recognized only relatively recently; and their application is now under development, essentially 25 years behind the synthetic zeolite field. The zeolites that occur in mineable deposits and which have molecular sieve properties of current interest are clinoptilolite, mordenite, ferrierite, chabazite, erionite, and phillipsite. An abbreviated genetic classification describing the geologic setting in which natural zeolites have crystallized can be given as follows: 1) alteration of siliceous volcanic pyroclastics on the ocean floor, in continental saline, alkaline lakes, and on the surface by ground waters; 2) regional burial metamorphism; and 3) deposition from hydrothermal solutions, including hot springs. The latter are not of industrial interest but do provide valuable information to design some synthetic systems to produce certain molecular sieve zeolites.

A classical contribution delineating an isothermal metastable phase transformation in a natural zeolite system is reported by Sheppard and Gude [9]. It reveals the close association between the problems encountered in the natural systems as have been found earlier in the synthetic systems. A great setback in research progress in this area undoubtedly was the irrational act of arson destroying their laboratory and files on zeolites.

Presently, the geological sciences have most to gain by applying the knowledge and techniques obtained in the synthetic systems to design experimental petrology programs to lead to an understanding of the conditions under which zeolites formed in the natural environment. The initial studies logically select the reactions of volcanic ash with various solutions. The first results have been very productive, and an outstanding example is that by Hawkins et al. [10] on the synthesis of alkali clinoptilolite which is the most abundant naturally occurring zeolite. Others, including those given at this conference, have made significant contributions to this developing field.

One of the criticisms given to the value of experimental petrology leading to an understanding of these low temperature systems is that the time involved is too long to be feasible. As a result we have found it necessary to approach this problem through unsupported undergraduate student research, the results of which were presented orally at a clay conference meeting some years ago but which have not yet been published. The results, however, are very promising. From geolo-

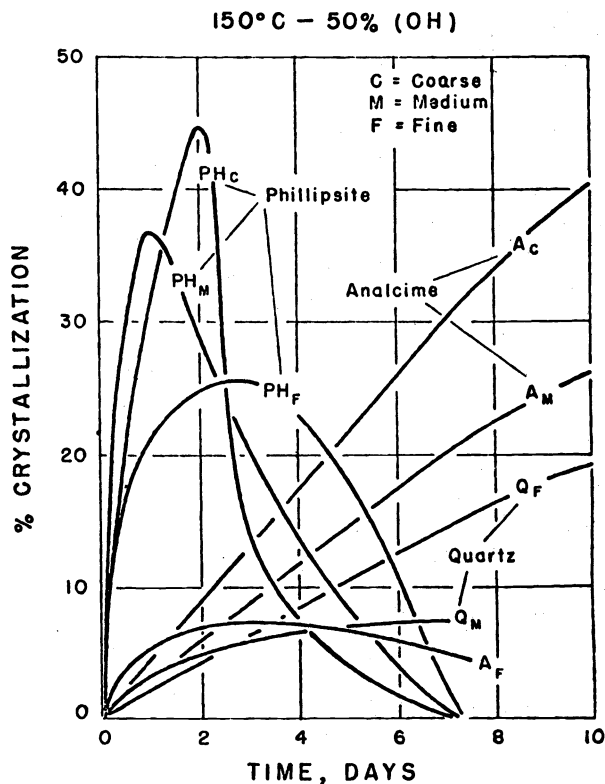


Figure 3. Crystallization curve of experimental reaction of rhyolite glass in size fractions of 6, 60 and 600 μ m with simulated Searles Lake brine.

gical evidence, for example, it is estimated that about one million years is required for zeolites to crystallize completely from volcanic ash on the ocean floor and for about one-hundredth of that time to crystallize in a saline, alkaline lake. By assuming first order hydroxyl concentration and using the Arrhenius extrapolation, a good initial correlation was achieved with the geological observations. An example of crystallization curves used to obtain this information is given in Figure 3 [11]. Another result which was obtained in this preliminary study was the effect of particle size of the volcanic ash as it affected the resulting zeolite phase assemblage due to the parameters of rates of reaction and the proportion of solution to solid reactant. This is regarded as important relevant to the problem of explaining sharp demarcations between zeolite beds in the same basin of deposition as a result of alteration of different ash falls with different particle size distributions.

One example of using the information gathered from studies of a zeolite crystallizing under hydrothermal conditions to design the experimental synthesis program was that for ferrierite in which the buffered system of carbonate-bicarbonate was found to be a key parameter [3]. The common association of calcite with ferrierite in the natural deposits led to designing the successful synthesis system.

DISCUSSION

In order to accelerate research progress on crystallization phenomena in both the synthetic and natural systems, particularly in

academic institutions where massive auxiliary support is not available, two principal bottlenecks must be overcome. These are in making the experimental runs and in quantitative identification of the phases by X-ray diffraction analysis to plot crystallization curves in the complex systems in which a number of crystalline phases grow and dissolve. In our laboratories we believe we have eliminated the latter bottleneck by interfacing a diffractometer, which has a 35-sample automatic slide changer, with a computer and a graphics terminal. This is being given as a progress report at this conference [12]. Slower progress is being made on significantly increasing the number of experimental runs per unit time that can be made by one researcher. The approach being tried is by the use of many small reactor vessels in a tray which automatically ejects the vessel from the oven into a quench tank at pre-set times. The subsequent steps of washing and drying are not considered serious bottlenecks once the other main problems are solved. Success in overcoming these two main obstacles to rapid data acquisition will be especially useful in investigating new synthesis systems, in determining mineral assemblages in natural systems, and in determining accurate crystallization curves for studies of morphological changes, composing isothermal metastable phase transformation diagrams, for delineating conditions for 100% yield of one phase for manufacture, and for following deterioration of crystallinity during use.

In the synthetic systems it is believed that the following areas in studying crystallization phenomena are important now and in the immediate future:

- the addition of large organic cations, surfactants, and other solution modifiers to create new species, perhaps even some with ports larger than 12-membered rings.
- the addition of anions to change and control the resulting morphology.
- studies of the nature of the silicate species in solution, both in the starting sodium silicate solution if used and in the solution phase during reaction, and the effects on the crystal polymerization.
- the growth of larger single crystals in the fluid and fixed bed ranges in high economic yields.
- the growth of large single crystals in small yield for crystal structure determinations and for basic studies of diffusion and separation mechanisms.
- particulation by in-situ replacement or pseudomorphic conversion of precursor reactant particles during synthesis.
- particulation of strong crystal aggregates by direct synthesis from powder reactants in certain systems.
- studies of crystallization phenomena in continuous stirred reactor system in addition to the batch systems [13,14,15,16].

In the natural systems it is believed that the following areas in studying crystallization phenomena are of current interest:

- to determine why the larger pore channels are restricted in the high silica zeolites like mordenite, clinoptilolite, and ferrierite.
- to determine the process giving sharp demarcation of zeolite beds in the same basin of deposition.

- to determine the kinetics of crystallization from volcanic glass in the low temperature environments using extrapolations of higher solution concentrations and temperature to circumvent the time factor.
- to continue phase equilibria studies of zeolites formed in the higher temperature environments.
- to determine the kinetics of phase transformations of zeolites formed in low temperature environments to other assemblages during burial metamorphism.
- to continue correlating the crystallization from volcanic glass as a function of location, laterally and vertically, in the basis of deposition.

Interaction between researchers concentrating on the synthetic systems and those concentrating on the natural systems has grown, primarily due to the increased industrial use of the natural zeolites. Zeolites were defined and classified since 1756 on the minerals, and it is remarkable what was accomplished by the early workers without the use of X-ray diffraction analysis. An illustrative example is the identification in 1875 of the fine-grained chabazite in the Bowie, Arizona deposit [17]. The molecular sieve field was started by sorption studies on natural chabazite, and crystal structure determination still are dependent primarily on using the naturally occurring crystals. Design of the experimental synthesis systems was, and is still the case to a more limited extent today, derived from the geological setting and associated mineral phases in the natural systems. It is very likely that the synthetic zeolites always will be most important commercially due to crystal and chemical purity and control; synthesis of zeolites, like the ZSM-5 series, which are not found in nature; and the great variety of tailor-made species possible through the synthesis route. Interaction is most important in the direct and personal exchange of knowledge, techniques, and concepts that can occur only at a conference. It is hoped that this conference will prove the merit of including contributions and attendance from both disciplines in the field.

CONCLUSION

This attempt to outline the current problems and opportunities in the area of zeolite synthesis and crystallization was directed primarily to those recently entering this branch of zeolite studies. It is my opinion, shared by others, that what has been accomplished so far is the basis for many more exciting new contributions.

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