

VERIFIED SYNTHESES OF ZEOLITIC MATERIALS

Second Revised Edition

**Harry Robson, Editor
Karl Petter Lillerud, XRD patterns**

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Preface to the second edition

The first edition of Verified Syntheses of Zeolitic Materials was published as Volume 22, Nos. 4-6 of Microporous and Mesoporous Materials (30 June 1998). Distribution was limited to subscribers to the Journal. The second edition is planned for publication in mid 2001 in time for distribution at IZC-13 (Montpellier, July 2001).

The format for the second edition is largely unchanged from the first. The intended audience is still the applications researcher, reasonably skilled in the art, who wants a particular phase enough to attempt its synthesis in the laboratory. In practical terms, this means approximately first year graduate students. With the exception of organic templating agents, zeolite synthesis does not require elaborate equipment or expensive reagents. As evidenced by the contributors list, many investigators in many different countries have been active in the synthesis field.

The current edition has reprinted all the recipes from the first edition plus 24 new recipes. The introductory articles on basic skills in zeolite synthesis includes the articles from the first edition (some with substantial revisions) plus five new articles. The XRD patterns have been recorded using different instrument settings from those in the first edition and are intended to conform to typical X-ray diffraction practice. In most cases, only the XRD pattern for the product as synthesized is printed here. The exceptions are those phases which show marked changes in the XRD pattern upon calcination.

Zeolite synthesis is an active field of research. As long as this continues, new phases will be discovered and new techniques for preparing existing phases will appear. The IZA Synthesis Commission hopes to continue and enlarge this collection to include all phases of interest to the zeolite research community.

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Previous IZA Special Publications

- W. J. Mortier, *Compilation of Extra Framework Sites in Zeolites* (1982)
- W. M. Meier, D. H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types*, 4th edition (1996)
- M. M. J. Treacy, J. B. Higgins and R. von Ballmoos, *Collection of Simulated XRD Powder Patterns for Zeolites*, 3rd edition (1996)
- H. E. Robson and K. P. Lillerud, *Verified Syntheses of Zeolitic Materials*, 1st edition (1998)

Introduction and explanatory notes

Accounts of synthesis experiments reported in the literature are nearly always cryptic leaving the reader who wants to repeat the experiment many choices of reagents and procedures. In most cases, there are multiple experiments producing similar products without a clear indication of which one the author(s) prefer. Characterizations of the products are often inadequate for an unambiguous choice for a new application.

Experts in the art of zeolite synthesis have learned to accept these ambiguities and persevere through early failures to reproduce the desired product in most, not all, cases. The neophyte may be less diligent; and early failures may be the end of the critical experiment leading to a new application. The IZA Synthesis Commission in preparing this volume seeks to improve the success ratio for synthesis experiments by encouraging the contributors to better define their experiments and adequately characterize their products.

The Organizing Committee, which preceded the Synthesis Commission, surveyed experts in the synthesis area and published an outline covering the essential points for reporting a zeolite synthesis [1]. The format for the recipes in this volume follows this outline. The table form is intended to assist the reader by placing the information in the same relative positions for all recipes. The table form supposes that all synthesis experiments follow the general sequence: batch preparation, crystallization, product recovery, and characterization.

1. Framework Type Codes

The three-letter codes (top line - far left) are arranged in alphabetical order as in the Atlas of Zeolite Structure Types [2]. They define the topography, but not the composition of the resulting phase. Unlike the Atlas, which has one entry for each code, this volume may contain multiple entries for a single code with differing Si/Al ratio products, products with differing T-atoms, or products of essentially the same composition produced by different synthesis procedures.

2. Product Name

The product name (top line - center) is the name by which the product is usually referred to in the literature. There may be several products of similar composition but different names. A more complete list of these names can be found in the Atlas section "Isotypic Framework Structures" for that framework type code. The choice among competing names has been left to the contributing author in most cases. The number of framework type codes is large but limited; the number of products or recipes is unlimited. As long as zeolite synthesis is an active field of research, there should be new recipes for later editions of this volume.

3. T-atom Composition

T-atom composition (top line - far right) refers to the elements which occupy tetrahedral positions in the framework and their relative numerical abundance (basis:100 T-atoms). The values are based on the elemental analysis of the product of the recipe as given in Product Characterization. In most cases, values are rounded to integer values except where a minor T-component has particular significance.

4. Contributed by

The name(s) indicate the person or persons who actually prepared the entry and is intended to identify the one most likely to respond to communications regarding the recipe. The entries are not intended for full scientific recognition for the research which produced the recipes; in most cases, recognition has already occurred elsewhere in the literature. Authors are identified by name only; academic titles and institutional affiliation are given in the contributors section. Single contributors are listed except where the authors expressly stated co-authorship.

5. Verified by

Verifiers are those independent investigators who have reproduced the synthesis experiment and obtained a satisfactory product by their own evaluation. Again, only names are given here; for institutional affiliation, see the contributors list. Only those verifiers who responded affirmatively are listed here. Negative responders, those who replicated the experiment but obtained a product other than the desired phase, are acknowledged in the contributors section. These reports, both positive and negative, are part of the record of the recipe and are available on request. In many cases, the responses of verifiers have prompted changes in the recipes.

6. Type Material

Type material refers to contents of the unit cell as indicated by the elemental analysis. In most cases, the product has been washed and dried but not calcined. Thus the template is often a component of the product composition. Water contents of the products are not consistent; only in some cases has the synthesis product been equilibrated under controlled humidity.

7. Method

Method cites the literature report on which the recipe is based, usually the author's report but sometimes an earlier, more general reference. Patent references have been avoided unless they are specific. It is the intention of this volume that the reader be directed to the single recipe which gives the best chance of immediate success in the synthesis.

8. Batch Composition

Batch composition refers to the product of batch preparation stated in ratios of oxides, template molecules and neutralization products. The basis is usually a single formula weight of Al_2O_3 or another trivalent oxide; occasionally the base is SiO_2 or P_2O_5 .

9. Source Materials

Source materials are those actual materials used to prepare the batch along with their purity and supplier. Generally the source materials are stated in the order in which they are used in preparing the batch. The authors have been encouraged to be specific as to the suppliers because many failures to replicate have been traced to the change of supplier for a source material, particularly in the case of silica or alumina. In most cases, the balance of the composition of the component is assumed to be H_2O and should be included in calculating batch composition.

10. Batch Preparation

Batch preparation refers to actual quantities of materials plus the preparation steps used to prepare material for the crystallization step. The estimate of product yield is intended for the reader's convenience. For each step, the materials added and the order of addition are indicated within the brackets. Order of addition has been found to be critical in some cases. Instructions for completing the step follow the brackets. Combination at room temperature is contemplated unless otherwise stated. Completion of the batch preparation in a matter of minutes or of hours is expected unless delay is specifically required.

11. Crystallization

Crystallization refers to the experimental conditions and temperature profile which converts the finished batch to a product slurry of zeolite crystals in a "mother liquor." The containing vessel is assumed to be inert except in special cases. Accidental seeding by residues of earlier experiments has been shown to be a problem. If autoclaves or their liners are reused, they

should be carefully cleaned. Rapid heat-up to the crystallization temperature is contemplated; rarely is the heat-up time a significant portion of the total treatment. Temperature fluctuations during treatment are to be expected.

Aging or incubation of the finished batch at ambient or some intermediate temperature is part of some treatments. Time / temperature tradeoffs are described in the literature; the intention here is to give the author's best guess as to the optimum treatment. Monitoring the progress of crystallization can be instructive, but it is difficult in closed autoclaves at temperatures above 100°C. Rather than sample at temperature or cool, sample, and reheat, the usual approach is to divide the batch into several vessels and treat the aliquots for progressively longer times.

Static treatments or only modest or intermittent agitation is the usual case. Continuous agitation may be required for specific preparations.

12. Product Recovery

Product recovery refers to the procedure for separating the desired product from the by-products of the crystallization process. Most zeolite products are micron-sized crystals which are easily filtered while the "mother liquor" is a solution of excess alkali silicate, excess template, etc. Very fine product crystals may require centrifugation for good product recovery. For alkaline synthesis, the pH drops as the washing proceeds; pH = 10 for the final wash is usually sufficient. For fluoride synthesis or AlPO_4 -type materials, other criteria for adequate washing are required.

Although most zeolite products are water stable, prolonged washing can produce subtle changes in their composition. Hydrolysis may replace cations with H_3O^+ ; salt or template inclusions may be reduced or eliminated. Some investigators prefer to wash with dilute NaOH rather than pure water. In general, washing conditions must be considered part of the synthesis.

Drying usually is accomplished in a laboratory oven at $\sim 110^\circ\text{C}$. It is good technique to equilibrate the dried sample at a constant 50% humidity to make it stable to handling in laboratory air. Yield here is expressed as percent of theoretical yield based on the limiting component (usually Al_2O_3 or SiO_2). In the literature, yield is sometimes expressed as percent by weight based on the finished crystallization batch.

12.1 Flocculation [3]

Sometimes flocculation, a method of agglomerating fine particles to filterable size, is advantageous. An example of an organic flocculant is a detergent-type molecule, which adsorbs with the hydrophilic end on the hydrophilic zeolite particle surface, with the hydrophobic end extending into the aqueous medium. The thus generated hydrophobic particles coagulate to form flocs or flocks, which can be filtered and washed on the filter with water.

Before applying such an organic flocculant, the alkalinity of the crystallized reaction mixture needs to be reduced. The application of an electrolyte, such as NaCl, as a flocculant, however, has the disadvantage that colloidal silica present in the mother liquor is coagulated as well, so that the crystallinity of, for example, zeolite alpha, will be $\leq 90\%$. If this is acceptable, NaCl is added with mild stirring (magnet bar) until, after turning off the stirrer, flocs become visible, first where the meniscus meets the glass. The flocculated product will settle, and the supernatant liquid can be decanted. The sediment may be filtered, but washing with water causes the flocs to disintegrate, and the crystallites will pass the filter again. Washing, however is not necessary. Instead, the filter cake is reslurried, and now an organic flocculant, such as Betz No. 1192, which is added in small portions of a 0.2% solution, until complete flocculation is observed, can be applied. The thus flocculated product can be filtered and washed with water.

If coagulation of the colloidal silica is to be avoided, the strongly diluted crystallized reaction mixture can be left undisturbed for settling, if necessary, for as long as a few days, or centrifuged. The supernatant solution is cautiously decanted from the sediment. If complete settling is not achieved, the small amount of solids left in suspension may be sacrificed. The sediment is then reslurried and flocculated with an organic flocculant, such as Betz No. 1192, filtered and washed, as described above.

13. Product Characterization

Product characterization identifies the crystalline product and compares its properties to those of known standards. For this volume, basic characterizations are the X-ray diffraction pattern, elemental analysis and crystal size and habit from SEM. For particular applications, several other characterizations might be desired, such as sorptive capacity, ion exchange properties, thermal analysis, nuclear magnetic resonance, etc. Not many authors report their products in such detail, and in some cases it is difficult to obtain data reproducible in another laboratory. Secondary characterization, when provided, are reported in the Notes section.

14. XRD

XRD refers to the principal phase as identified by comparison of its x-ray diffraction pattern with those in the literature. Unit cell parameters are usually given. When competing crystalline phases have been identified from extraneous lines, they are indicated plus an estimate of amorphous material from the background intensity.

A reference pattern for the product in the "as synthesized" is attached. In some cases a second pattern of the calcined product is provided. Some of the calcined materials, particularly AlPO_4 and GaPO_4 , are moisture-sensitive. For other cases the calcined material is virtually identical in the XRD pattern to the as-synthesized sample. In such cases no XRD trace of the calcined product is given. A separate article describes the instrument conditions for recording the XRD patterns.

15. Elemental Analysis

Elemental analysis gives ratios of metal cations present usually expressed as the ratios of their oxides. The editor prefers the direct analytical result (weight percent of the element or its oxide based on the dry sample). Most authors give ratios of the oxides based on one formula weight of Al_2O_3 or SiO_2 . In most cases, these were determined by inductively coupled plasma emission spectroscopy. In some cases, the content of water or template molecules in the product as indicated by thermal analysis is also included.

16. Crystal Size and Habit

Crystal size is an estimate of the crystallite size and/or the aggregate particle size. Habit is a qualitative description of the sample as observed in the SEM.

17. References

References indicate the primary literature report on which the recipe is based plus selected general references recommended by the author. This list is intentionally limited and is intended to start the user's search of the literature, not complete it.

18. Notes

The notes give additional instructions or information which the author believes helpful to the reader but which do not fit into the recipe format. The additional instructions are intended to substitute for a private conversation with the author before the reader/user begins the synthesis experiment. It is potentially the most valuable part of the contribution.

References

- [1] H. Robson, *Zeolites*, 13 (1993) 399
- [2] W. M. Meier, D. H. Olson, Ch. Baerlocher, *Zeolites*, 17 (1996) 1
- [3] G. Kühn, personal correspondence

Conditions for recording of XRD patterns reported in this book

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The X-ray diffraction (XRD) patterns were recorded with a SIEMENS D5000 diffractometer. The diffractometer was equipped with a Ge-focusing primary monochromator giving Cu-K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$), a BROWN 70 mm linear position sensitive detector (PSD) and a 40 position sample changer. The PSD is operated with 8° opening. A variable entrance slit giving a constant $6 \times 12 \text{ mm}$ exposed area is used.

The reported intensity distribution is for fixed slit geometry. The diffraction patterns are recorded with variable slit, but presented with at the intensity distribution recalculated to simulate fixed slit mode. The intensity scale (ordinant) for all patterns is K-Counts/second.

For comparison with measured diffraction patterns is it important to note that routine measurements are often performed with a slit that will expose more than the sample area at low angle. The observed intensities at low angle will therefore be too small compared with these reference patterns and calculated patterns.

In this version of the collection all patterns are scaled to the same absolute intensity. The diffraction patterns are presented in the as measured condition without any background subtraction or smoothing. Some samples contain elements that give raised fluorescence, like Fe and Co. No filter or secondary monochromator has been used to remove this radiation.

Source materials for zeolite synthesis

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1. Introduction

The chemistry of zeolite synthesis is subject to perturbations caused by impurities present in the source materials. Such contaminants may remain insoluble during the crystallization and cause undesired species to nucleate. They may be soluble and result in formation of different silicate or metasilicate species in solution, or they may cause an insoluble silicate species to precipitate. Therefore, it is desirable to apply pure chemicals as starting materials. Depending on the zeolite to be synthesized and the application intended for the product, less pure source materials are frequently employed, in order to reduce the cost. If the materials are not pure, they may vary from batch to batch and from different suppliers. It is of utmost importance to know the source materials for zeolite synthesis, and technical grade materials need to be assayed and analyzed for impurities. A few frequently used chemicals are discussed below.

2. Water Content

Clearly, when commercially available solutions of chemicals are employed, such as aqueous NaOH, H_2F_2 , or silicate, the water content of the solution has to be taken into account when the composition of the reaction mixture is established. Most other source materials contain more or less water, while the water content of fume silica may be only 3 wt.%, that of aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, is about 43 wt.%. Moreover, aluminum nitrate is deliquescent, and the water content will change once the jar has been opened and the chemical exposed to moist air. On the other hand, aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (48.6 wt.% H_2O), weathers by losing water upon exposure to the atmosphere. Technical grade aluminum sulfate usually contains about 14 H_2O .

Since the composition of a reaction mixture is given as ratio of oxides, any hydroxides employed are to be considered as oxides plus water, for example, $\text{NaOH} = 1/2\text{Na}_2\text{O} + 1/2\text{H}_2\text{O}$ (22.5 wt.% H_2O). Additionally, a small percentage of free water may be present, for example, sodium hydroxide pellets may contain about 97 or 98% NaOH. Similarly, an 85% H_3PO_4 contains 61.6 wt.% P_2O_5 and 38.4 wt.% H_2O . The water content of source materials may or may not constitute an important fraction of the total water content, and it is recommended that the water contained in these chemicals always be considered when the amount of water to be added in the preparation of the reaction mixture is calculated.

3. Sources of Aluminum

Some aluminum sources have been mentioned above. A disadvantage of using salts is that, after pH adjustment or addition of alkali silicate solutions, alkali salts are formed which have a strong electrolytic effect on gel formation. For example, such salts may cause sodalite to be crystallized instead of zeolite A type materials. For this reason, it is advantageous, particularly for reaction mixtures of low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, to introduce aluminum in the anionic form, that is, as sodium aluminate.

Sodium aluminate is subject to formation of aluminum oxide hydrates upon exposure to atmospheric carbon dioxide or just upon storage. It is not a widely used chemical, and, when obtained from a chemical supplier, is frequently aged to an extent that makes it unsuitable for zeolite synthesis. Sodium aluminate should dissolve completely with stirring in water at ambient temperature within a few minutes. If it does not, the precipitate or cloudiness usually can not be

dissolved by adding small quantities of alkali hydroxide, and the chemical is not suitable. Fresh sodium aluminate can be obtained in a technical form in larger quantities, such as 50-lb. bags. It is advisable to transfer the chemical with as little exposure to moisture and CO_2 as possible into small jars which should be sealed tightly and stored at or below room temperature. The composition of such technical sodium aluminate varies widely with Na/Al ratios from near 1.0 to 1.2 or higher so that a reliable assay is required. A small iron content manifests itself by the brownish discoloration of the otherwise clear sodium aluminate solution. This iron hydroxide can be removed by filtration or, for less critical preparations, just ignored.

In preparations containing phosphate, aluminum phosphate, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, is a viable alternative as it dissolves completely in alkaline phosphate or hydroxide solutions upon mild heating with stirring.

4. Silica Sources

A widely used silica source is aqueous sodium silicate, such as waterglass from PQ Corporation, Philadelphia, PA, USA. The PQ N-Brand product contains about 8.9 wt.% Na_2O and 28.7 wt.% SiO_2 . It usually is slightly cloudy, and it is recommended that filtered N-Brand be purchased. The precipitate can also be filtered off in the laboratory, but the vacuum filtration is slow and the filtrate has a reduced water content and needs to be reassayed. A small contamination with aluminum usually prevents zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios above ~600 to be crystallized.

When a lower aluminum content in the product is desired, colloidal silica sol, such as Ludox from E. I. DuPont de Nemours, Wilmington, DE, USA, can be used. This material is available in concentrations of 30 and 40 wt.% SiO_2 with different stabilizers employed. Without added aluminum, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the range of 3000 to about 3500 can be obtained.

Zeolites of still lower aluminum content can be prepared with fume silica as the silica source. Such materials are on the market as Cab-O-Sil (Cabot) or Aerosil (Degussa). The water content of fume silica is very low, ~3 wt.%. Products obtained when using fume silica as the silica source, without adding an alumina source, have $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios above 20,000.

Precipitated silica is available in different qualities. Hi-Sil (PPG Industries, Pittsburgh, PA, USA) contains about 90 wt.% of SiO_2 as well as ~1 wt.% of NaCl (it is recommended that the percentage of SiO_2 be determined; alternatively, the ash content minus 1% NaCl should approximate the SiO_2 content). The aluminum contamination prevents zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios above ~220. A somewhat purer material is Ultrasil (Degussa). The particle size of precipitated silica may need to be considered. Whereas finely divided fume silica may yield a thick paste of a reaction mixture, which is difficult to homogenize, a large-size precipitated silica, for example, Ultrasil VN3SP, may react too slowly to provide the desired aluminosilicate precursors in solution.

Tetramethyl- and tetraethylorthosilicate are available in high purity and yield the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Any noticeable aluminum contamination is likely brought in from other sources. The compounds are usually hydrolyzed, for example, in a stainless-steel beaker, prior to incorporation in a reaction mixture. It is recommended that the alcohol generated be removed by heating, although its effect on the crystallization of high-silica materials is generally slight.

In order to prevent contamination, plastic containers such as polypropylene or Teflon, are recommended for the preparation of all solutions, for the reaction mixture, and for the crystallization. Glass vessels should be avoided, as glass participates in the reaction, and silica, alumina, and boron are known to be leached out of glass. For example, the catalytic activity of a borosilicate or a ferrosilicate may be influenced by contamination with traces of aluminum. When pressure vessels are used for the crystallization, removable Teflon or stainless-steel liners are recommended. The reaction vessels should be thoroughly cleaned prior to use by heating with aqueous sodium hydroxide, if seeding is to be avoided. Teflon may also be cleaned with hydrofluoric acid.

Nucleation, growth, and seeding in zeolite synthesis

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1. Zeolite Crystallization

Crystallization from solution generally occurs via the sequential steps of nucleation of the phase, or phases, dictated by the composition of the solution, followed by growth of the nuclei to larger sizes by incorporation of material from the solution. Nucleation and crystal growth rates typically are governed by a driving force related to the supersaturation.

Molecular sieve zeolites usually are precipitated from aluminosilicate solutions in basic media, frequently at elevated temperatures and autogenous pressures. Most commercially interesting syntheses are preceded by the formation of an amorphous gel phase which dissolves to replace reagents consumed from the solution by crystal growth. Some experimental systems which are "crystal clear" have been developed that permit certain *in situ* analytical techniques to be used to study the crystallization process.

In hydrothermal zeolite systems it is more difficult to identify a "supersaturation," because of the myriad species present in the aluminosilicate solution, because of the role of structure directing agents in some cases, and because the relative concentrations of these in a batch system change as the crystallization proceeds. For these reasons, the issue of defining the precise driving force for zeolite nucleation and crystal growth has yet to be accomplished with any degree of certainty. However, recent progress has been reported in defining solubility products and crystallization diagrams for zeolites NaA and NaX, and further progress can be expected using the approach developed there. [1]

2. Zeolite Nucleation

It is expected that the crystallization processes occurring in hydrothermal zeolite precipitation are similar to those which are known to occur in simpler inorganic or organic crystallization systems. That being the case, one should note that nucleation mechanisms in liquid-solid systems have been divided into several categories, most notably [2,3]:

1. Primary Nucleation
 - Homogeneous
 - Heterogeneous
2. Secondary Nucleation
 - Initial breeding
 - Contact
 - Shear
 - Fracture
 - Attrition
 - Needle

Chapter 5 of the text by Randolph and Larson provides excellent background on these mechanisms. [2] The primary references contained in their bibliography also are quite informative.

Primary nucleation is characterized as being driven by the solution itself, either strictly within the solution, as in homogeneous nucleation, or catalyzed by extraneous material in the solution, as in heterogeneous nucleation. Certainly with the presence of amorphous gel in most zeolite synthesis systems, one might anticipate that heterogeneous nucleation on gel surfaces might be important. This has yet to be demonstrated unequivocally.

Secondary nucleation is catalyzed by the presence of parent crystals of the same phase, and occurs with a lower activation energy than primary nucleation. The parent crystals might be added as seed crystals at the beginning of a synthesis, or grown in the original unseeded system. Initial breeding results from the addition of seeds which will be discussed below. The other secondary nucleation mechanisms could stem from added seed crystals or crystals grown *in situ*.

For example, Culfaz and Sand reported that new mordenite crystals appeared to grow from seed crystal surfaces and break off acicular pieces, resulting in nuclei formation as the dendritic pieces grew to macroscopic sizes. [4]

The mechanisms involving secondary nucleation induced by fluid shear, contact (or collision) breeding, and fracture all require sufficient fluid motion to cause physical damage to the parent crystals, and thereby promote formation and release of secondary nuclei from the parent crystal surface. In many zeolite systems, there is no induced fluid motion, as by stirring, and crystal settling is generally viewed as insufficient to cause secondary nucleation. A review of the evidence suggesting that agitation-induced secondary nucleation is not important in zeolite systems was published recently. [5] More recently, an interesting study by Falamaki, et al, has suggested that severe agitation during synthesis of ZSM-5 was not sufficient to either promote nucleation or to break ZSM-5 crystals. [6]

The numerous works by Subotic, et al., and references contained therein, have pointed to the possibility that nuclei form within the amorphous gel matrix, and are released to become viable growing crystals as the gel phase dissolves. [7] This mechanism is still under review, and yet may be plausible given the new evidence that nanometer-sized particulates (or nanoparticles) have been observed in clear solution synthesis mixtures, and may be the origin of nuclei. [8] It has not yet been determined how or when these nanoparticles form, although recent progress has been made in determining that they form almost instantaneously in the MFI synthesis system. [9]

3. Crystal Growth

Most crystallization processes involve assimilation of material from solution via a growth process which can be described by the relation [2,3]:

$$\frac{dL}{dt} = G = Ks^a$$

Where a is an exponent expressing the dependence of the linear crystal growth rate, G , on the supersaturation, s , and K is a temperature-dependent rate constant. The value of a will be 1.0 for diffusional transport limitations to a planar crystal surface, and between 1-2 for most surface reaction limited growth processes. [2,3] Schoeman, et al. have analyzed the growth rate behavior for Silicalite in clear solutions using a chronomal analysis and concluded that its growth rate is limited by a first-order surface reaction with an activation energy of 42 kJ/mol. [10] A recent summary of several reports of activation energies for zeolite crystal growth showed values to be in the range of 43-96 kJ/mol, magnitudes which certainly suggest surface kinetics limited growth rather than diffusional limitations. [11]

A debate has arisen in the literature recently regarding what species actually add to the crystal surface to promote growth and whether an agglomeration mechanism plays a role in zeolite crystal growth. Schoeman used the DLVO theory for colloidal stability to predict that nanoparticle agglomeration would not be possible in a Silicalite synthesis solution. [12] He concluded that zeolite crystal growth was supported by addition of low molecular weight species, most likely the monomer. He also concluded that the nanoparticles, observed by several research groups, would be predicted to be stable in Silicalite synthesis solutions. However, Kirschhock, et al. extended Schoeman's work to show that growth by agglomeration of nanoparticles with crystal surfaces was possible. [13] Specifically, they noted that the nanoparticles should come to rest at about 7 Å from the crystal surface in an energy well, and have ample time to orient and chemically bond to the surface. More recently, Nikolakis, et al. analyzed Silicalite crystal growth and the energetics of nanoparticle-crystal interactions using atomic force microscopy. [14] They also extended the DLVO theory and concluded that zeolite crystal growth by nanoparticle addition was possible, even though their total potential energy curves showed no energy wells or negative values at distances greater than a fraction of an angstrom.

Nothing definitive can be said about this debate at this time. Thus, growth by addition of monomers, low molecular weight species, or nanoparticles cannot be ruled out. However, growth is suggested by the magnitudes of activation energies to be limited by surface reaction kinetics rather than diffusion from the bulk liquid to the crystal surface, and the nanoparticles would be expected to diffuse rather slowly, potentially at rate-limiting rates, due to their very large molecular weights. These observations might lead one to suspect that growth should be by addition

of low molecular weight species or monomers.

4. Seeding

Adding seed crystals to a crystallization system has typically resulted in increased "crystallization" rates. The enhanced rate might be due to simply increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. Understanding the precise role of seed crystals is an area of ongoing investigation.

The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off of seed crystal surfaces in a new synthesis batch, and has been reported in zeolite systems. [15] These microcrystalline fragments grow to observable sizes, and result in greatly enhanced "crystallization" rates due to the significantly increased crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed crystals to a synthesis system will introduce sub-micron sized crystallites into the system which will serve as nuclei.

Finally, it is worth noting that a recent study of initial bred nuclei using a clear synthesis solution [16] suggested that the initial bred nuclei themselves may be the same nanoparticles observed by Schoeman [8], Kirschhock, et al. [9], and independently elsewhere. [17]. That is, the same particulates which appear to catalyze zeolite nucleation in unseeded systems may remain in sufficient number to catalyze nucleation in seeded systems, since they are inherently present with the seed crystal sample, and may be impossible to eliminate by typical filtration techniques.

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Synthesis of high-silica zeolites and phosphate-based materials in the presence of fluoride

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1. Introduction

The most common mineralizer for silica-based zeolites is the hydroxide ion OH^- . The alkaline pH is generally adjusted by addition of an inorganic base or an organic base, especially when an organic species is used as a template. The replacement of the hydroxide anions by fluoride anions as mineralizers makes it possible to obtain zeolites even in slightly acidic media (pH \sim 5). At such pH values the solubility of silica, for example, increases significantly in the presence of fluoride because of the formation of hexafluorosilicate SiF_6^{2-} species. Such species were observed in particular in the mother liquor of fluoride Silicalite-1 by ^{19}F and ^{29}Si liquid NMR. It can be assumed that the hydrolysis of fluorosilicate anions yields polycondensable hydroxylated species whose condensation leads to the crystalline material. In the synthesis of Borosilicalite-1 the presence of the hydroxyfluoroborate anions BF_3OH^- and $\text{BF}_2(\text{OH})_2^-$ in addition to BF_4^- and SiF_6^{2-} was indeed evidenced by ^{19}F NMR [1].

2. Synthesis of silica-based zeolites - Usual synthesis conditions with fluoride

Typically the synthesis mixture is prepared by adding a silica source (such as fume silica, colloidal, precipitated silica), a source of framework elements if necessary (for example, B, Al, Fe, Ga, Ti), an organic species and a fluoride source. The temperatures of crystallization are similar to those used in the synthesis without F^- but the crystallization time is generally longer.

The crystals are usually of good quality and the size generally exceeds the values obtained in alkaline type synthesis.

When the crystallization is carried out in the presence of an organic cation, as in the case of silica-rich zeolites, fluoride is generally occluded in the pores of the solid as a compensating negative charge, in addition to the negative framework charge, of the organic cations. Fluoride is essentially completely removed on calcination.

The most common and preferred fluoride sources are NH_4F , NH_4HF_2 or HF. Fluoride may also be combined with the source of framework elements such as in $(\text{NH}_4)_2\text{SiF}_6$ or $\text{AlF}_3 \cdot \text{H}_2\text{O}$, and be released on hydrolysis. The calcination of the as-synthesized material then leads directly to the H form of the zeolite. However, in the case of aluminum-rich starting gels, the sparingly soluble salts NH_4AlF_4 and $(\text{NH}_4)_3\text{AlF}_6$ may be present in the as synthesized solid. They can be dissolved by washing with an aqueous alkaline dimethylamine solution.

Most of the syntheses employing the fluoride route have been carried out in aqueous medium. However, an essentially non-aqueous fluoride route has been developed for the synthesis of large crystals in the mm range using HF-pyridine or HF-alkylamines as mineralizers [2].

3. Synthesis of phosphate-based materials - Usual synthesis conditions with fluoride

In contrast to the alkaline pH values in the conventional synthesis of silica-based zeolites, the usual pH of the reaction mixture for the synthesis of phosphate-based materials such as aluminophosphates and gallophosphates is slightly acidic to slightly alkaline (typically, starting pH = 3-10). Therefore the pH conditions for the synthesis of phosphate-based materials in the

presence of fluoride are close to those that would be used in its absence.

Nevertheless, various beneficial effects are observed in the presence of fluoride. The crystallization times are generally shorter and the crystals usually larger and well formed. Thus, in the synthesis of the CHA-type materials SAPO-34 and CoAPSO-34, it was observed that, when F^- was present, the induction time was smaller (divided by about 3), but the rate of crystal growth was smaller than when it was absent [3]. It was assumed that the presence of fluoride favors the fast production of fewer nuclei, after which crystal growth consumes preferentially but slowly the precursors. The stability of the fluorocomplexes must not be so high that further reaction involving them is inhibited.

Another beneficial effect of the presence of fluoride is the production of a number of phases which do not form in a fluoride-free medium, thus showing a structure-directing role of the fluoride ion. For such phases, fluoride is generally part of the framework bonded to Al or Ga atoms as terminal or bridging species, or even trapped in double-four-ring units.

The preferred fluoride source is HF, the pH being adjusted by addition of an organic base. The presence of NH_4^+ or Na^+ cations is undesired in that case since ammonium or sodium aluminophosphates may be produced, for example $AlPO_4-15$ $NH_4Al_2OH(PO_4)_2 \cdot 2 H_2O$, may be produced. On calcination fluoride is removed together with the organic template.

For more information the reader is referred to the article entitled "The Opportunities of the Fluoride Route in the Synthesis of Microporous Materials" by Kessler, Patarin and Schott-Darie [4].

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Templating in molecular sieve synthesis

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Zeolite crystallization is a very complex phenomena that cannot be adequately described by the classical variables of reactant composition, temperature, and pressure. Crystallization also involves polymerization-depolymerization, solution-precipitation, nucleation-crystallization, and other complex phenomena encountered in aqueous colloidal dispersions.

In the early descriptions of molecular sieve synthesis, the species that formed the oxide framework (such as silicate, aluminate) were distinguished from extraframework species, such as exchangeable cations (Na^+ , K^+) and water. In some cases the "exchangeable" cations were not completely exchangeable without significant structural damage (such as K^+ in OFF). Nevertheless, the cations played an obvious role in the charge compensation of the alumina tetrahedra in the product. Less obviously, the frequent association of certain alkali cations with the presence of smaller cage structures led to the concept of a mechanistic role that was designated "templating." Templates were cationic species added to synthesis media to aid/guide in the polymerization/organization of the anionic building blocks that form the framework.

In one of the first broad studies of zeolite crystallization in the presence of mixed alkali-organic bases, Aiello and Barrer explained the observed structure specificity of the mixed cations by introducing the concept of templating of the different cage structures by the larger organic and smaller alkali cations. [1] In particular, the quaternary organic tetramethylammonium (TMA) appeared to play an important role in the formation of the OFF and MAZ structures, since these structures were not observed in its absence. The authors suggested that the TMA helped form the aluminosilicate precursor of the gmelinite cage building unit that was common to both structures through a templating action. In a subsequent study of the role of multiple cations, H. Khatami postulated that in the synthesis of zeolites from systems containing ternary, quaternary, or higher numbers of cations, "the zeolite framework structure is determined by one or at most two cations depending on their type and size. Additional cations, should they be included in the lattice, affect the zeolite properties but have minimal or no influence on the structure topology." [2]

In 1973 Flanigen reviewed the concepts governing zeolite crystallization and observed that cations play "a prominent structure-directing role in zeolite crystallization. The unique structural characteristics of zeolite frameworks containing polyhedral cages have led to the postulation that the cation stabilizes the formation of structural subunits which are the precursors or nucleating species in crystallization." [3,4,5] The many zeolite compositions and complex cation base systems

Table 1. Synthesis cation specificity for framework structures

Structure Type	Polyhedral Building Units	Synthesis Cations	Cation Specificity
LTA	D4R, sodal, α	Na, Na-TMA, Na-K, Na-Li	Na
FAU	D6R, sodal	Na, Na-TMA, Na-K	Na
KFI	D6R, α	Na-DDO, (Ba?)	Na-DDO
GME	D6R, gmel	Na, Na-TMA	Na
MAZ	Gmel	Na-TMA, Na-K-TMA, Na-Li-TMA	Na-TMA
OFF	D6R, gmel, canc	K-TMA, K-Na-TMA	K-TMA
ERI (with OFF)	D6R, canc (gmel)	Na-K, Ba-TMA, Na-Rb, Na-TMA Na-K-TMA, Na-Li-TMA, Na-K-BTMA	Na-K, Na-Rb, Na-TMA Ba-TMA
LTL	D6R, canc	K, K-Na, K-DDO, K-Na-TMA, Ba, Ba-TMA	K or Ba
CHA	D6R	Na, K, Na-K, Ba-K, Sr	Na, K, or Sr

D4R = double 4-ring, D6R = double 6-ring, sodal = sodalite cage, α = truncated cuboctahedron, gmel = gmelinite cage, canc = cancrinite cage.

were compelling examples of the structure-directing role of the cation and the cation "templating" concept. In this early context "templating" and "structure-directing" were synonymous.

Table 1 shows some of the early cation/structure relationships. It is clear from this table and other data that some structures exhibit a structural cation specificity (such as LTA and FAU for Na) while others do not (such as ERI, CHA). Table 2 further delineates the relationship between building units and cations in the early zeolite structures. The formation of a specific framework type and a polyhedral building unit depends on one or at most two cation species. The cation specificity is strong for the α -cage, sodalite cage, gmelinite cage and D4R unit. It is weak for the D6R unit. In some cases the cation (hydrated or anhydrous) is observed to fit nicely into the building unit; in others, multiple cations are present.

Table 2. Synthesis cation-building unit relationship

Building Unit	Structure-types containing building unit	Cation specificity for building unit
α	LTA, KFI	Na
Sodalite	LTA, FAU	Na or TMA
Gmelinite	GME, OFF, MAZ	Na or TMA
Cancrinite	ERI, OFF, LTL	K, Ba, or Rb
D4R	LTA	Na
D6R	FAU, KFI, CHA, GME, ERI/OFF, LTL	Na, K, Sr, Ba

In 1983 Lok, et al., reviewed the role of organic molecules in molecular sieve synthesis at a time when most new structures were the result of synthesis in the presence of different quaternary ammonium cations or amines. [6] The charge distribution and the size and geometric shape of the template were invoked to explain structure direction. These authors also addressed the persistent issue of template specificity. It was already known that in some instances: 1) one template can give rise to several different structures, 2) many templates can yield the same structure, and 3) some structures require the presence of a particular template. The solution to this dilemma was the interplay of templating and "gel chemistry" where "gel chemistry" represents all the other reaction parameters governing the gel, such as oxide composition, temperature, time, reagent type, pH. In a real sense the template was a necessary but not a sufficient condition for structure formation.

As larger and more complex organic cations were employed, the resulting structures had the organic species filling not just cages, but channels (such as 1,8-diaminooctane in ZSM-48) and channel intersections (such as tetrapropyl-ammonium in MFI). The ability of quaternary ammonium polymers to influence and to direct crystallization of zeolites was described by Rollmann et al. for a series of 1,4-diazabicyclo[2.2.2]octane-based polyelectrolytes. Examples are given in which the polyelectrolytes force crystallization of the large-pore zeolite mordenite where the small-pore species analcite would otherwise have resulted. Polymeric cations prevented stacking faults in a synthetic gmelinite, faults which had hitherto restricted access to the 12-ring channels of both natural and synthetic samples of this zeolite. [7]

In addition to the more numerous and readily available quaternary ammonium cations, other classes of nitrogen-free, cationic templates have also been used successfully. Complexes of alkali cations with crown ethers have been exploited to make novel structures (such as EMT) and known structures with novel compositions (such as FAU, KFI, RHO). [8] Balkus found that a variety of stable, cationic, substituted metallocenes could also be used to template novel structures. [9,10]

More recently, there have been several reviews that address structure-direction in high-SiO₂ zeolite crystallization. The concepts of structure-directing agent (SDA) and pore filling agent have been used to describe the relationship between the relatively hydrophobic organic cations and the oxide lattice with little or no framework charge. Davis and Zones and their coworkers [11,12] have attempted to correlate the ability of an organic cation for structure-direction in zeolite synthesis with its hydrophobicity and rigidity. The hydrophobicity of a variety of SDA's was evaluated by measuring the phase transfer behavior of the iodide form from H₂O to CHCl₃. The

rigidity was evaluated from the number of tertiary and quaternary connectivities. SDA's with intermediate hydrophobicity were found to be most useful for high-SiO₂ molecular sieve synthesis. In terms of SDA geometry, a bulky, rigid molecule with limited conformational variability tends to template a single structure. The use of relatively flexible molecules with a minimum diameter of ~5Å gives more than one molecular sieve, depending on the gel chemistry. Zones and coworkers have designed and prepared numerous bulky, rigid templates and used them to synthesize a great variety of new high-SiO₂ molecular sieves.

Lobo, et al., have also reviewed the concepts of structure-direction in the synthesis of clathrasils and high-silica zeolites with emphasis on the energetic interactions between the organic guest and the inorganic framework. [13] The effects of size, geometry, and the chemical nature of the organic structure-directing agent on the crystalline structures that are formed were discussed beginning with clathrasils and ending with 12-ring zeolites with 3-dimensional pore systems. The application of structure-directing concepts is described using the syntheses of ZSM-18 and SSZ-26 as examples, and the control over long-range order in zeolites by structure-directing effects is illustrated by the purposeful variation of the stacking probability of SSZ-33/CIT-1 and FAU/EMT intergrowths.

Although amines have been used to successfully synthesize some high silica zeolites, they have been particularly effective in the synthesis of crystalline aluminophosphate-based molecular sieves and the concept of templating persisted. A wide variety of neutral AlPO₄ molecular sieve frameworks have been prepared using quaternary ammonium cations or amines, where these organic species occupy cages, channels, and intersections. Additional AlPO-based compositions and structures resulted when the framework incorporation of one or more additional elements (such as Si, Mg, Mn, Fe, Co, Zn) generated negative charge. [14] Cationic templates were still the norm, since the organic amines were predominately protonated in the more acidic synthesis media. Most of the AlPO-based molecular sieves were prepared without the need for any alkali or alkaline earth cation. In these systems the structure-directing role of the template is dominated by stereospecific space-filling and stoichiometry between the template and the framework, and is influenced to a lesser extent by framework charge compensation. With the synthesis of alkali-free forms of the CHA, ERI, FAU, SOD, and LTA structure-types, it was also clear that many structure-cation specificities are likely to be framework composition dependent.

Among the goals of zeolite science are the understanding of zeolite shape selectivity and the synthesis of new zeolite structures with desirable properties. Harris and coworkers have combined computer simulation of host/guest interactions and experimental data to understand how organic templates interact with zeolite structures. [15] In the cases of ZSM-5, ZSM-11 and SSZ-33 they found that modeling can reveal details of the complex interaction of templates with zeolite frameworks and correctly predict which silicate structure a template will make. They also observed that in the NON and CHA structure types, the zeolite template interaction energies correlate extremely well with experimental crystallization times, indicating participation of the template in the rate determining step of crystallization. [16]

A combination of several computer modeling techniques has been applied to investigate the ability of organic molecules to template microporous materials. [17] The efficacy of a template was rationalized in terms of the energetics of the host-template interactions. The calculated geometries of the template/framework combinations are in excellent agreement with the experimental structural data. The procedures used can successfully identify optimum templates for a given host. These results suggest that in the future it may be possible to design a theoretical zeolite structure and design a template to make it, all by computer simulation.

Catlow and his collaborators have recently achieved half the objective by using *de novo* design techniques (available in the computer code ZEBEDDE) to predict that 4-piperidinopiperidine would produce a previously known structure, an aluminophosphate molecular sieve with the CHA structure. The authors demonstrated the successful application of computer aided materials design, through the identification of critical parameters in the synthesis and the computational design of a suitable template, and then used the template to synthesize a microporous material possessing predefined structural and physical properties. [18,19] The material was structurally characterized using a combination of diffraction and EXAFS techniques. [20] It now only remains to design a theoretical structure and the template to make it, then use that template to make the target

structure.

Although most templating or structure-direction has been attributed to cations, the fluoride anion has also shown a templating effect in molecular sieve synthesis. [21] Fluoride has long been known to have a mineralizing (or mobilizing) effect in synthesis. This effect applies especially to silica-based materials which may thus be prepared in media with pH lower than 10-11. The structure-directing effect was found when F^- enabled the formation of three entirely novel materials (the silica form of the AST structure type, LTA-GaPO₄ and CLO-GaPO₄). In each of these structures F^- is incorporated into D4R units of the material and contributes strongly to the stabilization of the structure, as do the organic template molecules. This effect is chiefly observed when the framework has no charge or if its charges are auto-compensated. F-synthesis has been most recently exploited by Corma and coworkers to make a variety of pure SiO₂ structures. [22] In many of these structures the fluoride appears to be bonded to the SiO₂ lattice imparting a temporary negative charge to balance the cationic template charge. [23] Thermal treatment removes both F and organic.

In summary, alkali cations are most effective in templating low Si/Al zeolites from basic media. Quaternary ammonium cations are best at templating medium to high Si/Al zeolites and AlPO-based molecular sieves. Amines have been used to template AlPO-based molecular sieves and high-Si zeolites, and it is believed that the effective form of the amine is certainly the protonated form in AlPO-based synthesis and probably the protonated form even at the higher pH range typical of the high Si zeolites. Quaternary ammonium cations and amines have been very effective templates for phosphate-based structures, in general. The effectiveness, variety, availability, stability, and cost of the nitrogen-based cations as templates has not yet been rivaled.

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