

VERIFIED SYNTHESES OF ZEOLITIC MATERIALS

**Third Revised Edition
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N. Barrier, XRD Patterns**

**Second Edition
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of the International Zeolite Association**

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Verified Syntheses of Zeolitic Materials

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I. Preface to the third edition

The first edition of Verified Syntheses of Zeolitic Materials was published in Microporous and Mesoporous Materials (1998) Volume 22, 4-6. Distribution was limited to subscribers to the Journal.

The second edition was published on behalf of the Synthesis Commission of the International Zeolite Association in 2001, Elsevier, ISBN: 0-444-50703-5. The 2nd edition of the book reprinted all the recipes from the first edition plus 24 new recipes. The introductory section includes the articles from the first edition (some with substantial revisions) and five new articles.

The current 3rd edition (ISBN-10: 0-692-68539-1) has reprinted all the recipes (72) from the second edition plus 36 new recipes (total 108 recipes). The introductory section contains 14 new articles reporting on the very recent developments in the area of zeolite synthesis. The introductory articles present the state of the art topics related with zeolites including: synthesis of new molecular sieves using novel structure-directing agents, design of new molecular sieves via new synthesis approaches, synthesis of zeolites with nanosized dimensions, synthesis of single-unit-cell hierarchical zeolites, synthesis of aluminophosphate analogues of zeolites, and post synthesis modifications of zeolites. Additionally, the main approaches used for characterization of zeolites including: diffraction methods, advanced spectroscopic methods, and adsorptive separation techniques are revealed. Important contributions on modeling of zeolites from the unit cell to the crystals and development of new zeolite-based catalytic processes are added. The intended audience of this book is researchers, specialists from academia and industry in the area of zeolites, zeo-type porous materials. Additionally, students at undergraduate, PhD and Post Doctoral levels involved in the syntheses of zeolites and related materials will use it as a reference book. This book will be of interest for specialized master courses in Materials Science and Practice.

The XRD patterns presented in the third edition have been recorded using different instrument from those in the first and second editions.

Zeolite synthesis is an active field of research. The 2nd edition of this book was published in 2001 when the zeolite structures known during that time were about 130. Due to the great interest in the zeolite synthesis, which is driven by the need for existing and new applications, the number of zeolite structures increased substantially, and in 2016 more than 231 different zeolites are available. With the development of new synthesis approaches and modeling of the syntheses processes, many new zeolites types were synthesized. Besides, known zeolites with unique properties were prepared by applying new synthesis methods combined with novel techniques for characterizations.

These zeolitic materials find great applications in catalysis, sorption and ion exchange processes. Additionally, zeolites become attractive materials for nanotechnology applications, medicine, cosmetics, pharmaceutical, and food industries. The IZA Synthesis Commission (<http://www.iza-online.org/synthesis/default.htm>) prepared the 3rd edition of the book in order to enlarge the existing collection and to include new materials of interest to the zeolite research community. Besides the introductory articles revealed the most important developments from the last decade associated with synthesis, characterization and application of zeolites.

The IZA Synthesis Commission will continue to enlarge this collection and will include all phases of interest to the zeolite research community.

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III. Introduction and explanatory notes

The Synthesis Commission consists of experts in the synthesis area of zeolite and zeo-type materials. The format for the recipes in the 3rd edition of the book follows the style of the previous two books. The table format is intended to assist the reader by placing the information in the same relative positions for all recipes.

The table form describing the synthesis experiments follows the typical 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 (<http://www.iza-structure.org/databases/>). They define the topography, but not the composition of the crystalline materials. The third edition of the book contain multiple entries for a single code with differing Si/Al ratio products, products with differing T-atoms, products of essentially the same composition produced by different synthesis procedures, and materials with different particle sizes.

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. 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.

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 contributor's section.

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. Negative responders, those who replicated the experiment but obtained a product other than the

desired phase, are acknowledged in the contributors' section. 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 authors 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 that 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 readers' convenience. For each step, the materials added and the orders 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 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 authors 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. Any particular conditions of hydrothermal treatment of zeolites if apply are added in the section "Notes".

12. Product Recovery

Product recovery refers to the procedure for separating the desired product from the byproducts 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 = 7-10 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. Additional information on the purification of nanosized zeolite crystals via high-speed centrifugation is added to the specific recipes.

Drying usually is accomplished in a laboratory oven at ~100C. It is good technique to equilibrate the dried sample at a constant 50% humidity to make it stable to handling in laboratory air. Freeze-drying technique is applied for drying of nanosized zeolites in order to avoid post synthesis agglomeration of nanocrystals.

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

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 floes, 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 <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, particle size, 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, is 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 users 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.

IV. Conditions for recording of XRD patterns

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36 new samples included in the 3rd edition

The powder X-ray diffraction (PXRD) patterns were recorded with a BRUKER D8 advance diffractometer in Bragg-Brentano geometry. The diffractometer was equipped with a Ge-focusing primary monochromator giving Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), a Lynxeye detector operated with 3.5° opening. A fixed divergence slit of 0.6 mm was used as well as primary and secondary Soller slits of 2.5° . A beam knife and an 8 mm anti scattering slit placed in front of the Lynxeye detector were also used. All diffraction patterns were recorded within the 2θ range $2 - 50^\circ$ with a step size of $\sim 0.014^\circ$ and a time per step of 4 s. Since no diffraction peaks are observed below $4^\circ(2\theta)$ all patterns were rescaled on the 2θ range: $4 - 50^\circ$. The diffraction patterns are presented in the as measured condition without any background subtraction or smoothing.

All samples have been intimately crushed in an agate mortar and then placed on back loading sample holders to limit preferential orientation. For samples in too small amounts the powder was deposited on a flat silicon zero-background sample holder.

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72 samples reproduced from the 2nd edition

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 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 (ordinate) for all patterns is K-Counts/second. For comparison with measured diffraction patterns it is 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.

V. Contributors

The authors of recipes with mailing addresses and institutional affiliation in this volume are identified by name only in the recipe. A truthful effort has been made to update or verify addresses from the second edition recipes, which are included in the third. Changes of affiliation are to be expected.

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VI. Introductory Articles

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Introduction

The origin of zeolites comes from microporous aluminosilicates. Today, the word 'zeolite' is no longer restricted to this type of materials. It refers to any silica-based crystalline microporous solid in which some of the silicon is replaced by other elements T such as the trivalent elements T = Al, Fe, B, Ga, etc., or tetravalent elements T = Ti, Ge, etc. Depending on the Si/T molar ratio, the materials are classified into two groups; zeolites when the Si/T < 500 and zeosils with the Si/T > 500.

Zeosils and clathrasils form the two classes of silicic materials in the porosil family. Phosphate-type crystalline microporous solids are commonly called related microporous solids. Generally, the microporous solids are characterized by a 3D framework resulting from the stringing together of tetrahedral units TO₄ with shared oxygen vertices (T = Si, Al, P, Ge, Ga, etc.); channels and/or cavities with molecular-sized cross-sections, connected with the surrounding medium. The formed channel systems are 1-, 2- or 3-dimensional. Microporous materials with cage structures are 0-dimensional.

Real structures may deviate from this ideal definition by the presence of units with non-tetrahedral coordination, e.g., TX₅, or TX₆ polyhedra, where X = O, F, or non-bridging neighboring units, e.g., T–OH, T–F or T–O⁻ end groups as in interrupted frameworks. The structural code comprises three capital letters, which are attributed by the structure commission of the International Zeolite Association (IZA) to each structure obtained in this way. If the framework is interrupted, the 3-letters are preceded by a hyphen. In the case of zeolites crystallizing as disordered structures, a star precedes the 3-letters codes. Only few structures have both [1].

Synthesis of zeolites and related materials

Zeolite and related materials are usually obtained by hydrothermal crystallization of a gel comprising a liquid and a solid phase. The reaction medium contains:

- a sources of framework elements T = Si, Al, P, etc.,
- a sources of mineralizing agents OH⁻, F⁻,
- an inorganic cations and/or organic species (neutral molecules or cations),
- a solvent (usually water).

Zeolites are generally synthesized in a basic medium at temperatures below 200°C and low pressures (autogenous pressure < 20 bar). In the case of related microporous materials (aluminophosphates, etc.), the pH of the reaction medium is general in the range 3–10. The anions OH⁻ [2] or F⁻ [3-5] solubilize the reactive species in the gel (formation of silicates and fluorosilicates) and enable their transfer to the growing crystals. The time required for this kind of synthesis is extremely variable, but generally somewhere between a few hours and several days.

The nature of the reactants and their purity can have a huge impact on the synthesis of these solids [6]. The presence of impurities can cause undesired species to nucleate. It can be the case for the synthesis of zeosils (pure-silica zeolites) where a pure-silica source has to be used as reactant. Indeed, the silica source can be contaminated by traces of aluminum used for shaping for instance. Therefore, zeolites with high silicon to aluminum ratio are obtained instead of pure zeosils. In some cases, less pure reactants can be used to prepare zeolites but their composition can be varied from one batch to the other and from one supplier to the other. Therefore, the source materials for zeolite synthesis and technical grade materials need to be assayed and analyzed for impurities. A description of the most popular reactants is given below.

Sources of silica

Several kinds of silica sources can be found, fumed silica, precipitated silica or colloidal silica. As mentioned above, depending on the type of microporous solids to be synthesized, the choice of the silica source can be crucial.

Zeosils can be prepared using fumed silica. These silica sources correspond to pure SiO₂. Such sources are on the market. The water content is very low (about 3 wt. %) Such silica sources allow to get zeosils with Si/Al molar ratios above 10,000.

Other pure silica sources are the tetraalkylorthosilicates. The most common source is the tetraethylorthosilicate (TEOS). Its hydrolysis leads to the formation of SiO₂ and four molecules of ethanol. Be careful, the presence of alcohol can change the synthesis medium; the main solvent being not water but a mixture of water/ethanol. Although the effect is slight, this can lead to synthesis of non-desired compounds. However, ethanol can be removed before synthesis (evaporation by heating). With such silica sources, pure zeosils can be synthesized.

When Si/Al ratios above 6,000 are acceptable, colloidal silica solution can be used. These sources are available with different SiO₂ concentrations; the water coming from the silica source has to be taken into account for the molar composition of the reactant mixture.

Precipitated silica allows to obtain zeolites with Si/Al molar ratios above 200. A widely used silica source is aqueous sodium silicate also known as water glass or liquid glass. According to the manufacturer, it contains different amount of water. It is slightly cloudy; a small contamination with aluminum prevents zeolites with Si/Al ratios above 300 to be crystallized.

Sources of aluminum

Sodium aluminate may be used in zeolite synthesis in particular for zeolites with a low Si:Al molar ratio. This is because CO₂ gas present in air reacts with sodium aluminate just upon storage, forming Na₂CO₃ and aluminum hydrate and therefore lowering the pH of solutions. Therefore, it is recommended to use fresh prepared sodium aluminate solutions. An interesting aluminum source is pseudoboehmite of formula AlOOH. Among the aluminum salts, hydrated aluminum sulfates Al₂(SO₄)₃ is often used in zeolites synthesis. Alkoxides are also sources of aluminum; the most used is aluminum isopropoxide. For high Si/Al molar ratios, the presence of isopropanol after hydrolysis in the reacting mixture has a less influence on the synthesis but this is not true in the case of the synthesis aluminophosphate for which the Al:P molar ratio is often 1. Metallic aluminum dissolves in alkaline solution may represent an alternative when other salts do not enable the formation of zeolites. Finally, a zeolite itself like Y zeolite may be used as a source of aluminum; in this case a dissolution-recrystallization process during the hydrothermal treatment is involved.

Sources of hetero T elements

The most widely synthesized metallosilicates are borosilicates, gallosilicates, zincosilicates, titanosilicates and ferrisilicates [7]. Another main family is germanium-containing zeolite (germanosilicates and silicogermanates) [8-9]. It is important to note that the presence of hetero-elements (other than silicon or aluminum) can direct the synthesis and promotes the formation of structures unobtainable in their absence. The nature of the heteroatom associated to silicon can have a real structure-directing role. This is the case of zinc or beryllium, which allow the crystallization of different topologies in (Si,Al) medium, forming 3-membered ring cycles (3-MRs) occupying preferably [10] like for the zincosilicate VPI-7 [11] and beryllsilicate OSB-1 [12]. Other heteroelements such as boron or gallium allowed to obtain original microporous solids such as the borosilicate RUB-13 [13] or gallosilicate TNU-1 [14].

The main sources of boron are boric acid and sodium borate [15]. Also, calcined boron- α zeolite has been advantageously used as reactant [16]. Gallium halide salts and gallium oxide or oxy hydroxide obtained by slow calcination at 300°C under air of gallium nitrate are usually the gallium sources. Germanium halide salts, amorphous GeO₂, which dissolves easily in basic solutions, are mainly used as the germanium sources but fine powder of crystallized Ge-quartz is also possible.

The isomorphous substitution of Si by Ti atoms into a zeolite framework is achievable but in a less extent in comparison with aluminum. The first titanosilicate molecular sieve described was Ti-silicalite-1 (TS-1) [17]. The titanium sources are tetraethylorthotitanate, titanium tetrabutoxide or halides TiCl₄ and TiF₄. Iron halides, nitrate and sulfate more or less hydrated are used to synthesis iron containing zeolites [18].

Sources of mineralizing agent

In alkali media, the mineralizing agent is OH⁻ [2], alkali hydroxide (NaOH, KOH), sodium aluminate and hydroxide salts of organic structure directing agents are the main sources. Fluoride anions are generally introduced as HF, NaF, NH₄HF₂ or NH₄F salts in the synthesis mixture. In the case of porosils, the fluoride route has the important advantage to lead to materials with a much lower density of defects due to the charge balance role of the fluoride anions against the positive charge of the organic cations [19-20]. Apart from their mineralizing role, the fluoride anions can play a co-structuring role by stabilizing certain units in the building of the inorganic structure, in particular for the double-four membered rings units (*d4r*) [5,19-20].

Structure-directing agents

The structure-directing agent (SDA) can have multiple roles. It may compensate the charge of the inorganic structure (in the case of a cation). The properties of the synthesis mixture may be modified, e.g. it contributes to an increase of the pH of the reaction gel in the case of cations having OH⁻ as counter ion. Finally, these species have a structuring effect, i.e. the ability to direct the synthesis to a specific zeolite. There are two types of structure-directing agents in zeolite synthesis, inorganic (ISDA) and organic (OSDA). Alkaline and alkaline earth metals are the main ISDA that play a crucial structure-directing role in zeolites synthesis [21] in particular for zeolites with a low Si/Al molar ratio prepared in highly basic media. Since their first use [22], OSDAs allowed the increase of the number of zeolitic frameworks with different chemical compositions. Many of these topologies have not a natural counter-part. Typically, they are primary, secondary, tertiary, and quaternary amines. Other molecules like alcohols [23] and crown ethers [24] are used. They increase crystallinity and influence the Si/Me molar ratio of the framework. Generally, cationic OSDAs possess a single positive charge but dicationic OSDAs leading to several new SDA topologies, there are diquaternary ammonium

salts [9]. More recently, phosphonium and diphosphonium salts have been successfully used in the synthesis of new zeolites [25-26].

Several behaviors of the OSDA molecules have been identified and classified into three categories [27]. First, the true "OSDA", they correspond to organic species that lead to a zeolite framework to adopt specific geometric and electronic configurations of the OSDA. This is a very rare case illustrated by the example of zeolite ZSM-18 [28]. The second category concerns "structuring agents", i.e. OSDAs that lead to a zeolite type, and are therefore specific to that topology. Finally, the third category of OSDAs is represented by species that act as "pore-filling" and are therefore not specific to a topology: a given molecule will yield several different materials depending on the synthesis conditions and compositions of the reaction mixtures. Simple OSDAs are commercially available but most of those used by zeolite chemists are home made in laboratories.

Water content

Dilution of synthetic gels is an important parameter. Indeed, gels differing only by the water content can lead to the crystallization of different structures. Thus, in the pure silica system, high concentrated synthesis media (very low amount of water, H₂O/Si molar ratio below 10) led to pure-silica *BEA-type zeolite [29]. This is also particularly true in the (Si,Ge) and (Si,Ge,Al) system and well illustrated by the ITQ-33 example [30]. It is recommended that the water contained in reactants always must be considered in the preparation of the synthesis mixture [6].

Summary

Hydrothermal synthesis of zeolites and related inorganic microporous materials requires mainly inorganic reactants but the presence of organic species as structure-directing agents may be necessary. These reagents are mixed together to form a gel whose composition must be controlled. For that, it is imperative for the zeolite chemists to check carefully the chemical composition of the reactants before undertaking a synthesis. In this introductory section, we list different sources of reactants that are used for the hydrothermal synthesis of zeolites or related molecular sieves.

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2. Synthesis of new molecular sieves using novel structure-directing agents

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Introduction

Tremendous progress has been made in zeolite synthesis over the past half century through the pioneering innovations of the zeolite community. At the center of these advancements is the use of organic structure-directing agents (SDAs). Since the early work of Barrer and many others, [1, 2, 3, 4] SDAs have been used to create over 230 unique structural frameworks and any number of different chemical compositions. Initially, small simple molecules, such as tetraalkylammonium cations, were utilized as SDAs, but today, diquatery and triquatery ammonium cations, along with phosphonium- and sulfonium-based SDAs are frequently considered in the synthesis of novel zeolites. Figure 1 highlights the key innovations that have driven the field forward and that will be discussed in this article. Using different amine reactions, researchers have created libraries of ammonium SDAs using commercially available reagents. [5, 6, 7, 8] The diversity of SDA sizes, shapes, and charge densities has allowed for the discovery of many new zeolites under a variety of inorganic conditions.

While the mechanism of zeolite nucleation is often related to zeolite-SDA interaction energies, it is well-known that zeolite crystallization is a kinetically controlled process. In addition to SDA choice, several synthesis factors can influence phase selectivity, such as the silica and alumina sources, alkali/alkaline earth cations, hydroxide/fluoride mineralizing agents, gel concentration, and hydrothermal processing conditions. Still, some general rules about SDA size and shape have been observed. For example, large SDAs generally produce large cage-based structures, whereas clathrates and small cage zeolites are templated by smaller SDAs. The synthesis of one-dimensional zeolites is often directed by linear SDAs, while branched SDAs tend to create multi-dimensional frameworks. [9] These trends have been discussed further by others. [10, 11]

The utility of an organic compound as a zeolite SDA is additionally dependent on its stability at the high temperature and pH typical of hydrothermal syntheses. For example, quaternary ammonium SDAs can undergo the Hofmann elimination reaction to an amine and an alkene in the presence of a base and heat. Additionally, organic compounds selected for use as SDAs need to be adequately soluble in water. Zones and co-workers demonstrated that SDAs with an intermediate C/N⁺ ratio (between 11 and 16) have the highest tendency to crystallize high-silica zeolites, as they are soluble in water but sufficiently hydrophobic such that there is preferred interaction with the silicate species. [12]

In this article, we highlight a few novel and inventive uses of SDAs that have recently been developed to create new frameworks, compositions, and morphologies. Many reviews have been written on SDAs and their role in zeolite synthesis, [13, 14, 5] and we refer the reader to these papers for further information.

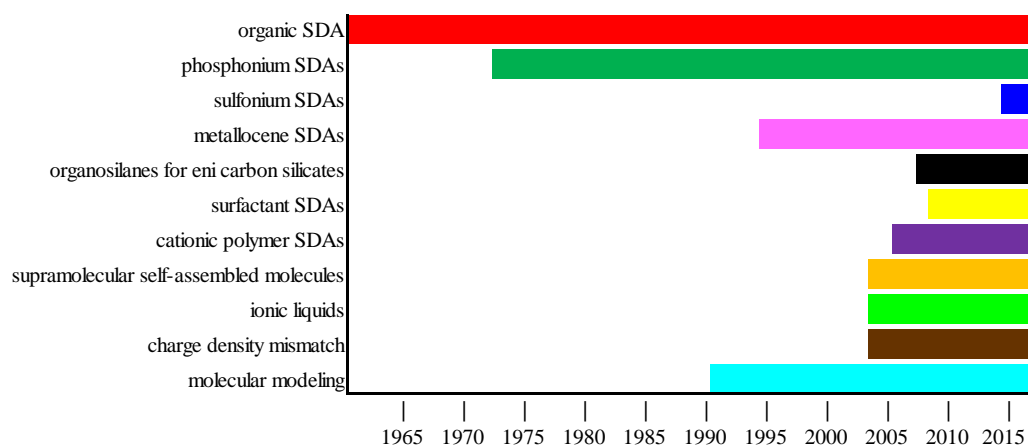


Figure 1. Timeline of key SDA innovations.

Novel SDAs

Non-Ammonium SDAs

In an effort to discover new zeolite materials, many research groups have begun to explore novel types of SDA chemistries. For example, phosphonium-based SDAs, which have been in use since the early days of synthetic zeolites, [15] have recently enabled the discovery of new zeolite structures. Importantly, unlike ammonium SDAs, phosphonium analogues do not degrade via the Hofmann elimination reaction and can therefore be used at higher pH and temperature. Corma and co-workers have recently found several new structures using novel phosphonium-based SDAs, including ITQ-26, ITQ-27, ITQ-34, ITQ-40, ITQ-47, ITQ-49, ITQ-52, and ITQ-53. [16] In related work, Sano and co-workers have studied the interzeolite conversion of FAU to 8-ring zeolites using phosphonium SDAs and have shown that the phosphorus in the SDA can be used as a modification agent to the zeolite. [17]

Application of phosphazene chemistries that enable the synthesis of SDAs from smaller phosphonium and amine building blocks have also caught the attention of the zeolite community. Due to the large number of commercially available amines with various alkyl groups, this SDA synthesis route is ripe with possibility. Moreover, because these compounds are highly basic, the silica is easily mobilized in these types of zeolite synthesis gels. Corma and co-workers have applied this idea to create the first synthetic example of boggsite, which is a 10- x 12-membered-ring (MR) zeolite with catalytic potential. [18]

As another example of novel non-ammonium SDAs, Ryoo and co-workers recently used sulfonium-based SDAs in their discovery of an aluminosilicate MEL and three germanosilicates. [19] Two of the germanosilicates, ISV and ITT, were previously synthesized using mono and diquatery ammonium SDAs, respectively, and the third germanosilicate is a new 15- x 12- x 12-MR open framework structure. Whereas ammonium-based SDAs are typically limited to C/N⁺ ratios between 11 and 16, those made from sulfonium can have higher C/S⁺ ratios due to the higher solubility of the sulfonium compounds in water. In turn, this opens up the opportunity to create new structures with extra-large pores from larger and bulkier SDAs.

Two more innovations serve as final examples of the use of non-ammonium SDAs. Balkus and co-workers discovered the first 14-MR zeolite using a cobaltocene complex as the SDA. [20] Importantly, this was the first extra-large pore silicate-based material; previously, extra-large pore materials were phosphate-based. In the work of Bellussi and co-workers, the organic was incorporated into the silica source, resulting in the discovery of a new class of materials called eni carbon silicates (ECSs). By using a

series of organosilanes, Bellussi's team synthesized a number of new organic-inorganic hybrid ECSs with highly porous and complex structures. [21]

Surfactant and Polymer SDAs for Hierarchical Zeolites

In order to accommodate larger reactant molecules and increase mass transfer, the zeolite community has long desired a material with both micropores (< 2 nm) and mesopores (2-50 nm). Early attempts to synthesize these hierarchical materials employed a co-templating strategy where both traditional SDAs and surfactants were added to the synthesis gel. In theory, the desired zeolite framework is dictated by the SDA, and the surfactant templates ordered mesopores from micelle-like structures. However, in practice, a physical mixture of separate microporous and mesoporous materials usually results. More recent co-templating strategies have resulted in true hierarchical zeolites by controlling either the synthesis parameters or the surfactant. [22, 23]

The landmark work of Ryoo and co-workers demonstrated that lamellar zeolite nanosheets could be grown using a single SDA in a one-pot synthesis. The first organic molecule used in this synthesis approach combined a long alkyl chain (to prevent crystal growth in the z-direction) with a diquatery ammonium head group known to direct the synthesis of MFI. [24] By changing the ammonium head group, lamellar BEA, MRE, MTW, AEL, AFI, and ATO frameworks were also synthesized. [25, 26]

Xiao and co-workers have used cationic polymers to create hierarchical materials. Here, the cations are similar to traditional ammonium SDAs, which direct for specific zeolite frameworks. However, the longer length scale of the polymerized cations causes the molecule to act as a porogen, resulting in the formation of disordered mesopores. Using this strategy, Xiao's team has developed hierarchical BEA, MFI, and FAU. [27, 28, 29]

Supramolecular Self-Assembled Molecules as SDAs

In order to create extra-large pore zeolites (> 12 MR), many groups have endeavored to synthesize bulkier SDA molecules. However, as previously discussed, solubility of the organic in water requires that the C/N⁺ ratio be kept below ~16. As a way to circumvent this issue, Corma and co-workers used organic compounds with aromatic rings that can self-assemble through pi-pi interactions into larger dimers and trimers. [30] Moliner recently wrote a good review on this subject from which a few important examples have been selected for discussion here. [31]

..... The original demonstration of supramolecular self-assembled molecules as SDAs by Corma's group provided a route for the synthesis of pure-silica LTA. Subsequently, Yan and co-workers found that the same SDA enables crystallization of either LTA or AST, depending on the SDA concentration. [32] Both Yan and Gómez-Hortigüela's groups studied this SDA system in solution and in the framework and found that the molecular aggregation behavior depends on the SDA concentration. Consequently, there is some degree of control over the void space in the resulting nanoporous network. [32, 33]

As an extension of this work, Gómez-Hortigüela and co-workers have performed studies using several supramolecular molecules to prepare different types of both AIPO and SAPO structures. Specifically, ICP-1, a new 1D aluminophosphate structure, and three new layered aluminophosphate structures have been discovered. [34, 35] In the latter example, the organics self-assemble between the layers in a manner similar to nanosheets developed by Che and co-workers. [36] Like the surfactant chain on Ryoo's SDA, the pi-pi interactions between the aromatic rings prevent crystal growth between lamellar layers. In related work, Corma and co-workers synthesized ITQ-51 (a silicoaluminophosphate form of IFO) [37] by using 1,8-bis(dimethylamino)naphthalene

as the SDA. This molecule is highly basic and acts as a proton sponge, which allows it to be protonated in the high pH solutions typical of zeolite syntheses. In turn, this favors the organic-inorganic interactions that are necessary for the nucleation and crystallization of zeolites.

Alternative Synthetic Approaches

Ionic Liquids

..... Ionic liquids have been used in zeolite syntheses to simultaneously serve as a solvent and an SDA. [38] These compounds are attractive solvents because they are environmentally benign and non-flammable. Furthermore, ionic liquids have tunable physicochemical properties due to the large range of commercially available cations and anions, which makes them excellent at solvating a wide variety of organic and inorganic compounds. Finally, the high autogenous pressures typically produced during the hydrothermal synthesis of zeolites may be avoided when ionic liquids are employed because these unique solvents have negligible vapor pressure, low melting temperatures, and are thermally stable.

..... Use of ionic liquids in zeolite synthesis was first demonstrated by Morris and co-workers and led to their discovery of several AIPO-type materials. [39] Tian and co-workers subsequently produced AIPO forms of AFI and ATV, [40] and both groups continue to have success creating MAPO materials. [41, 42] However, the synthesis of siliceous zeolites from ionic liquids is more difficult and requires careful attention to the poor solubility of silica in this medium. Morris and co-workers recently showed that by partially exchanging the bromide anion for hydroxide on imidazolium-type ionic liquids, dissolution of silica can be sufficiently improved so as to enable the synthesis of pure-silica MFI and TON. [43]

Charge Density Mismatch

..... The Charge Density Mismatch (CDM) approach was developed by Lewis and co-workers at UOP. [44] In this zeolite synthesis technique, a relatively large organocation is first added to a synthesis mixture containing an excess of negative charges due to a low Si/Al ratio. Then, a stoichiometric amount of a smaller cation with a high charge density (e.g., a small organocation or halide salt of an alkali/alkaline earth cation) is added to compensate the charge; crystallization occurs through cooperative templating between the larger and smaller cations. Importantly, this method provides a route for the synthesis of new materials and does not require the use of novel or exotic SDAs. Furthermore, identification of unique cation combinations allows for some amount of rational design of new structures and new compositions. Using this technique, the UOP group has discovered a new phase UZM-5 (UFI) (Lewis, Miller, Moscoso, Wilson, Knight, & Wilson, 2004), as well as several new compositions of existing structures. Hong and co-workers have expanded on the CDM method by finding many new combinations of SDAs, high-charge density cations, and temperatures resulting in novel compositions and structures. [45] In addition, they have further studied the mechanism of this synthesis technique. [46]

Rational Design of SDAs and the Role of Molecular Modeling

Molecular modeling and simulation have found several uses in the zeolite field. [47] While the ultimate goal is *a priori* design of an SDA that promotes nucleation of a targeted hypothetical zeolite framework, there are several more modest and yet notable ways modeling aids in the rational synthesis of zeolites. For example, guest-host energy values determined by molecular dynamics provide a measure of the relative “goodness” of the SDA, and in some studies have enabled the discovery of new SDAs for existing

zeolite structures. In addition, computational techniques have led to the development of theoretical zeolite databases and provide a means for simulating zeolite nucleation.

Many groups use modeling to find the optimum SDA configuration in zeolite frameworks. Although inorganic synthesis conditions also play a role in phase selectivity, SDA-zeolite interaction energies allow researchers to rationalize zeolite phase selectivity. As an example, Burton, Zones, and co-workers calculated the stabilization energies of several cyclic and polycyclic SDAs in cage-based 8-MR zeolites and found that the energies were strong predictors of the phase selectivity for a given set of inorganic conditions. [48] In addition, Harris and Zones identified a strong correlation between template fit and crystallization rate. [49]

Several groups have also used modeling techniques to identify alternative SDAs for known zeolite frameworks. Through computations, Schmitt and Kennedy discovered two new SDAs for ZSM-18, [50] and Corma and co-workers used molecular modeling to find an SDA that selects for ISV over BEC. [51] Deem and co-workers devised a computational method where they can "sprout and grow" an SDA within a zeolite framework from a library of commercial chemical precursors that react through known chemical reactions (e.g., Menshutkin reaction). [52] Using this technique, Deem, Davis, and co-workers synthesized STW, AEI, and SEW using computationally predicted SDAs. [53, 54, 55] This method follows on the pioneering work of Lewis and co-workers where new SDAs for LEV and MFI were identified. [56]

Conclusions

..... Step-out thinking has led to the development of a variety of new zeolite templating approaches and ultimately to the discovery of many new microporous materials. Innovations in SDA use, along with new inorganic synthesis methods, will continue to move the area of zeolite synthesis forward. While new zeolite discoveries are often initially a result of using novel and expensive SDAs, research aimed at finding cheaper SDAs for potentially useful zeolites will also prove important. [57]

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3. Synthesis design of new molecular sieves

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Introduction

Despite the fact that there are today 229 different zeolitic structures recognized by the International Zeolite Association (IZA), [1] the discovery of new crystalline molecular sieves with novel and targeted physico-chemical properties is a matter of much interest for their use in traditional and emerging applications. [2] To achieve this, the design of zeolites with predefined pore structures, and well-controlled active sites, would be highly desirable.

Unfortunately, the complete understanding of the mechanisms involving the nucleation and crystallization processes of zeolites is far from being achieved, and this lack of fundamental knowledge is the main limitation to rationalize the design and synthesis of new molecular sieves.[3] Nevertheless, the accumulated experience in zeolite synthesis during the last 50 years has allowed remarkable insight into the influence of different chemical variables in the synthesis of new molecular sieves.[4] In this sense, some of the most relevant organic and inorganic directing effects described recently in the literature allowing the crystallization of new zeolites will be highlighted below.

Organic structure directing agents (OSDAs)

The incorporation of organic moieties, such as tetraalkylammonium cations, into the synthesis media was a key breakthrough to synthesize new zeolites.[5] In general, the properties of these organic molecules, including size, shape, flexibility, and hydrophobicity, clearly influence the chemical and structural properties of the crystallized molecular sieves.[4,6] Systematic studies of different families of tetraalkylammonium cations acting as OSDAs, have not only allowed the discovery of several new zeolitic structures but have also introduced fundamental directing roles of the OSDAs depending on their size and shape.[6] For instance, increasing the size and rigidity of the organic molecules results in the crystallization of new zeolites with larger pores and/or cavities within their structures (see Figure 1), while using branched organic molecules allows synthesizing multidimensional zeolites.[6]

In the last years, the synthesis of zeolites presenting interconnected pores of different dimensions (multipore zeolites),[7] and small pore zeolites presenting large cavities within their structure have received significant attention.[8] On one hand, the presence of interconnected pores of different dimensions, may allow preferential adsorption and diffusion pathways for reagents and products, inducing unique catalytic activities and selectivities.[7] On the other hand, the recent application of small pore zeolites with large cavities in different industrially-relevant chemical processes, such as methanol-to-olefins,[9] or selective catalytic reduction of NO_x,[10] has aroused the attention on this type of framework topologies. The preferred OSDAs for the synthesis of high silica small pore zeolites with large cavities in their structure are cyclic or polycyclic ammonium cations that are able to fit and stabilize the presence of the large cavities (see Figure 2). [8]

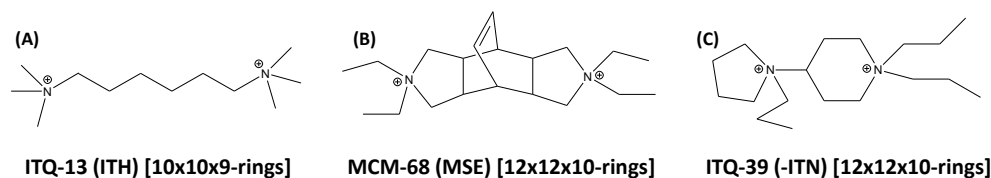


Figure 1. OSDA molecules used for the synthesis of zeolites with different size and flexibility.

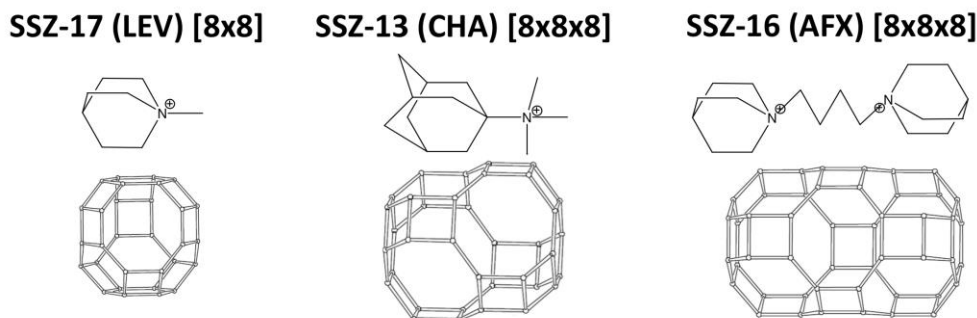


Figure 2. Polycyclic ammonium cations for the synthesis of small pore zeolites with large cavities.

In addition to the classical ammonium-based OSDAs for the synthesis of zeolites, the use of phosphorous-based organic molecules as OSDAs (P-OSDAs), such as phosphonium and phosphazenes, has allowed the preparation of different new zeolitic structures with different pore architectures depending on the size and shape of the P-OSDAs (see Figure 3).[11] P-based OSDAs are more stable and show different properties compared to classical ammonium-based OSDAs, influencing the nucleation and crystallization processes and permitting the growth of new molecular sieves.

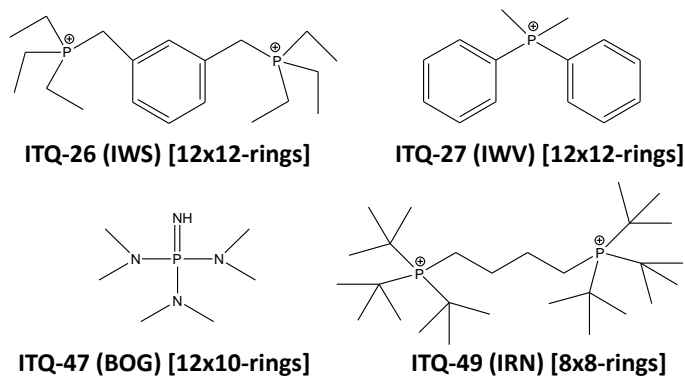


Figure 3. P-Based OSDAs used for the synthesis of zeolites.

In order to reduce the diffusion pathways through the pores of the zeolites when bulky reactants or products are involved, the synthesis of new layered or 2-D zeolite structures is highly desired, and different top-down (A) and bottom-up (B) preparation methods have been designed using different organic molecules.[12] In that way, delaminated zeolites, such as ITQ-2 (see Figure 4A) and ITQ-6, have been synthesized by exfoliating layered zeolite precursors using surfactants and controlled pHs,[12a] while the use of bifunctional di-quaternary ammonium-type surfactants has allowed the direct synthesis of zeolite nanosheets (see Figure 4B). [12b]

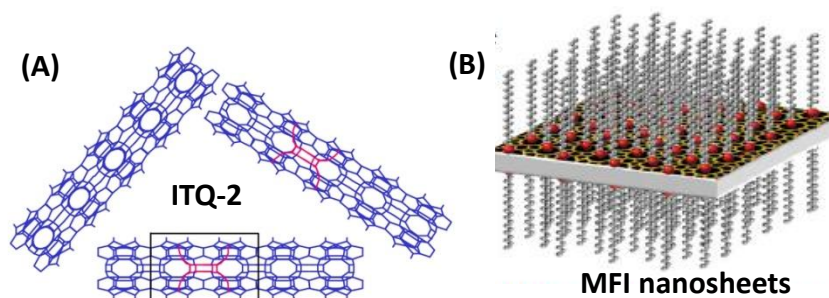


Figure 4. (A) Structure of the ITQ-2 zeolite and, (B) MFI nanosheets. Reproduced from references [12a] and [12b].

Directing effects of inorganic zeolite components

Besides the structure directing effects of the above described organic molecules, there are remarkable inorganic structure directing effects that permit the crystallization of new zeolitic structures.

In this sense, it is well-known that the introduction of some heteroatoms in the synthesis gel favors the formation of some particular secondary building units (SBUs), permitting the crystallization of zeolite structures that would be less stable without these specific heteroatoms.[4] Probably, the most outstanding inorganic directing effect has been achieved by the introduction of germanium atoms in the synthesis media, allowing the crystallization of several new zeolitic structures with very low framework densities (FD), large micropore volumes and, particularly, containing extra-large pores (see Figure 5).[13] The reason for that is because germanium atoms are able to stabilize double-4-rings (D4R) and double-3-rings (D3R) secondary building units (SBUs), and the presence of these small cages favors the crystallization of zeolites with lower FD and larger pore dimensions, even with smaller organic structure directing agents.[14] The fact that the introduction of Ge would favor the formation of these SBUs has been theoretically and experimentally shown.[15] Most interesting is that some of the silicogermanates have also been later synthesized without Ge, such as zeolites ITQ-17 and ITQ-24.

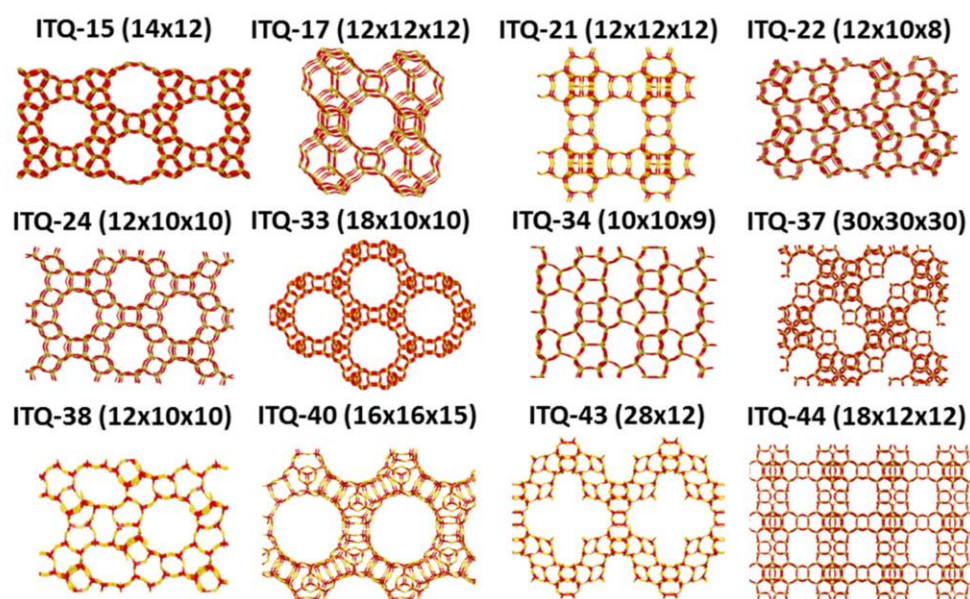


Figure 5. New zeolitic structures with different pore architectures synthesized by introducing germanium atoms in the synthesis gel. Reproduced from [4b].

Synthesis of zeolites by postsynthesis treatment of existing ones

A different methodology to prepare new zeolitic structures is based on secondary post-synthesis treatments, transforming pre-crystallized layered precursors into new crystalline structures by pillaring the interlayer region with other atoms. New zeolites have been recently synthesized following this pillaring method, such as APZ-4 (12x10-rings), [16] and COE-4 (10x10-rings), [17] which have been achieved by pillaring with silicon atoms the PRE-FER and PRE-CDO layered precursors, respectively. Finally, different new zeolite structures have been synthesized through the so-called Inverse Sigma Expansion, [18] or Assembly-Disassembly-Reassembly (ADOR) methodology (see Figure 6). [19] These procedures are based on the selective removal of a layer of Ge framework atoms, in germanosilicates previously synthesized, followed by a structure reassembly that enables the synthesis of new materials with different pore architectures. This method has allowed the transformation of the germanosilicate UTL (ITQ-15, 14x12-rings), [13a] in different multipore high-silica zeolitic structures, such as IPC-2 or COK-14 (12x10-rings), [18,19] IPC-4 (10x8-rings), IPC-6 (12x10x8-rings), and IPC-7 (14x12x10-rings). [20]

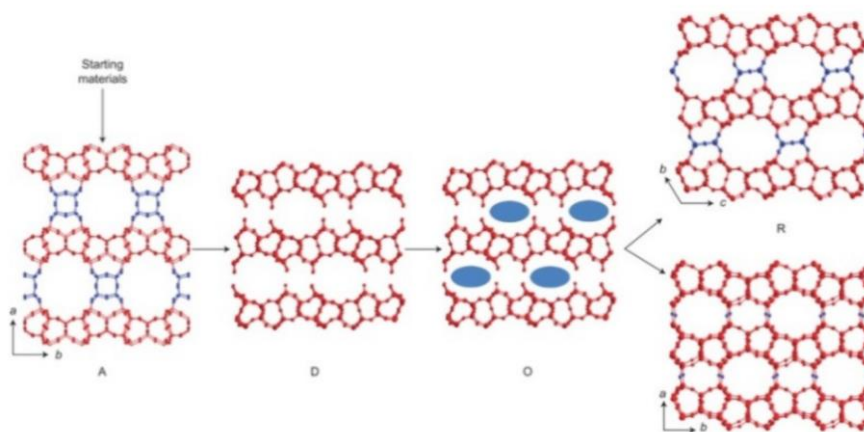


Figure 6. New zeolitic structures synthesized following the ADOR methodology. Reproduced from reference [19a].

Conclusions

As it has been shown, the rational use of different organic and inorganic structure directing agents in the synthesis of zeolites has allowed the crystallization of many new zeolitic structures. It is expected that original and innovative advances in designing new OSDAs, by combining theoretical calculation and innovative synthesis methodologies, allow the crystallization of new molecular sieves with controlled chemical compositions and pore topologies. We are contemplating a strong revival in the field of zeolites that involve the synthesis of new and older modified materials, electron diffraction techniques for solving crystalline structures, and applications in the fields of gas molecular separation, catalysis, molecular control releases, sensors, among others.

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4. Zeolite nanocrystals

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Introduction

Nanomaterials and nanotechnology are not words that are used solely in the scientific vocabulary. These terms are now adopted and largely employed in the daily language, which demonstrates the high interest of the society in the developments in this field. This interest is related to the expectations that nanomaterials and nanotechnology will make most products lighter, stronger, cleaner, less expensive, and more precise. These expectations are already reality for a number of materials and technologies, which motivates academic and apply scientists to perform more extensive research and developments.

In the material science *nano* is a synonym of extremely small (size, time interval, etc.). The goal is usually to accentuate the property of interest and thus to improve material's performance. The decrease of the size of particles changes the ratio between surface and bulk atoms. A major difference between dense and porous materials is in the accessible fraction of atoms. In the case of porous materials, the intra crystalline pores make a larger part of atoms accessible.

This short overview is devoted to nanosized crystalline zeolite-type materials. Zeolite crystals, known also as molecular sieves, are built of corner sharing SiO_4 - and AlO_4 - tetrahedral units that form channels and cages with sizes below 2 nm. The well-defined pore systems and flexible chemical compositions are the origin of the unique characteristics of zeolites, namely shape selectivity, high specific surface area, high thermal and chemical stability, and controllable hydrophilic/hydrophobic properties. Consequently, zeolites are the most widely used materials in the chemical process industry.

The uniform pore dimensions of a zeolite allow separation of molecules with size below 1 Å. This shape selectivity, however, is coupled with diffusion limitations that bring a number of undesirable side effects. For instance, the pore blocking and active sites deactivation is the most important drawback in the use of zeolite catalysts. The decrease of zeolite crystals size is a straightforward solution to this problem. Crystallites of nano dimensions offer also a number of other advantages such as improved reaction kinetics and large external surface areas. Zeolite nanocrystals in colloidal form can be used for the preparation of supported zeolite layers by employing rapid deposition techniques as spin- or deep-coating.

Besides the traditional catalytic and separation applications, nanozeolites and particularly these with narrow particles size distributions and colloidal properties have shown potential for application in areas such as optics, electronics and medicine. These considerations motivated the research on nanozeolites during last two decades

Synthesis of nanozeolites

In general, the synthesis of zeolites takes place in a close system, where the gel molar composition, the type of the reactants and the physical conditions of the synthesis determine the physicochemical characteristics of the final product. In a conventional

synthesis, the size of the crystallites is about 1 μm . Much smaller crystallites, usually below 100 nm, are considered as nanocrystals and much larger crystals, 10 to several tens of microns, are considered as large or even giant crystals. The nucleation rate in the system determines to a great extent the final size of the crystallites, since the reaction stops with the exhaust of the nutrient pool. Hence, the synthesis of nanosized crystals requires abundant nucleation and simultaneous growth in the zeolite yielding system (Figure 1).

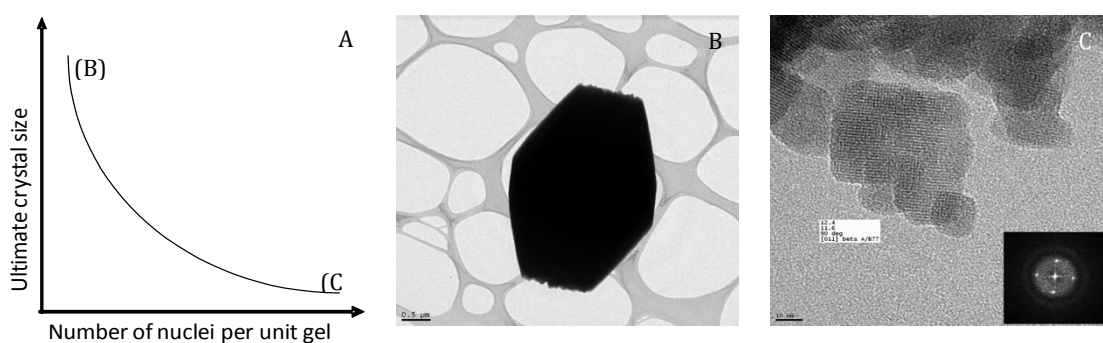


Figure 1. A) Number of nuclei - crystals size relationship in a zeolite yielding system; B) Large single zeolite Beta crystal synthesized in fluoride medium at 170 °C; C) Nanosized zeolite Beta crystals synthesized from a clear precursor suspension at 90 °C. Note: insets (B) and (C) in Figure A represents the products yield in low and high nucleation rate, respectively.

The first study devoted to the synthesis of nanozeolites was presented in 1992 during at 9th International Zeolite Conference. In this study, Meng et al. reported the synthesis of zeolite L with size of 30-70 nm. [1] Several years later the preparation of nanosized Al-LTL and Ga-LTL, including crystals in the form of colloidal suspensions, was patented by Verduijn et al. [2] First systematic studies on the synthesis of nanozeolites were performed in the early 1990s by Schoeman and colleagues. [3] They used clear precursor suspensions containing only discrete gel particles. The nucleation in such systems is abundant and simultaneity of crystallization events results in crystals with narrow particle size distributions in the form of stable colloidal suspensions. Important zeolite materials such as FAU- and LTA-type zeolites were synthesized using optically clear precursor suspensions. [3] This group has also reported the synthesis of MFI-type zeolite. [4] The system employed for the synthesis of Al-free MFI-type material (silicalite-1) was 9TPAOH:25SiO₂:480H₂O:100EtOH, where TPAOH is tetrapropylammonium hydroxide and the ethanol (EtOH) is product from the hydrolysis of the silica source (tetraethylorthosilicate, TEOS). Subjected to hydrothermal treatment at 100°C for 24, the system yields single crystallites with a size of 95 nm. In contrast to the conventional systems where a vast diversity of (alumino)silicates species is present, the initial solution prepared by hydrolysis of TEOS with TPAOH contain a limited number of well defined discrete (3-4 nm) amorphous precursor particles. [5] This is particularly important for investigation of labile zeolite precursor particles. Briefly, the use of such a system facilitates the interpretation of the results and ambiguous conclusions are in general avoided. Consequently, the system with slight variations of H₂O/SiO₂ content was employed in many fundamental studies devoted to the zeolite nucleation. [6-9]

Zeolite Beta is another important zeolite that was synthesized in the form of a stable colloidal suspension. [10] Thus, in late 1990s all important from industrial point of view zeolites were available in nanosized form. In these syntheses, clear suspensions and relatively low crystallization temperatures were employed in order to favor the

nucleation over the growth and thus as small as possible particles to be obtained. It is worth mentioning that the stabilization of a clear precursor suspension requires very careful choice of initial reactants in order to control the polymerization reaction between initial species and avoid the formation of large, chemically inhomogeneous precursor particles. Usually the alkali metal content is kept very low in order to avoid the aggregation of gel particles. The low content of alkali metals is compensated by the abundant use of organic cations. The use of such initial systems and relatively mild synthesis conditions usually results in low crystalline yield. The conversion of (alumino)silicate precursor could vary between several wt. % to several tens wt. %, but in any case is substantially lower than the yield of a conventional hydrogel precursor. In summary, the first decade of intense research on nano-zeolites was marked by the efforts to obtain different zeolitic materials with nanosize dimensions without much attempt for optimization of the crystallization process. [11]

In the last decade this gap was fulfilled to some extent since much more research was targeted to the optimization of synthesis parameters and the increase of crystalline yield. [12] Microwave (MW) heating or sonication was used to promote uniform nucleation in zeolite yielding systems and thus nanocrystals to be obtained. Different non-conventional methods of zeolite synthesis were also developed in order to decrease the crystals size and increase the crystalline yield. Soft and hard templates were used to confine the growth of zeolite nanoparticles. Another approach was the use of silane coupling agents or multivalent surfactant for restricting the growth of zeolite particles. A substantial reduction of particle size was achieved, but the zeolite particles were heavily aggregated. Similar was the result of dry gel conversion, where substantial reduction of particle size and heavy agglomeration of the crystallites was observed. Although some interesting results were reported, the non-conventional methods remain marginal in the synthesis of nanozeolites.

A lot of work was devoted to the optimization of the nucleation and growth in conventional hydrogel systems free of organic template. The advances in the understanding of zeolite nucleation in such systems opened the door to more rational design of initial systems and control of the nucleation process. [13,14] It was found that the polymerization reaction between alumina and silica species can be controlled by the excess of NaOH in the system and the way of mixing. The use of very low temperature (4 °C) during mixing of the reactants also contributes to the controlled polymerization and the stabilization of discrete gel particles. Clear suspensions rich of alkali metal hydroxide were stabilized as the size of primary particles and their uniformity was similar to the ones obtained by the use of extensive amounts of organic structure directing agents (SDAs). Moderate temperatures, close to ambient, were preferred to convert the amorphous material into a zeolite and to suppress as much as possible the Ostwald ripening. Under such conditions, the transformation of the amorphous precursor particles into zeolite crystals, without substantial change of the particle size, was achieved (Figure 2).

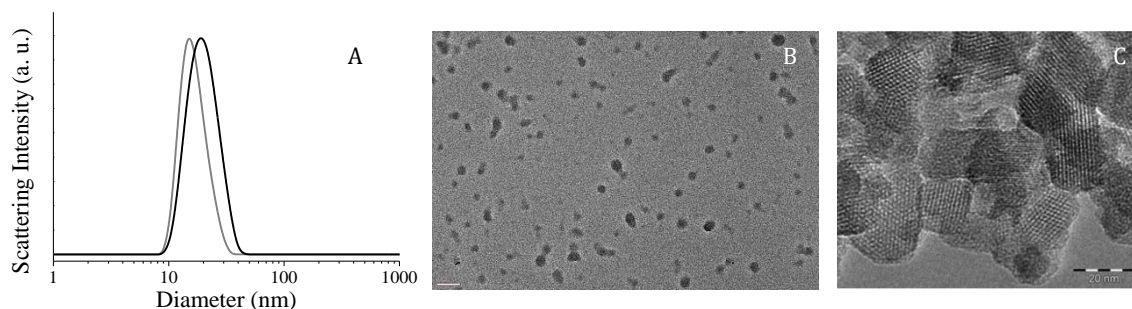


Figure 2. DLS curves of the zeolite precursor suspension (grey) and final crystalline product (black) in a FAU-type zeolite yielding system (A). TEM micrographs of the initial gel particles (B) and the ultimate zeolite nanocrystals (C).

This approach was used in the synthesis of EMT, which is the hexagonal counterpart of the largely used FAU-type zeolite. Until recently, this material with a high industrial potential was obtained only by the use of 18-crown-6 ether as SDA, which was the major obstacle to practical uses. By careful control of gel composition, the zeolite was obtained in a Na-rich system that does not contain any organic additives. First colloidal precursor particles with sizes of 10-20 nm were stabilized. Upon moderate heating (30 – 40 °C), the primary particles were transformed into pure EMT-type material with similar size. The use of a relatively low temperature allowed not only to synthesize nanocrystals with narrow particle size distribution, but also to avoid to formation of competing zeolite phases such as FAU-, LTA-, GIS- or SOD-type. Another advantage of the low temperature synthesis is that the kinetics of the growth can be controlled and the transformation to a denser phase to be avoided. The synthesized EMT-type material exhibited hexagonal shape, as the crystal dimensions were 13-15 to 3-4 nm in *a* and *c* direction, respectively. [15] The crystalline yield was more than 60 wt %, which was close to the value in a conventional zeolite synthesis.

Another important breakthrough was the synthesis of nanosized FAU-type (Y and X) zeolite in organic template free system. Zeolite Y is the primary active component in fluid cracking catalysts (FCC) and its impact on petroleum refining is enormous. The synthesis of nano zeolite Y, with high yield (> 60 %) using solely Na⁺ as SDA is a big step to the application of nanocrystals. Again, the colloidal precursor particles were stabilized and upon moderate heating they were transformed into nanozeolite crystals with narrow particle size distributions (Figure 2A and B). [16] Well shaped octahedral crystallites with a size of 10-20 nm were synthesized (Figure 2C). The micropore volume of FAU-type crystals is equal to that of micron-sized ones confirming the high crystallinity of the zeolite. These high quality nanocrystals exhibit narrow particle size distributions and colloidal stability similar to their counterparts synthesized with organic structure directing agents.

Conclusion and prospects

There are 232 zeolite framework types at present. Less than 10 % of these crystalline molecular sieves are synthesized in the form of nanocrystals. Increase of the number of structure types synthesized, as nanocrystals is an important issue that zeolite scientific chemists will certainly address in the future. This short overview provides some general guidance of the synthesis of zeolite nanocrystals. However, there is not a general approach to nanocrystals that could be applied to any zeolitic material.

Therefore, new synthetic procedures will have to be developed and if possible generalized to a particular group of crystalline microporous materials.

Although the number of zeolites synthesized in the form of nanocrystals is not large, most of the industrially important zeolites are already available in the form of nanocrystals. Thus, FAU-, MFI and BEA/BAB-type nanocrystals with different framework compositions, controllable size and very high yield can be readily synthesized. The availability of high quality and cheap zeolite nanoparticles makes possible their use in large-scale processes, where nanozeolites are expected to overcome at least partially the negative impact of slow intra-pore diffusion. Improved adsorption/desorption kinetics is the straightforward effects of the replacement of conventional micron-sized zeolites with nanozeolite materials. In addition, the nanozeolites offer the advantage of large external surface areas that could be used for processing of bulky molecules that cannot reach the micropore space.

The synthesis of colloidal zeolite crystals from organic template free systems is important step ahead to new applications. Such products do not require a calcination step, which results in heavy and irreversible aggregation of zeolite particles. Consequently, discrete zeolite nanoparticles can be processed in the desired final form of the material. Further, the use of zeolites synthesized solely with alkali metal cations is favorable from economic and environmental points of view.

This overview of the nanozeolites is far from being comprehensive. More information can be found in recent review papers that address different aspect of the synthesis, properties and application of nanosized zeolites and related porous materials. [17,18]

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5. Synthesis of single-unit-cell zeolites

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Introduction

Single-unit-cell zeolites have attracted attention due to potential applications in the areas of catalysis and separations. [1, 2] They are derived from layered precursors containing zeolite nanosheets arranged in parallel stacking though structure directing agents (SDA) placed in-between them. Single-unit-cell zeolites can be prepared by delaminating or pillaring of these layered zeolite precursors. [1,2] Recently, a direct synthesis method based on sequential rotational intergrowth has been developed. [3] Here, we provide a brief introduction of single-unit-cell zeolites. More extended reviews can be found in ref. (1, 2).

Top-down approach

MCM-22, the zeolite precursor of which (MCM-22(P)) consists of single-unit-cell thick layers, was reported in the early 1990's. [4] MCM-22(P) has an independent intralayer sinusoidal 10-MR channel and 12-MR cups on the surface of the layers. As a result of the condensation of hydroxyl groups between layers after thermal treatment of the layered precursors, a 10-MR interlayer pore opening connected to 12-MR supercages is created. If instead of calcination, the layered precursor is swollen with a cationic surfactant and pillared, a pillared zeolite with microporous layers is created. [5] If the swollen precursor is delaminated, then single unit cell zeolite layers can be obtained. [6] MCM-22 layers contain porosity within the layer but there are no pores perpendicular to the layer (the transport limited apertures are 6-MR). Other zeolite layered precursors exhibit similar lack of open porosity perpendicular to the layer. [7,8] In 2009, a layered MFI zeolite, named multilamellar MFI, was successfully created by using a bifunctional structure directing agent (SDA).[9] It is the first example of zeolite layers with 10-MR pores perpendicular to the zeolite layer. Conceptually, its synthesis is based on the idea that the di-quaternary head of the SDA directs the zeolite growth and the long tail serves as a space-filler between the zeolite layers (Figure 1).

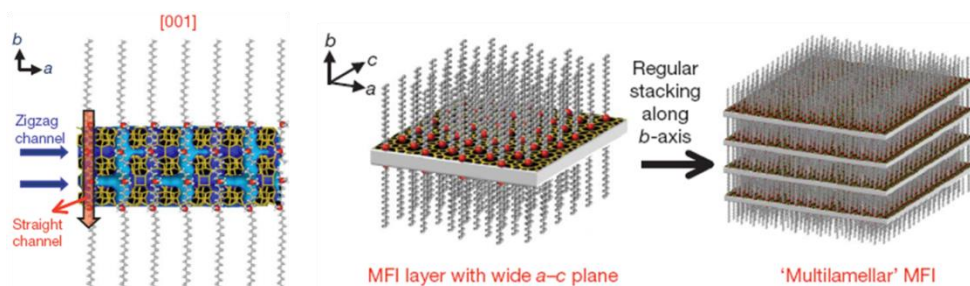


Figure 1. Structure model for the MFI nanosheets. From ref. [9]

Swelling of the layered zeolite precursor could be achieved by using long chain surfactants that interact with the silanols between the layers and expand the inter-layer spacing. Such swelling is not required for multilamellar MFI since the long chain of the

SDA serves this purpose in the as-made material. Oxide pillars can then be intercalated in the interlayer space [5, 10] or delamination can be realized by washing in acidic solution and sonication of the swollen material (Figure 2).[6] The delaminated zeolite is of interest for catalytic applications but also could be considered as a building block for ultrathin molecular sieve membranes.[11] For the later application, the preservation of the layer structure is critical and could be ensured by swelling, pillaring and delamination under mild conditions.[12, 13] Incorporation of heteroatoms into single-unit-cell hierarchical zeolites can be achieved by known synthesis and post-treatment methods as reported, for example, for delaminated Ti-MWW, pillared Ti-MWW and pillared Sn-MWW.[14-16] Generally, post-synthesis modification can be applied to all layered zeolite precursors to prepare single-unit-cell hierarchical zeolites. [17]

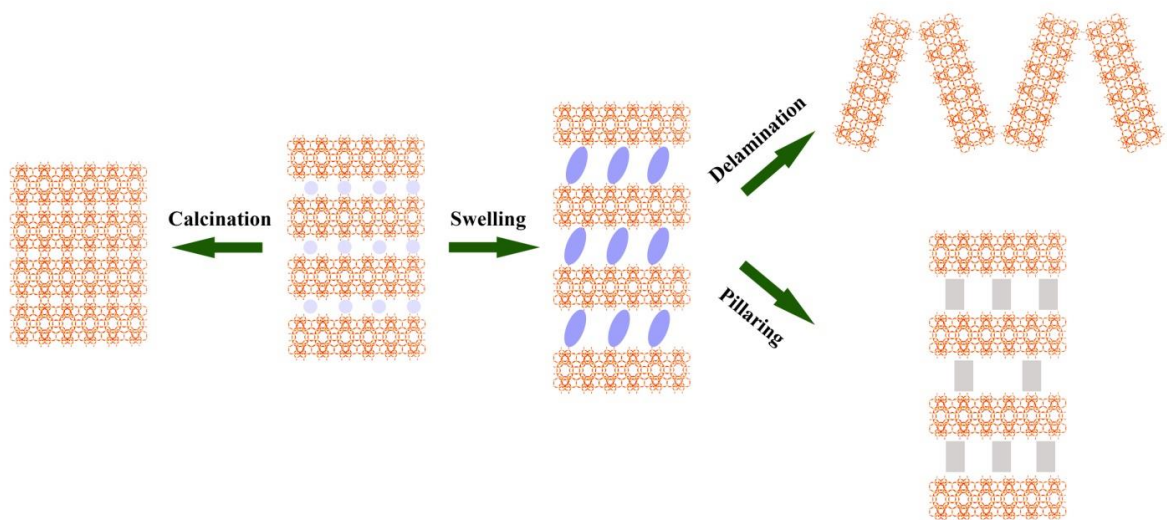


Figure 2. General process for single-unit-cell hierarchical zeolite preparation from layered zeolite precursors (shown here for ITQ-2 and MCM-22(P)).

For certain applications, it is required to remove the SDA from the single-unit-cell zeolite without using calcination. For example, for membrane applications it is important to avoid aggregation of nanosheets and this cannot be achieved when exfoliated powders are calcined. In this context, removal of SDA using solution-based approaches has been explored and it is now possible to prepare SDA-free non-aggregated suspensions of zeolite nanosheets (Figure 3). [18]

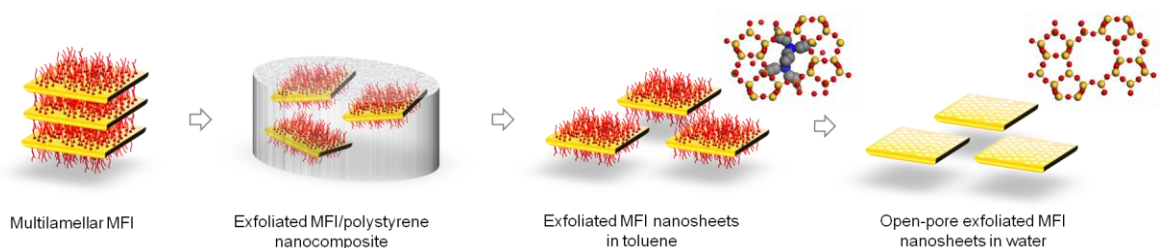


Figure 3. Schematic for the preparation of water suspension of open-pore MFI nanosheets from multilamellar MFI. [18]

Bottom-up approach

Bottom-up approach (direct synthesis) is attractive because the *top-down* approaches rely on multiple steps (hydrothermal synthesis of the layered zeolite precursor, followed by swelling of the precursor and then pillaring or delamination of the swollen materials) making them costlier to implement. In 2012, a one-step synthesis strategy of single-unit-cell zeolites was introduced. Conceptually, it is based on sequential rotational intergrowths of certain zeolite framework types, like MFI and MEL. [3]

When two crystal structures with different symmetry can intergrow at the single-unit-cell level, the higher symmetry one may act as a linker to connect single-unit-cell elements of the lower symmetry structure causing branching of the latter and a rotational intergrowth or twinning (Figure 4C, top). Self-pillared layered materials can be produced by the repetitive branching caused by such rotational intergrowths. For instance, self-pillared pentasil (SPP), a material formed by the intergrowth of MEL and MFI (Figure 4), can be synthesized using the readily available SDA tetrabutylphosphonium (TBPOH) or tetrabutylammonium hydroxide (TBAOH). [3, 19, 20] MFI and MEL frameworks can be described based on a common building unit (the pentasil chain) arranged with different symmetry operations. TBPOH and TBAOH are known to encourage the intergrowth of MFI and MEL. Under certain conditions, MEL domains can be inserted onto the predominantly MFI nanosheets during the synthesis of SPP using TBPOH or TPAOH as the SDA. The symmetry of MEL is higher than that of MFI. Thus, after MEL is formed, it can act as the linker and new MFI layers can emerge out of MEL. If MEL is inserted on the newly formed MFI layers, a new MFI branch can emerge, and the process can be repeated until the end of the crystal growth. As a result of this growth process, the zeolite lamellae are intergrown in a house-of-cards arrangement (Figure 4 C, bottom).

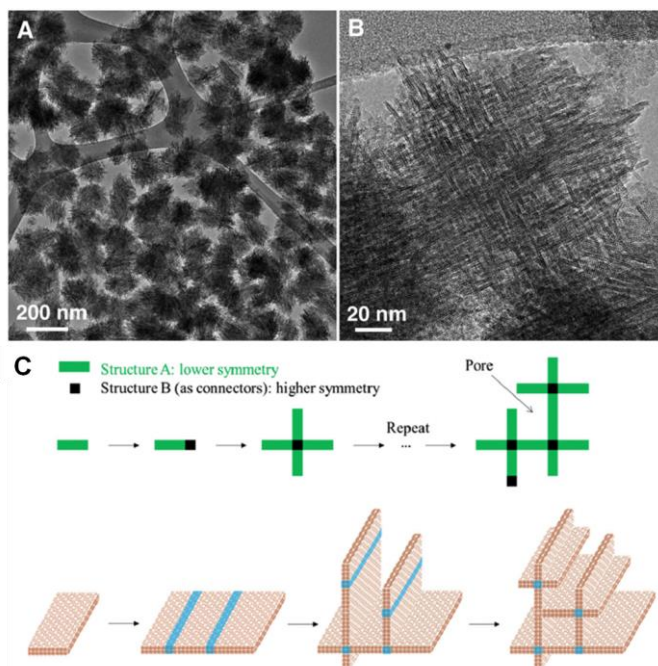


Figure 4. Low-magnification (A) and high-magnification (B) TEM images of the self-pillared pentasil (SPP) zeolite particles; Schematic growth of SPP (C) via intergrowth of MEL and MFI. [3, 19]

This approach does not rely on pillaring and/or use of long-chain surfactant SDA and, consequently, it is attractive for its simplicity and cost effectiveness. In addition to MFI, faujasite hierarchical materials have been prepared based on FAU/EMT intergrowths with a distinct branching mechanism caused by small amounts of EMT. However, in hierarchical faujasite, the layers are much thicker than single-unit-cell and are unlikely to be reduced further to single-unit-cell thickness. [21, 22]

In addition to the self-pillared materials discussed above, direct synthesis of non-intergrown single-unit-cell nanosheets has been reported. For example, the bifunctional template, which was used to prepare multilamellar MFI can also direct the synthesis of unilamellar MFI. [9] Recently, delaminated MWW zeolite nanosheets were synthesized directly using bifunctional templates (Figure 5) [23] as well as by use of a dual-template synthesis approach. [24] However, the direct synthesis of non-intergrown large-area zeolite nanosheets, which is desirable for thin film uses is yet to be achieved.

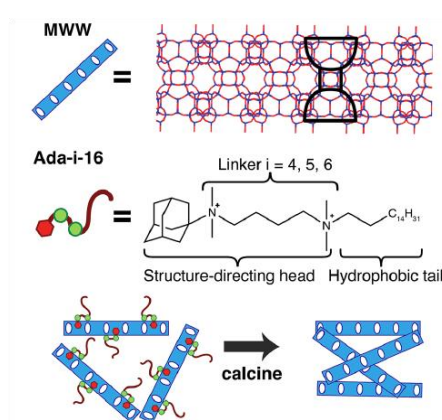


Figure 5. One-pot synthesis strategy to prepare delaminated MWW zeolite nanosheets. [23]

Conclusions

Single-unit-cell hierarchical zeolites have been successfully prepared first by pillaring or delamination (*top-down*) approaches and more recently by direct one-step (*bottom-up*) synthesis. Synthesis of non-intergrown zeolite nanosheets with large basal dimensions remains elusive.

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6. Synthesis of aluminophosphate analogues of zeolites

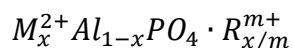
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Introduction

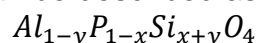
Aluminophosphates (AIPOs) were reported for the first time in 1982 by Flanigen and co-workers at Union Carbide. [1] The AIPOs are zeolite-like materials (zeotypes) having neutral frameworks consisting of alternating corner-sharing aluminate and phosphate tetrahedra (Al/P = 1, known as Flanigen's rule). The difference in electronegativity between Al (1.61) and P (2.19) makes AIPOs moderately hydrophilic, compared to the hydrophobic behaviour shown by silicas (pure silica zeolites). At present, of the 229 framework type codes recognised by the SC-IZA, 53 are known to occur as AIPO-based framework (Table 1). [2] Some AIPOs possess structural types analogous to those of zeolites (*i.e.* AFX, AEI, CHA, SOD), [2] while others possess structure types not yet prepared in aluminosilicate form (*i.e.* AFT, AFV, AVL). [2] Due to the crystal-chemical requirement that AlO_4 and PO_4 must alternate, only frameworks containing even-numbered rings are formed. The only exception, so far, has been reported by Strohmaier et al., where SAPO ECR-40, analogous to that of ZSM-18 (MEI), contains three-member rings. [3] The presence of Si, ordered within the framework, is required. The limitation of forming odd-numbered rings tends to restrict the structural complexity of AIPOs, although Lee and co-workers recently reported the structure of a new medium-pore AIPO, denoted PST-6 (PSI), which has 36 crystallographically distinct tetrahedral sites within the asymmetric unit and a one-dimensional pore system consisting of parallel 10- and 8-ring channels. [4]

A large range of heteroatoms have been introduced into AIPOs by substitution at both Al and P sites. [5] By comparison with zeolites, the more ionic character of the AIPOs and the conditions of their synthesis (starting gel typically pH 6-8) allow more metal cations to be in solution during crystallisation and to be incorporated in the lattice. Aliovalent substitution of Al^{3+} by divalent metal cations such as Mg^{2+} , Mn^{2+} , Co^{2+} and Zn^{2+} results in the formation of MAPOs, [6] which have a negatively-charged framework. In the as-prepared material the negative charges are usually balanced by organic structure directing agents (SDAs);



whilst in the calcined material the protons on bridging hydroxyl groups or Lewis acid sites generated by incompletely tetrahedrally-coordinated heteroatoms, compensate the negative framework charge. Al can also be replaced by trivalent elements (isovalent substitution) such as B and Ga resulting in the formation of so-called BAPOs [7] and GAPOs, [8] respectively.

The aliovalent replacement of phosphorus by silicon generates silicoaluminophosphates (SAPOs), a class of materials with important catalytic properties. [9] Furthermore, other elements such as vanadium and titanium can substitute P atoms within the framework (VAPO and TAPO, respectively). [10] The general composition for SAPOs can be described as:



Three mechanisms were initially proposed for the incorporation of silicon atoms in crystalline aluminophosphate frameworks: [11] SM1 in which an aluminum atom is

replaced by a silicon atom, forming a positively charged crystalline framework; SM2 where a phosphorus atom is replaced by a silicon atom resulting in a negatively charged framework; SM3 in which two silicon atoms replace one aluminium and one phosphorus atom, resulting in an electrically neutral structure. The net frameworks charge resulting from the three different mechanisms of substitution would be +1, -1, and 0, respectively. Until now only negatively-charged frameworks have been synthesized; the SM1 mechanism seems not to occur. [12] The SM2 mechanism gives Si surrounded by four Al second nearest neighbors, giving a single ^{29}Si MAS NMR signal (at ca -90 ppm). By contrast, substitution of the silicon by a combination of SM2 and SM3 mechanisms results in the formation of aluminosilicate silicate islands within the AlPO framework which display a number of signals in the ^{29}Si MAS NMR, corresponding to a range of environments. [13]

The charge-balancing H^+ ions in calcined SAPO materials can be replaced to some extent by transition metal cations, and the ion-exchanged products are denoted as Me, H-SAPO. The introduction of transition metal cations into framework sites of SAPOs is also of interest for the design of novel catalysts (MAPSOs). There are several ways to incorporate metals: impregnation, ion-exchange, vapour deposition and isomorphous substitution in which the transition metal ion salt is incorporated directly into the synthesis.[14] Recently, a new synthetic approach has been developed that utilises copper-polyamine or copper-aza-macrocyclic complexes as templates, and enables the direct inclusion of complexed Cu^{2+} cations in the solids.[15-20] Calcination then releases the Cu^{2+} cations to extra-framework sites distributed throughout the crystals and removes the need for a cation-exchange step. This process was first demonstrated for SAPO STA-7, [15] and subsequently for SSZ-13, [16] SAPO-34, [17-19] and very recently for SAPO-18[20] giving active, selective and hydrothermally stable catalysts.

Synthesis of Aluminophosphate-based Zeotypes

Aluminophosphate-based zeotypes are usually prepared by hydrothermal synthesis. Typically, a gel is prepared by mixing together framework-building inorganic species such as aluminates (*i.e.* aluminium hydroxide, pseudoboehmite, aluminium isopropoxide), phosphates (*i.e.* orthophosphoric acid) and silicates (*i.e.* fumed silica, colloidal silica, CabOSil) with metal salts (*i.e.* acetates or sulphates) in water with the addition of organic structure directing agents, which also act to modify the pH (*i.e.* amines or hydroxides). Fluoride can also be employed as mineralising agent. F^- offers multiple benefits: (i) reduction of the crystallisation time; (ii) formation of larger and well defined crystals; (iii) crystallisation of a number of phases which usually do not form in a fluoride-free medium. [21]

The organic structure-directing agents (OSDAs) are added to the gel in order to favour the arrangement of tetrahedral anions and the crystallisation of desired structures. Quaternary ammonium cations, generally used in their hydroxide form (*i.e.* tetraethylammonium hydroxide) and secondary and particularly tertiary amines, protonated at the reaction pH (*i.e.* tri-*n*-propylamine and protonated diethylamine), are the most commonly used OSDAs for the synthesis of aluminophosphate zeotypes. Primary amines, tend rather to favour the formation of layered or chain aluminophosphate structures, where the nitrogen atoms of the amines are hydrogen-bonded to phosphate oxygens that are not shared with framework cations. [22] In addition to promoting the crystallisation of specific structures, the addition of amines or alkylammonium hydroxides permits the pH of the starting gel to be controlled. The pH of

the overall gel must be close to neutral to favour the dissolution of the various components, thereby allowing the nucleation and growth of zeotype crystals. In fact, a pH lower than 3 causes the appearance of dense phases and one higher than 10 usually affects the final yield adversely. [23] The homogeneous gel made up of these components is then heated to a temperature between 100–200 °C in a Teflon-lined stainless steel autoclave (PTFE) for a period that can vary from few hours to several days.

Zeotypes have also been prepared employing the ionothermal synthesis methodology reported by Morris and co-workers. [24] In this method ionic liquid (*i.e.* alkylimidazolium-based or pyridinium-based ionic liquids) acts as both the solvent and the template provider. The absence of other solvents into the reaction mixture, apart from trace water, implies that there are no other molecules present to act as space fillers during zeotype synthesis. Therefore, the ionothermal synthesis ideally removes the competition between template–framework and solvent–framework interactions that are commonly present in hydrothermal preparations. Typically, under working conditions, a small fraction of the ionic liquid cations can decompose, resulting in smaller template cations which may preferentially act as the. Due to the very low vapour pressure of ionic liquids, syntheses may be carried out at ambient pressure, eliminating safety concerns associated with high hydrothermal pressures.

A similar synthetic strategy, named aminothermal synthesis, has been reported by Liu et al. for the preparation of SAPO-34, SAPO-18 and of a new silicoaluminophosphate denoted DNL-6 which possesses the RHO framework type. [25] Triethylamine or diethylamine were used as the solvent and template in the syntheses. However, in this case syntheses are carried out in PTFE-lined autoclaves at autogenous pressure. AIPOs and SAPOs can even be prepared solvothermally, where alcohols (*i.e.* di, tri, and tetraethylene glycol, butane-1,4-diol) are used as the solvent. [26] It is worth noting that most solvothermal preparations of molecular sieves are not truly anhydrous, and the presence of small amount of water is essential to the crystallisation process.

Compared to the conventional hydrothermal crystallisation, microwave heating of zeotype synthesis mixtures offers the possibility to drastically reduce the crystallisation time and often to obtain small crystals less than a micron in size. For more details, the reader is referred to the review “Microwave Techniques in the Synthesis and Modification of Zeolite Catalysts” by Cundy. [27]

Table 1. List of AlPO-based framework types.

Framework type	Name	AlPO or M(S)APO	B	Co	Fe	Ga	Ge	Mg	Mn	Ni	Si	Ti	V	Zn
AEI	AlPO-18	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
AEL	AlPO-11	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
AEN	AlPO-53	✓	✗	✗	✗	✓	✗	✗	✗	✗	✓	✓	✗	✗
AET	AlPO-8, MCM-37	✓	✗	✗	✓	✗	✗	✗	✓	✗	✗	✓	✗	✗
AFI ^a	AlPO-5	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
AFN	AlPO-14	✓	✓	✓	✗	✓	✓	✗	✓	✗	✗	✗	✗	✗
AFO ^b	AlPO-41	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓	✓	✓	✗
AFR	AlPO-40	✓	✓	✓	✓	✓	✓	✗	✗	✗	✓	✓	✗	✓
AFS	AlPO-46	✓	✓	✓	✗	✓	✓	✓	✗	✗	✓	✗	✗	✗
AFT	AlPO-52	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✓	✗	✗
AFV	AlPO-57	✓	✗	✗	✗	✗	✗	✓	✗	✗	✓	✗	✗	✓
AFX	AlPO-56	✓	✗	✗	✗	✗	✗	✓	✓	✗	✓	✓	✗	✗
AFY	AlPO-50	✓	✗	✓	✗	✗	✗	✓	✓	✗	✓	✗	✗	✓
AHT	AlPO-H2	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
ANA	AlPO-24	✓	✗	✓	✗	✗	✗	✗	✗	✗	✓	✗	✗	✗
APC	AlPO-C, AlPO-H3	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
APD	AlPO-D, APO-CJ3	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
AST ^c	AlPO-16	✓	✓	✓	✓	✓	✓	✗	✓	✗	✓	✓	✓	✗
ATN	AlPO-39	✓	✓	✓	✓	✓	✓	✓	✗	✗	✓	✗	✗	✓
ATO ^d	AlPO-31	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
ATS	AlPO-36	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓	✓	✗	✓
ATT	AlPO-33, AlPO-12	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
ATV	AlPO-25	✓	✗	✗	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗

AVL	AIPO-59	✓	✗	✗	✗	✗	✗	✓	✗	✗	✓	✗	✗	✓
AWO	AIPO-21	✓	✗	✓	✗	✓	✗	✗	✗	✓	✗	✗	✗	✗
AWW	AIPO-22, AIPO-CJB1	✓	✗	✗	✗	✗	✗	✗	✗	✗	✓	✗	✗	✗
BPH	AIPO-65, STA-5	✓	✗	✗	✗	✗	✗	✓	✗	✗	✓	✗	✗	✓
CGF ^e		✗	✓	✗	✗	✓	✗	✗	✗	✗	✗	✗	✗	✓
CGS ^f		✗	✓	✗	✗	✓	✗	✗	✗	✗	✗	✗	✗	✓
CHA ^g	AIPO-34, AIPO-44, AIPO-47	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CLO ^h		✓	✗	✓	✗	✓	✗	✗	✓	✗	✗	✗	✗	✓
CZP ⁱ		✗	✓	✓	✗	✓	✗	✗	✓	✗	✗	✗	✗	✓
DFT ^j	DAF-2, UiO-20	✓	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✓
EDI ^k		✓	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✓
ERI	AIPO-17	✓	✓	✓	✓	✓	✓	✓	✗	✗	✓	✓	✓	✗
FAU	AIPO-37	✓	✓	✓	✓	✓	✓	✗	✗	✗	✓	✓	✓	✓
GIS	AIPO-43	✓	✗	✓	✓	✗	✗	✓	✓	✗	✓	✗	✗	✗
JRY	CoAPO-CJ40	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
JSN	CoAPO-CJ69	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
JSW	CoAPO-CJ62	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
LAU ^l		✗	✓	✗	✓	✓	✗	✗	✓	✗	✗	✗	✗	✓
LEV	AIPO-35, AIPO-67	✓	✓	✓	✓	✓	✓	✓	✗	✗	✓	✓	✗	✓
LTA	AIPO-42	✓	✓	✗	✗	✓	✓	✗	✗	✗	✓	✓	✗	✓
LTL		✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
MEI	ECR-40	✓	✗	✗	✗	✗	✗	✗	✗	✗	✓	✗	✗	✗
MER		✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
PSI	PST-6	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗
RHO		✓	✗	✓	✗	✗	✗	✓	✓	✗	✓	✗	✗	✗
SAF	STA-15	✓	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗	✗

SAO	STA-1	✓	✗	✗	✗	✗	✗	✓	✗	✗	✗	✗	✗	✗
SAS	STA-6	✓	✗	✗	✓	✗	✗	✓	✓	✓	✓	✗	✗	✗
SAT	STA-2	✓	✗	✗	✗	✗	✗	✓	✗	✗	✓	✗	✗	✗
SAV	STA-7	✓	✗	✓	✗	✗	✗	✓	✗	✗	✓	✗	✗	✓
SOD ^m	AIPO-20	✓	✓	✓	✗	✓	✓	✓	✓	✓	✓	✓	✗	✗
THO ⁿ	ZCP-THO	✓	✗	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗	✓
VFI	AIPO-54, VPI-5, MCM-9	✓	✗	✓	✓	✗	✗	✗	✗	✗	✓	✓	✗	✗
ZON	UIO-7	✓	✗	✓	✗	✓	✗	✗	✗	✗	✓	✗	✗	✓

The symbols ✓ and ✗ indicate whether a given element has been replaced within a AlPO-based framework. (a) Ca, Sn, Be, Cr, Cd, Mo, Zr. (b) Zr. (c) Cr. (d) Cd, Cr. (e) CoGaPO-5, ZnGaPO-5. (f) ZnGaPO6, CoGaPO-6. (g) Zr. (h) MnGaPO, ZnGaPO. (i) ZnBPO, MnGaPO, CoZnPO. (j) FeZnPO, ZnCoPO. (k) CoGaPO. (l) CoGaPO, FeGaPO, MnGaPO, ZnGaPO, ZnAlAsO. (m) CoGaPO, ZnGaPO. (n) GaCoPO.

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7. Disassembly as a route to new materials

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Introduction

Pushing and extending the synthetic limits of zeolites

Zeolites are traditionally perceived as regular three-dimensional (3D) frameworks built from silicon tetrahedra by sharing oxygen corners. However, in last two decades there has been an increasing interest in two-dimensional (2D) zeolites, a family of materials numbering now about 15-20 members [1-3]. Unlike 3D zeolites, layered materials may vary in the spatial arrangements of lamellas, which significantly affect their textural properties and consequently their catalytic performance [2]. Although most of them (if not all) are still only the subject of basic-science interest and not real industrial application, they have proved their importance by offering an alternative way to overcome diffusion limitations usually connected with bulk zeolites. Overall, zeolitic science seems to have the tendency to leave the chemistry of bulk rigid crystals and lean more towards zeolitic materials with decreased crystal proportions, e.g. with hierarchical, nano or layered nature. Such zeolites usually excel by facilitating mass transfer while keeping the advantages of zeolitic frameworks.

The solvothermal synthesis of zeolites is the most common synthetic approach applied for both 3D and 2D zeolites. This bottom-up method leads to energetically most favourable structures according to energy-density correlation, which causes some limitations to the diversity of synthesizable zeolites (more discussed later). There have been many efforts to modify the solvothermal conditions to expand these potential borders, e.g. using different mineralizing agents, ionic-liquids instead of water solvent, heating via microwaves, using new ammonium, phosphonium and phosphazene-based SDAs etc.

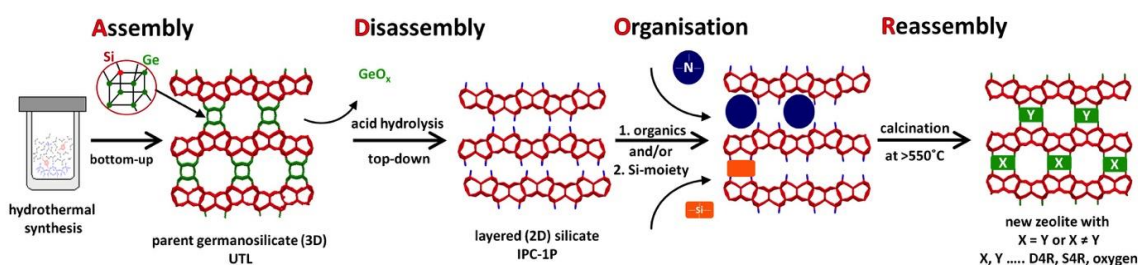
In 2011 top-down synthesis was developed as an alternative approach based on germanosilicates [4]. The novel synthesis protocol based on 3D-2D-3D transformation was called ADOR (Assembly-Disassembly-Organisation-Reassembly).

Step by step to novel structures

The ADOR abbreviation stands for four fundamental steps leading to new zeolites: Assembly, Disassembly, Organisation, Reassembly (see Scheme 1). The first means to synthesize the parent material (Assembly), a germanosilicate, by well-described bottom-up protocols. Germanosilicates are generally hydrolytically sensitive and it had been believed that their framework uncontrollably collapses in time when exposed to air moisture. Despite this fact, it was found that under specific conditions some germanosilicates can transform chemically selectively from 3D framework into 2D layered materials rather than totally and irreversibly collapse [4]. It proceeds by hydrolyzing and removing of specific secondary building units (e.g. double-four-rings, D4R, double-three-rings, D3Rs) located between the layers and preferentially occupied by sensitive dopant, here specifically germanium. This step is denoted as Disassembly. The third step, Organisation, can very closely follow the Disassembly or can be

performed as a separate treatment. The purpose is to organise the layers into an appropriate position towards each other to guarantee their full reconnection during the last Reassembly step (calcination at $< 500^{\circ}\text{C}$).

Although ADOR was already demonstrated on a couple of germanosilicates [5], zeolite UTL remains the most explored representative; therefore, here it will be used to demonstrate the ADOR potential. Germanosilicate UTL consists of almost purely siliceous layers with D4R units connecting them. D4R units are mostly composed of germanium atoms. The Assembly step of UTL is just a conventional synthesis published in many Refs. [6,7]. Disassembly was studied very carefully using various water solutions of 0-12M hydrochloric acid [8]. As germanium is a hydro-sensitive dopant in less than 5 minutes more than 90% of germanium is washed out of the UTL framework independently on the acid molarity. In the following Organisation step, we distinguish two types: I. *self-organisation*; and II. *organisation by intercalation of additive molecules*. The latter type is performed as a separate step and thus it will be discussed in the next section. Independently of the further modifications, the character/topology of the layer is identical with the parent zeolite UTL [4, 9].



Scheme 1. The schematic view on the whole ADOR method showing the individual step.

Self-organisation directly follows the Disassembly step. Depending on the acid molarity two processes may occur presenting in fact two competing mechanisms - de-intercalation and re-organisation (Scheme 1). In pure water or diluted HCl solutions ($< 0.1\text{M}$) the de-intercalation prevails leading to removal of any hydrolysed D4Rs debris. The resulting layered material is called IPC-1P. During the Reassembly, surface silanol groups condense with the opposite counterparts forming Si-O-Si oxygen bridges. The final zeolite IPC-4 (IZA code PCR) has 10-8-ring channel system. On the other hand, the highly acidic solution like 12M HCl supports making-breaking of -Si-O-Si- bonds. It initiates a re-organisation of some framework atoms. Thereby some Si atoms, originally located intra-layers, may move to the layer surface and build precursors for novel layer connections. During the calcination it forms siliceous S4R units between the layers giving rise to 12-10-ring perpendicular channels of IPC-2 zeolite [8]. IPC-2 is topologically identical to zeolite COK-14 [10] (IZA code OKO), they have the same connectivity although different symmetry.

By careful control of the molarity one may balance between de-intercalation and re-organisation rates. With increasing $[\text{H}^+]$ the re-organisation starts occurring and at certain point the equilibrium between de-intercalation and re-arrangement can be reached. In this case, specifically at 1.5M, about half of the layers are de-intercalated and half undergo rearrangement. Reassembled zeolite consists of $\sim 50\%$ layers connected with Si-O-Si bridges and 50% with S4R units and it was called IPC-6 [8]. At 5M it was found another staged material denoted IPC-7 containing $\sim 50\%$ of S4R connections and 50% of siliceous D4R connections [8]. Novel zeolites have two independent channel systems, 12-10- and 10-8-ring in IPC-6, and 14-12- and 12-10-ring system in IPC-7 (see Scheme 2).

Layer manipulation enabling structural diversity

The first product of the top-down synthesis, the layered IPC-1P, is by its properties similar to any other layered zeolites. Similarly to them, the interlayer space in IPC-1P can be variously modified pursuing two different objectives [1, 2]: 1) to increase the interlayer space and thus permanently separate the layers; or 2) to organise the layers in suitable positions in order to subsequently reconnect them into 3D frameworks. The first target is easily reached by well described swelling and pillaring treatments. Both inorganic (amorphous SiO₂) [9] and organic [11, 12] pillars may be built up between the layers. The incorporation of organic pillars like silsesquioxanes has a great potential for preparing a bifunctional acid-base catalyst.

In order to link the layers of any topology into 3D framework one should apprise the properties of the layer surface, particularly the surface silanol density, inter-silanol distances *etc.* [13-15]. It determines their possible mutual arrangement and consequently their new inter-layer linking. IPC-1P has the quadruplets of the silanols as a result of D4R hydrolysis. Based on the calculations performed with the periodic model consisting of two interacting IPC-1P layers at the density functional theory (DFT) level, the most stable arrangement was found for unshifted layers [13, 14]. This is exactly the inter-layer arrangement, which occurs during the self-organisation in the acid solutions (as described in the previous chapter). Nevertheless, there are at least three more possible inter-layer arrangements although they are energetically less favourable. To achieve the lateral shifts of adjacent layers one has to introduce an appropriate organising molecule.

Organic amines and ammonium cations showed a good ability and suitability to be intercalated between the layers [5]. For instance, octylamine nicely fits into the space between two unshifted layers [14]. The unshifted layers may be directly calcined forming zeolite IPC-4 with 10-8-ring channels. Alternatively, extra-silicon source like diethoxydimethylsilane (DEDMS) can be added. DEDMS molecules incorporate between the unshifted layers via bonds to the surface silanols. During the calcination they form new S4R units as interlayer links giving rise to 12-10-ring channels of zeolite IPC-2 [14]. On the other hand, choline molecules bind to the layers in other specific way (dependent as well on its amount), which forces the layers to shift with respect to each other. As a result, the direct reassembly of the laterally shifted layers leads to zeolite IPC-9 with unusual channel system 10-7-ring [16]. When DEDMS is incorporated before reassembly, another zeolite with S4R units can be formed. It is denoted IPC-10 and contains 12-9-ring channels [16] (Scheme 2).

The perspectives for ADOR

The main advantage of the ADOR method lies in the predictability of the final zeolite structure. It is not a matter of coincidence and luck as it has been with the bottom-up synthesis of most known zeolites. Here, the structure of the layers in parent and daughter zeolites is preserved and the nature of novel inter-layer connections can be easily controlled by choosing appropriate hydrolysis conditions or by intercalating suitable organic and silicon molecules. This greatly facilitates the structure solving, which may be very difficult and demanding for a completely unknown zeolitic structure.

More importantly, one can design the overall porosity of the system, *i.e.* the size and shape of the channels [8]. It is given by selecting the inter-layer links as discussed above. The control over the porosity is highly desired for any application, particularly in

catalysis where shape-selectivity is very appreciated as a mighty tool to inhibit undesired side reactions [17]. Thus, the ADOR shows that chemical weakness in the material (like low hydrothermal stability of germanosilicates) can be beneficial if you find the appropriate purpose or application [18].



Scheme 2. The energy versus density plot (on the left) shows the distributions of thermodynamically accessible structures (black dots) and also linear fit of energy versus density for the known zeolite structures as solid red line (reprinted from Ref. [19]). The novel zeolites prepared by ADOR from parent UTL are marked on the plot as red dot for UTL, IPC-2, IPC-4, IPC-6 and IPC-7 as yellow dots and IPC-9 and IPC-10 as pink dots. Their structures with the connecting units are shown on the right.

Although ADOR was demonstrated on other germanosilicates, e.g., ITH [5], still UTL remains the most fruitful example. This germanosilicate stands at the beginning of the synthesis until now 6 daughter zeolites varying in diversity of the size and shape of the individual channel system and a number of hybrid materials. The uniqueness of UTL probably lies in its two-dimensional channel system giving rise to compact solid layers after hydrolysis and the appropriate surface-silanol density allowing the layer manipulation. The limits and perspectives of the ADOR method are overviewed in a review paper Ref. [5].

One more and probably the most important advantage is connected with the ADOR. In 2009 Deem et. al constructed a database of computationally predicted zeolite-like materials where are over two millions of unique structures [19]. About 10% lie within the +30kJ/mol Si energetic band above α -quartz, which is considered as a reasonable area for zeolite frameworks. Nevertheless, all known zeolites are located on the low-density edge shown as a red line in Scheme 2. To evaluate the feasibility of hypothetical zeolite-like materials, so called feasibility factor was introduced [19]. It presents how far away from the low-density edge of the distribution is the hypothetical zeolite-like material. It is supposed that materials lying further away from the red line are less feasible. Thus, the question arises, why can we not prepare zeolites away from this line? As some scientists already suggested [19] the hitch might be in the synthetic protocol, the bottom-up crystallization, which usually proceeds from a low-density solution toward a high-density solid material. And here the ADOR offers an alternative route as the top-down method avoids other solution-assisted crystallization beside the initial one for the synthesis of the parent zeolite. Scheme 2 shows the location of the parent UTL zeolite very close to the red line (as it supposed to be) and all daughter IPC zeolites. It is clear

that zeolites IPC-9 and IPC-10 broke the rules of feasibility as they are high energy materials located on energy-vs.-density plot far from any other known zeolite. This is the most striking consequence of the ADOR, opening the pathway to novel zeolites 'unfeasible' via traditional bottom-up protocols.

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8. Synthesis of zeolites: seeding approach

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Introduction

In the industrial crystallization including zeolite syntheses, the employment of seeding results in multiple advantages such as shorten induction period, higher product yield, controlled particle size distribution, and improved product quality. Seeding is also employed for special purposes, such as polymorphs control and production of single handedness in organic syntheses [1]. Furthermore, a unique use of seeding was reported for some zeolites. For the synthesis of CON-type zeolite (CIT-1), seeding of *BEA-type zeolite (beta) is considered to be essential although the detailed mechanism has not yet been clarified [2].

The zeolite synthesis process involves:

- Mixing of the initial sources in water to obtain a starting gel
- Aging at room temperature (if necessary)
- Heating
- Product recovery (after crystallization)
- Drying
- Calcination when an organic structure-directing agent (OSDA) is employed.

During the aging at ambient conditions as well as the heating, aluminosilicate mixtures are considered to convert into zeolite precursor. This is followed by the crystallization of zeolites, which consists of two steps: nucleation and crystal growth. The induction period before the nucleation is considered to be due to its high activation energies. The nucleation process can be altered by the use of seeds. They can act as nuclei and provide active surfaces for product growth. Once crystals start to grow, activation energies for the growth are considered to be lower, and crystal growth is faster than nucleation. Several mechanisms have been proposed in addition to a simple mechanism involving liquid-mediated supply of the dissolved (alumino)silicate species to the surface of the seed zeolite crystals. For example, secondary nucleation via the initial breeding mechanism caused by microcrystalline dust washed out from seed surfaces has been investigated. Polycrystalline breeding formed over seed crystals has been also reported as a potential pathway [3].

Although seeding methods have been well known and often used for the zeolite synthesis, the new aspects of seeding are recently developed focusing on the OSDA-free synthesis and on ultrafast synthesis of zeolites. These two trends will be described below in detail.

OSDA-free synthesis of zeolites by seeding

The OSDA is essential for the synthesis of some specific zeolites and especially the one with high silicon to aluminum ratio (SAR). However, the cost of OSDAs accounts for a large portion of the total cost of the starting materials. In addition, calcination and waste gas/water treatment are additional processes. Several recent publications revealed that OSDA-free synthesis of *BEA- [4–6], MTW- [7] and RTH-type zeolites [8]

were achieved by seeding approach in spite of using the classical synthesis in the presence of OSDAs. Moreover, it was shown that liquid-mediated crystal growth was dominant [9]. Secondary nucleation has not been observed so far. Using OSDA-free synthesis, more than 10 zeolites have been synthesized [10,11]. The OSDA-free synthesis of zeolites is summarized in Table 1. The data provide information about seed crystals and products obtained by the use of seeding approach. It is important to notice that without seeding, other zeolites, silicates, or amorphous matters are obtained.

The amount of seed crystals ranges from 0.5 to 33.3 wt.% relative to the silica sources used for the preparation of the initial mixtures. Seeds clearly direct the crystallization of targeted zeolites, and the products have the same framework types in the most cases. However, seeds and products have shown different structures in two cases: synthesis of MTW from *BEA [11] and NES from EUO [12]. Figure 1 schematically illustrates the difference between conventional and recently developed seeding methods.

Table 1. Summary of OSDA-free synthesis of zeolites.

Seeds				Products		References
Framework type code	Material name	SiO ₂ /Al ₂ O ₃ ratio	Amount (wt% to silica)	Framework type code	SiO ₂ /Al ₂ O ₃ ratio	
*BEA	Beta	No data	10	*BEA	No data	[4]
*BEA	Beta	52	0.5–2.5	*BEA	7.8–9.0	[5]
*BEA	Beta	14–24	1–10	*BEA	10.4–13.2	[6]
*BEA	Beta	20.4, 23.2	10.3	*BEA	Core:26.6, Shell:10.6	[11]
*BEA	Beta	50	9.1–33.3	*BEA	14.6–22	[11]
*BEA	Beta	No data	5	*BEA	9.8 SiO ₂ /Fe ₂ O ₃ = 100	[11]
*BEA	CIT-6	∞ SiO ₂ /ZnO = 13	10	*BEA	10.9–21.4	[11]
*BEA	Beta	24	10	MTW	31.8–46.4	[11]
EUO	EU-1	15	10–15	NES	14.0–25.8	[12]
LEV	RUB-50	19.4	4.6	LEV	No data	[11]
LEV	Not specified	21.4	5–17	LEV	9.2–12	[11]
LEV	RUB-50	19.5	1.5–5	LEV	8.1	[11]
MAZ	Omega	5.6	10–20	MAZ	6.4–8.2	[13]
MAZ	Not specified	7.8	9.1–33.3	MAZ	9.6–12.8	[14]
MEL	ZSM-11	66.0	10	MEL	17.6	[11]
MSE	MCM-68	22	10	MSE	12–14	[15]
MTT	ZSM-23	No data	10	MTT	40	[16]
MTW	ZSM-12	101	10	MTW	No data	[11]
MTW	ZSM-12	94.6	1–10	MTW	23.4–32.4	[11]
PAU	ECR-18	No data	10	PAU	No data	[11]
RTH	RUB-13	∞ SiO ₂ /B ₂ O ₃ = 46	2	RTH	82 ([Al]-TTZ-1), 216 ([Al, B]-TTZ-1.) SiO ₂ /B ₂ O ₃ = 42–54 SiO ₂ /Ga ₂ O ₃ = 504	[8]
SZR	SUZ-4	No data	1	SZR	No data	[11]
TON	ZSM-22	No data	1–10	TON	88	[17]
VET	VPI-8	SiO ₂ /ZnO = 13	10	VET	295–351, ∞ SiO ₂ /ZnO = 12.3–16.6	[18]

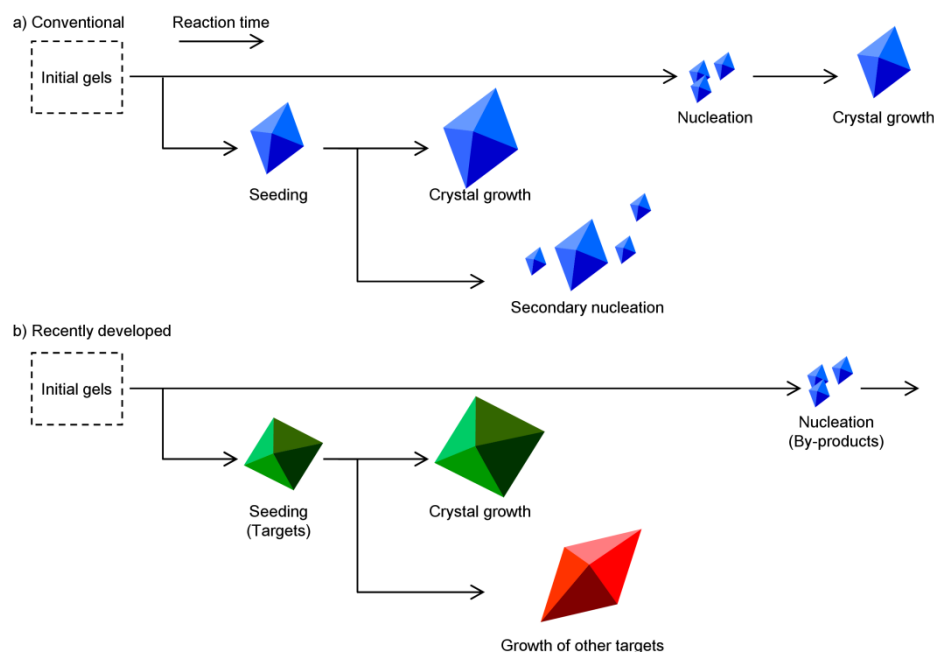


Figure 1. Schematic illustration of a) conventional and b) recently developed seeding methods.

The products obtained by this method have common characteristic features. Firstly, the products are well faceted, and the defects within the products are less than those synthesized with OSDAs. This is due to the fact that the crystallization process is focusing on the crystal growth, and that it is not necessary to calcine the product in order to remove the OSDAs, which often leads to dealumination and creation of defect sites. Moreover, the SARs of the products are lower than those synthesized with OSDAs. If necessary, a post-synthetic dealumination is applied to control the chemical composition of the final phase [15].

Ultrafast synthesis of zeolites by seeding

The synthesis of zeolites usually takes few hours up to few weeks during which the crystallization process is completed. Recently, seeding approach combined with fast heating in a preheated oil bath by employing a tubular reactor reveal that the crystallization of zeolite and related materials is completed within several minutes, i.e., one minute for AIPO-5 [19] and 10 minutes for SSZ-13 [20].

As shown in the introduction, the process of the zeolite synthesis consists of several steps in view of unit operation. In view of phenomena, it consists of precursor formation (conversion of starting mixture), nucleation and crystal growth of zeolite. In typical Teflon[®]-lined autoclaves with convection ovens, the heating rate of the gel is not high enough, and the heat transfer rate gives a significant influence on the crystallization time. Which is the rate-determining step?

Firstly, the heating problem was resolved by the use of a reactor made of stainless steel tube (1/4" OD) without Teflon[®]-lining instead of autoclave. In addition, preheated oil bath was employed in place of an air oven. The main advantage of a tubular reactor is continuous operation useful for mass production. Thanks to the fast heat transfer between the oil and the tube, through the tube wall and between the tube and the gel, the gel was heated to a targeted temperature within one minute although it took one hour for the conventional case. The solution of the heating problem resulted in reduction in

the crystallization time; however, further reduction was necessary to apply for the continuous operation. Moreover, skipping nucleation process was investigated when the seeding was employed. In OSDA-free synthesis, the problem of the dissolution of seeds during the heating was a common issue beyond the types of the zeolites. Thus, the most important point in seed-assisted synthesis is to match the timing between the conversion of the starting mixture to the precursor and the survival of seeds crystal during heating. In the fast heating system developed here, the damage of the seed could be reduced. In general, the conversion of the mixture to the precursor proceeds in aging (before heating) and heating steps. In the case of fast heating, the role of the aging step is more significant since the heating-up time is shortened. High temperature condition is advantageous in view of the crystal growth rate; however, OSDAs tend to be degraded more at higher temperature. It is the competition between the crystal growth and the degradation of OSDAs. If the heating time can be reduced by fast heating, the loss of the OSDAs before the onset of the crystal growth is effectively reduced. By tuning all the factors described above, ultrafast synthesis of zeolites was successfully achieved

The key aspect necessary for the successful, ultrafast synthesis of zeolites are summarized as follows:

- Preparation of suitable gel by tuning the composition with aging
- Removal of thermal time lag by fast heating
- Skipping nucleation stage by seeding
- Enhanced crystal growth at high temperature
- Limited degradation of OSDA by fast heating.

These results show that the crystal growth of zeolites itself is not as slow as they had been believed, compared with heating process of a conventional autoclave as well as the precursor formation and the nucleation processes.

Conclusions

From both scientific and engineering points of view, the OSDA-free synthesis and ultrafast synthesis have attracted considerable attention of researchers and engineers. These two cases show the importance of avoiding avoid high energy burrier of nucleation as well as the efficiency of seeding approach for zeolite syntheses. Although, so far these methods have been applied to limited structure types and compositions, it is expected that the applicable zeotypes will be broadened in near future. Moreover, there might be other advantages of seeding method beyond OSDA-free and ultrafast synthesis. There are still many unexploited routes for the synthesis of zeolites that left to be discovered.

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9. Post synthesis modification of zeolites

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Introduction

New nanoporous materials enable breakthrough improvements in catalytic and adsorptive processes in the refining, petrochemical, gas processing industries and in many other areas of technology. Although the discovery of new zeotype structures continues to be a fruitful materials research focus for these various applications, there are many cases where modification of zeolite and related materials after their synthesis can also lead to incremental and breakthrough improvements in applications. In fact, there are a greater number of research groups throughout the world that stress post-synthesis modification to generate new functional materials than focus on new zeolite structure discovery, perhaps because such modifications have led to many commercially significant materials.

For the purpose of this short review the various major post-synthetic modification chemistries are grouped according to the modification approach. Initial discovery of the impact of post synthesis modification on the properties and performance of zeolites dates back to 1950's starting with ion exchange to remove alkali metals from extra framework charge balancing positions. The major approaches outlined in this review include chemistries that are additive, subtractive, substitutive, and transformative. Additive chemistries start with as-synthesized or calcined zeolites and seek to modify the properties by adding to the bulk composition, usually at the surface of the zeolite material. Subtractive chemistries involve the removal of some of the mass, usually attempting selective removal in some way, to adjust acidity, diffusion behavior, or other properties. Substitutive methods sometimes are accomplished via an initial subtractive step, followed by insertion of components that lead to significant modification of acidic or perhaps framework charge properties. Ion exchange processes such as framework stabilization by rare-earth exchange can be viewed as substitutive as well and are often used in combination with other modification strategies. Transformative modifications have been accomplished in many forms, including using one zeolite as a reagent in the synthesis of another, exfoliation of layered materials to create high surface area "layered" zeolites, and reactions to connect layered zeolites through their interlammellar spaces, forming three-dimensional zeolite topologies.

Additive Methods

The general method of selectivation has been the subject of a great number of patents and a few of the early examples are referred to here.[1,2] Early pioneering work on zeolite surface passivation with phosphorus and boron compounds were carried by Kaeding et al.[3] The main processes that have been used in commercial applications have been selective in-situ or ex-situ coking of zeolite surfaces or ex-situ solution or perhaps gas phase silylation of the zeolite surface, mostly using MFI zeolite. The modification thus becomes either a carbon coke coating or silica coating of the zeolite

surface. These processes sometimes dramatically increase methyl benzene transformation selectivity to para-xylene by one or more mechanisms, which include passivation of the acid sites on the zeolite external surface and/or narrowing of the zeolite pores to increase shape selectivity. An interesting perspective on the chronology of development of para-selective zeolite catalysts at Mobil Oil Corporation has appeared. [4] Patents continue to issue in this area; modification procedures continue to increase in complexity and include more specific procedural steps. [5]

The mutual interaction of zeolite, binder and matrix components has been exploited in FCC and other catalysts for many years by industrial scientists. It is naïve to assume that binders are inert spectators in catalyst composites, necessary only for the purpose of minimizing pressure drop and loss of active catalytic phase from the reactor under operating conditions. This is because the chemistry involved in creating the binder and the subsequent calcination that produce the porous ceramic forms create new bonds between the binder/matrix and zeolitic and other catalyst components; and these bonds may generate new types of active sites in the finished catalyst.

Only recently have academic groups begun to focus on the chemistry of the binder/zeolite interaction. [6,7] This late focus on such important phenomena is likely due to the complexity of finished catalyst materials chemistry, structure, and the associated difficulty in thorough characterization aimed at eventual fundamental understanding of local structures and active sites. The dramatic improvements of many characterization techniques including solid state NMR, various forms of microscopy and imaging; powder diffraction and PDF analysis, tomographic methods, X-ray spectroscopy and new developments in operando and combined techniques, have finally begun to enable characterization of these complex composites. [8,9]

Subtractive Methods

The phenomenon of zeolitic aluminum expanding its coordination sphere and thereby becoming susceptible to removal from the framework is well established and long utilized in the preparation of industrial catalysts. Dealumination can be carried out using a number of liquid and gas phase chemical treatments using acids, steam, ion exchange and other chemical manipulations, in many cases a combination of one or more of these processes. Steam-stabilization was used to make the so-called 'Ultra Stable' Y family of Y zeolites, a commercially important family of materials that still is extensively used. Secondary synthesis methods based on steam stabilization caused significant porosity modification. The precise, geometrically defined, pores of zeolites measuring in the range of 5-13 Å were augmented by large 200-300 Å pores which are thought to enhance access of larger feed molecules to active sites and improve diffusivity.

A number of early patents outline the evolution of dealumination technology.¹⁰ Dealuminated zeolites have numerous properties that increase commercial applicability including significant mesoporosity,[11] increased acidity,[12] and increased thermal and hydrothermal stability.[13] More recent work casts some doubt on the utility of mesoporosity derived from dealumination alone, however.[14] This realization has led to very active research targeting precise creation of 'mesoporosity' and 'macroporosity with the goal of overcoming the limitations of small, geometrically defined, pores.

These developments were critical in enabling the wide use of zeolites in key refining and petrochemical processes, including fluidized catalytic cracking and hydrocracking, and resulted in their major economic and societal impact. The mechanisms by which these modification methods led to framework stabilization and

enhanced catalytic performance were the subject of vigorous scientific debate in the zeolite catalysis literature. [15] Eventually it became clear that the enhanced stability, and improved performance, derived from these modification schemes were due to better control of indiscriminate framework de-alumination which otherwise led to framework collapse. The models eventually adopted by workers in the field suggest that steam stabilization, when carried out in a controlled manner, involved the hydrolysis of framework aluminum followed by 'healing' of the (more silicious) framework by insertion of silicon derived from other parts of the framework or from amorphous phases.

Desilication is a currently active area of zeolite modification. However, the dissolution of silica from zeolites using basic solutions was first studied long ago. [16] The example originally given was synthetic mordenite, although the inventors stated analogous results were obtained with other high silica zeolites. The inventors also indicated enhanced porosity and lowered Si/Al ratio in their treated materials, which are the major claimed advantages in the much more recent reports as well. A later patent combined acid treatment with subsequent base treatment in NaOH to enlarge pores in mordenite. [17] Several publications in the 1990s further outline the incongruent dissolution of aluminosilicate zeolite in basic solutions. [18]

Basic media used in desilication include alkali hydroxides and tetraalkylammonium hydroxides. A 1994 report indicated that mesoporosity can be generated by treatment of MFI zeolite with sodium carbonate solutions. [19] An extensive series of desilication studies have been carried out by the Perez-Ramirez group; representative references are listed. [20] In 2002, Goto et al reported and patented the desilication of zeolites in NaOH in the presence of surfactants. [21] Later Ying and Garcia-Ramirez reported similar materials. [22]

Substitutive Methods

A number of reports of realumination have appeared over the years, starting with one in 1977. [23] Subsequent independent studies by other groups both questioned [24] and supported [25] the original authors contention that aluminum could be reinserted by treatment of dealuminated zeolites with aqueous basic reagents after a dealumination process such as steaming or acid treatment. In light of recent studies of desilication of zeolites under similar conditions, however, it is possible that the original reports of realumination in basic solutions were at least in part unrecognized desilication reactions.

It has been claimed that acidic realumination also can take place, [26] however there are also studies that question acidic realumination as well. [27] One theory for realumination is that defects that are very similar to the original aluminum site, called hydroxyl nests, analogous to such defects found in hydrogarnets, [28] are easily "refilled" with aluminum cations by appropriate treatments. Recent studies have sought to disprove the existence of hydroxyl nests in zeolites, however. [29]

The early flurry of framework modification activities described above was followed by more elegant synthetic approaches employing chemical substitution methods. Silicon reinsertion has also been claimed by a number of authors. [30] The claimed mechanism for silicon insertion often invokes the filling of hydroxyl nests, similar to the proposed mechanism for re-alumination reactions. The reactions generally involved halo-silicate reagents such as SiF_6^- , or SiCl_4 , or simple fluoride reagents such as NH_4HF_2 . The driving force for the substitution reactions, which are dissociative in nature, is the reinsertion of Si after the extraction of aluminum and concomitant formation of soluble halo-aluminum species.

Transformative Methods

Transformative post-synthetic treatments of zeolites range from solid state phase transformations to complete dissolution/recrystallization reactions. Many of the solid state transformations are carried out on layered zeolite precursors or three-dimensional zeolites with periodic weak or reactive links within the structure. Dissolution/recrystallization reactions have been carried out widely on a number of zeolite compositions and structures.

Layered zeolite precursors have been known for some time.[31] Delamination and pillaring has been carried out on layered zeolites similar to manipulations of layered clays.[32] A number of studies have appeared over the last 15 years or so on the conversion of layered zeolites to three dimensional zeolite structures either by direct fusion of the layers,[29] by prior addition of pillaring agents followed by conversion to a three-dimensional material,[33] or by removal of some portion of a three-dimensional zeolite, for instance germanium oxide units, followed by re-conversion of the resulting two-dimensional material to a new three-dimensional zeolite.[34] The most broadly applicable method is the direct conversion of layered zeolites to three-dimensional zeolites, the latter two methods being less general and perhaps only feasible in a limited number of cases.

The use of zeolites as reagents in zeolite synthesis has been studied extensively for decades and could warrant a separate article on its own. The earliest reference, the original zeolite B patent from 1961, indicates that zeolite B forms via conversion of other known zeolites at long reaction times. [35] Recent examples of such transformations are the hydrothermal conversion of FAU-type zeolite to MSE and CHA types. [36,37]

Summary

A number of other post synthesis modifications have been carried out on zeolite materials, although some of the more commercially relevant methods have been mentioned in this essay. An extensive review has also recently appeared. [38]

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10. Diffraction methods for zeolite structural characterization

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Introduction

In the context of zeolite syntheses, diffraction methods are indispensable in the initial structural characterization of a product. Is the phase crystalline? Is it the desired phase? Is it a known phase? Is it pure? Is it novel? These questions can usually be answered by applying simple X-ray powder diffraction (XPD), electron diffraction (ED) and/or electron microscopy (EM) techniques. Each method has its strengths and weaknesses, but they are highly complementary, so with a judicious choice of techniques, the desired information can be obtained. For example, an XPD pattern can be used as a fingerprint for identification purposes, and scanning electron microscopy (SEM) will reveal the size and morphology of the crystallites and whether or not impurities are present. However, more information can be derived, if needed (Table 1). Therefore, it is important to know where the information can be found and how to extract it. For example, high resolution transmission electron microscopy (HRTEM) can also show the pores/channels and TO₄ tetrahedra in a zeolite, but the technique requires a certain level of expertise. Here we describe a few practical considerations for collecting and interpreting simple XPD, ED and EM data.

Table 1. Information that can be derived by applying different XPD and ED/EM techniques.^a

Information	XPD	ED	EM
Crystallite morphology			SEM
Crystallite size	profile fitting		SEM
Crystalline impurity	unindexed peaks	different patterns	SEM
Amorphous impurity	high background	No diffraction	SEM
Stacking faults	broad peaks	streaking	HRTEM
Unit cell dimensions	reflection positions (1D but accurate)	reflection positions (3D but approximate)	HRTEM
Symmetry	systematic absences (obscured by overlap)	systematic absences (no overlap)	HRTEM
Crystal structure	reflection intensities	reflection intensities	HRTEM

	(obscured by overlap) (kinematical)	(no overlap) (dynamical)	(phase information)
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^a The recommended technique for obtaining each kind of information is shown in bold.

X-ray powder diffraction

Data Collection

It is not possible to go into detail in the space available here, but the basic considerations for XPD data collection and a few common sources of error will be discussed. For more information, the reader is referred to the volume entitled "Modern Powder Diffraction" edited by Bish and Post [1] or to the article entitled "Practical Aspects of Powder Diffraction Data Analysis" by Baerlocher and McCusker [2].

Peak positions

If an XPD pattern is to be indexed (*hkl* assigned to each of the peaks and thereby the unit cell dimensions derived), it is essential that the peak positions be determined accurately. In this case, the 2θ scale of the diffractometer needs to be calibrated using a standard material (e.g. NIST Silicon standard 640d). The sharper a peak, the better its 2θ value can be determined, so the diffractometer should also be adjusted to optimize the sharpness of the peaks. As a guide, almost any laboratory instrument can be adjusted to give a full width at half maximum (FWHM) for the Si 111 reflection ($28.44^\circ 2\theta$ with $\text{CuK}\alpha_1$ radiation) of $0.08^\circ 2\theta$ or less. The measured 2θ values for the peaks in the pattern of the standard material should agree with the literature values to within $0.01^\circ 2\theta$.

If the sample is off-center, this will affect the 2θ zeropoint correction, so ideally, the sample should be mixed with a small amount of the standard (that is, measured with an internal standard), so that the 2θ calibration can be done simultaneously. However, if care is taken in positioning the sample, a 2θ calibration using an external standard is usually sufficient. In reflection mode, thin samples are preferred for peak position determination, so effects of sample transparency can be eliminated, but care should be taken to ensure that the crystallites are randomly oriented or not all reflections will be recorded.

Peak intensities

For indexing purposes, the intensities of the reflections are irrelevant, but for identification or for structure analysis, accurate relative intensities are essential. There are three commonly ignored factors that can have a significant effect on the relative intensities measured: (1) sample thickness, (2) preferred orientation, and (3) divergence slits.

Bragg-Brentano (reflection) geometries require an "infinitely thick" sample. That is, it is assumed that the sample is thick enough that all impinging X-rays interact with the sample (by absorption or diffraction) before they reach the sample holder. In this way, the volume of sample effectively irradiated remains constant as 2θ changes. If this is not the case, the intensities must be adjusted for the transparency of the sample. In general, the intensities of the low angle reflections will be too large if the "infinite thickness" criterion is not met. For transmission geometries, on the other hand, the sample must be thin enough that the X-rays are not too strongly attenuated by absorption.

Most powder diffraction data analyses assume that the sample consists of millions of randomly oriented crystallites. If this is not the case, relative intensities will be

distorted. For example, if the crystallites have a plate-like morphology, they are likely to lie flat. Assuming that the c-axis is parallel to the short dimension, crystallites aligned in the 001 diffraction condition will be overrepresented, and those in the $hk0$ diffracting condition underrepresented. This will then lead to a bias in the relative intensities recorded. Various sample preparation techniques have been used to reduce preferred orientation (such as back or side loading of flatplate sample holders, mixing amorphous glass beads with the sample, or spray drying), but none is foolproof. Measurements in transmission mode with the sample loosely packed in a rotating capillary are less susceptible (but not immune - needles will tend to align themselves with the capillary) to this problem.

A related problem is that of a "rock in the sand". That is, if a larger crystal is present, its diffraction pattern will distort the measured intensities, because its orientation will be overrepresented, so the assumption of random orientation will not be met. This non-random distribution cannot be corrected for in the subsequent analysis, so care should be taken to assure that the crystallites are of similar sizes and/or that they are free to tumble.

In Bragg-Brentano geometry, the X-ray beam is spread over a larger surface of the specimen at low angles than it is at high angles. To ensure that the X-rays interact only with the sample (and not the edges of the specimen holder) a divergence slit is inserted between the X-ray source and the sample to confine the beam to the sample. As the 2θ angle increases, this slit can be opened wider to allow more X-rays through and thereby increase the counting rate, but then the resulting data must be corrected for the increased volume of sample irradiated. The slit size can be varied during the measurement either continuously (using an automatic divergence slit) or manually (using a series of calibrated slits). For data comparison purposes, the data should then be transformed to constant sample volume (single constant slit) data. In many laboratories, data are recorded using a relatively wide single slit that is appropriate for higher angle data, but not for the lower 2θ values. In such a measurement, the intensities of the low angle peaks will appear to be too low, because only part of the X-ray beam interacts with the sample.

Phase identification

In a zeolite laboratory, powder diffraction data are most commonly used to identify a newly synthesized material or to monitor the effects of a post-synthesis treatment. In both cases, the measured pattern is compared with an existing one, whether it is a pattern in the Collection of Simulated XRD Powder Patterns for Zeolites [3], the Powder Diffraction File (PDF) of the ICDD [4] or an inhouse data file. Such comparisons are not easy for zeolites, especially if the data collection or sample preparation conditions differ. A few practical considerations are presented briefly below.

- (1) Intensities are important for identification, so the data should be collected accordingly.
- (2) Data should be in the form of a constant volume measurement if the Collection, the PDF or any of the common databases is to be used in a search/match procedure.
- (3) Peak position information is often given in terms of d -values rather than 2θ values, because d -values are independent of the X-ray wavelength (λ) used. ($d = \lambda / (2 \sin \theta)$)
- (4) The low angle reflections are the ones most strongly affected by non-framework species [2]. These reflections are usually more intense in the calcined material than in the as synthesized form, and similar materials containing different cations or different organic species may have quite different relative intensities at low angles. However, the intensities of the higher angle reflections can be compared quite well.

(5) Different synthesis conditions or different post-syntheses treatments can cause subtle distortions in a zeolite framework structure that can complicate identification. The symmetry may be reduced, although the basic framework connectivity remains unchanged. In this case, indexing the pattern can facilitate identification.

Electron Diffraction

Electron diffraction (ED) is complementary to XPD, and can also be used for phase identification and structure determination. Each crystallite in a powder sample behaves like a single crystal in ED, and there is no peak overlap. While an XPD pattern provides information on the entire bulk sample, each ED pattern gives information on individual crystallites in the sample. Thus ED has a unique advantage for studying multiphase samples. Here the basic considerations for ED data collection and applications will be discussed. More information can be found in the book by Zou et al. [5] or in the review articles [6-7].

Sample preparation and data collection

Samples for TEM investigations are prepared by dispersing the powder in absolute ethanol, and transferring a droplet of the suspension onto a copper grid coated with a holey carbon film. An ED pattern is obtained by selecting one crystallite, aligning it along a crystallographic axis (zone axis), and recording the pattern of the selected crystallite. Recently new 3D ED methods were developed, i.e. automated diffraction tomography (ADT) [8] and rotation electron diffraction (RED) [9], for collecting a series of ED patterns from an arbitrarily-oriented crystal. Almost complete 3D ED data can be collected by ADT and RED. For phase identification, it is important to calibrate the camera length and ensure that the crystal is at the eucentric height so that the d -values are determined accurately. For structure determination, it is important to collect the ED data from very thin crystals (< 100 nm) in order to minimize dynamical effects and thereby obtain more kinematical ED intensities.

Phase identification from zone axis ED patterns

An ED pattern is a 2D section of the 3D reciprocal lattice that can be used as a fingerprint for phase identification. The two shortest reciprocal lattice vectors (in \AA^{-1}) and the angle between them can be determined from the ED pattern. They are compared with those calculated for a given zeolite. If these three values fit, it is likely that the ED pattern is from that zeolite. However, in some cases, more than one zeolite might give a good fit to an ED pattern, especially if the ED pattern is taken along a zone axis with high indices or if the zeolite structures have some identical projections. In order to resolve the ambiguity, more than one ED pattern should be taken from the same crystal and all ED patterns and the tilt angles between them be used to search for the best fit [5]. The program PhIDO was developed for this purpose [10].

Phase identification and structure determination from 3D RED data

Phase identification is more easily done using 3D ED data. The 3D peak positions and peak intensities can be extracted from the ADT/RED data and combined into a 3D reciprocal lattice. The unit cell parameters can be determined directly from this reconstructed reciprocal lattice [8-9]. Possible space groups can be deduced from the systematically absent reflections. The unit cell and space group are used to identify the zeolite. If no zeolite is found to have similar unit cell parameters and space group, the structure of the crystal is likely to be new. In such a case, the ED intensities extracted

from the 3D ED data can be used together with the unit cell and space group to determine the structure of the new zeolite. The procedure is similar to that used for determining a structure from single-crystal X-ray diffraction data. Indeed, the same software can be used for both X-ray and ED data [6-7,9].

The values of reciprocal lattice vectors (in \AA^{-1}) and angles from ED often have larger errors than those from XPD. It is sometimes difficult to distinguish between zeolites that only have small differences in their unit cell parameters. In such cases, intensities and systematic absences from ED and chemical composition from energy dispersive spectroscopy (EDS) might provide further information to facilitate the phase identification. One drawback of ED is that the unit cell parameters and symmetry can change in the TEM as a result of the vacuum or interaction of the sample with the electron beam.

Complementary electron microscopy (EM) techniques

SEM is very useful for finding the size and morphology of the crystallites. The morphology often reflects the symmetry (point group) of the crystals. If more than one morphology is apparent in the SEM images, the sample may contain impurities. While crystals usually have well-defined shapes, an amorphous impurity has an ill-defined one. HRTEM images can also be used for phase identification and structure determination, but this technique is more demanding [6]. The crystallographic phase information that can be obtained from HRTEM images can also facilitate both space group and structure determination. HRTEM has unique advantages for studying disordered zeolite materials, because the local atomic arrangement can be seen directly. Finally, chemical compositions can be obtained by EDS on both SEM and TEM.

Conclusion

By applying the appropriate combination of simple XPD, ED and EM techniques to a zeolite material, much can be learned about its structural characteristics. The morphology of the crystallites can be ascertained (SEM), the unit cell dimensions can be determined (ED, XPD), the purity of a sample verified (XPD, SEM), a known phase can be identified (XPD, ED), and disorder can be visualized (HRTEM). The techniques are highly complementary and the combination needed depends upon the information required. More sophisticated data analysis can also lead to the determination of the structure of a novel zeolite material.

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11. Advanced methods applied on zeolites

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Introduction

Recent advances in the development of *in situ* techniques that are able to obtain both spatial and chemical information simultaneously, are paving the way to obtaining an increased understanding of catalytic solids, in particular zeolites. These *in situ* micro-spectroscopic techniques offer a toolbox, in which a technique (or a combination thereof) can be selected based on the scientific question at hand. In this article, we highlight some recent examples from our group of innovative lab-based and synchrotron-based methods, applied on zeolite-based systems. Not only do we focus on zeolite powders and model single crystals, but also on industrial-scale catalysts, namely Fluid Catalytic Cracking (FCC) particles (50-150 μm) and zeolite-based extrudates (mm-sized), showing the full range of possibilities of these systems.

Lab-based micro-spectroscopy

The coupling of a microscope with a spectrometer offers several advantages for studying zeolites, mainly in linking structural and chemical information in a spatiotemporal manner, such as zeolite pore structure and molecular species present therein. Depending on the type of molecules and whether they are produced within the zeolite over time (*i.e.*, during a reaction), or introduced (*i.e.*, as guest molecules to study absorption properties), determines the technique(s) required, whether it is electronic (UV-Vis, fluorescence) or vibrational (IR, Raman) micro-spectroscopy.

The combination of *UV-Vis and confocal fluorescence microscopy*, make an interesting proposition to study several catalytic properties of zeolites. Taking a staining probe reaction such as styrene oligomerization, which forms light absorbing species, UV-Vis microscopy can spatially resolve the types of species formed during the reaction. [1] A unique feature of this system is that the same *in situ* cell used for the UV-Vis microscopy experiments can be transferred to a confocal fluorescence microscope in order to obtain a 2-D/3-D chemical map of the molecular species formed on Brønsted acid sites inside the ZSM-5 crystals. This involves the use of multiple laser line wavelengths to selectively excite individual groups of molecules within or at the surface of the zeolite material.

Recently, a combination of UV-Vis and confocal fluorescence micro-spectroscopy was employed to study binder effects and Brønsted acidity in partially and fully proton-exchanged Na-ZSM-5-based SiO₂-bound extrudates. [2,3] Using acid-catalyzed thiophene oligomerization as a probe reaction, the activity and selectivity of the materials were monitored using time-resolved UV-Vis microscopy. An understanding of the type and relative quantity of oligomers produced inside the 2-6 μm Na(H)-ZSM-5 crystals were determined. It was found that fully proton-exchanged samples containing a higher Brønsted acid site density favored the formation of ring-opened species (thiol-like compounds). This was in contrast to the further oligomerization route taken by partially proton-exchanged samples, due to the lower Brønsted acid site density present. Confocal fluorescence microscopy experiments on the same samples showed that the

partially proton-exchanged samples obtained a non-homogeneous distribution of acid sites, which is in contrast to the homogeneous distribution in the fully proton exchanged samples.

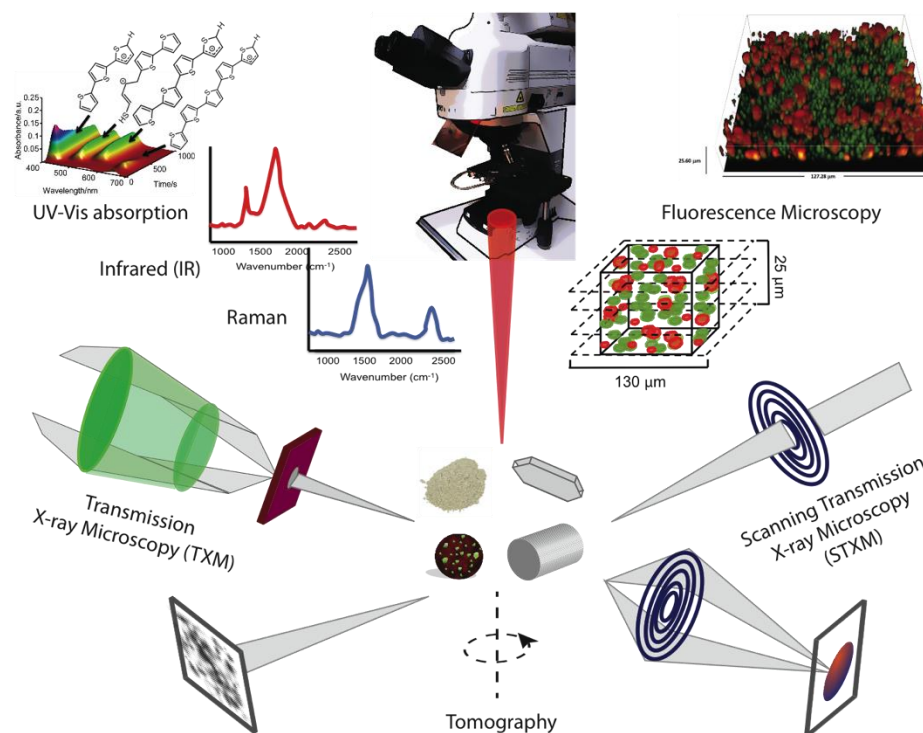


Figure 1. Schematic depicting advanced lab- and synchrotron-based micro-spectroscopic techniques applied on zeolite-based materials. From zeolite powder, model zeolite crystals to industrial-scale zeolite-containing catalyst bodies, these techniques are an arsenal to probe zeolite properties in significant detail.

Given the unique nature of the various zeolite pore architectures and their shape-selective properties, fluorescence microscopy has been shown to provide an exemplary means to study such features using polarization and staining probe molecules. The acid-catalyzed oligomerization of 4-fluorostyrene is one such example, which Sprung *et al.* applied on industrial FCC particles and large ZSM-5 crystals (100 x 20 x 20 μm) in order to develop structure-activity relationships, by linking the distribution of active phase and pore structure therein with oligomer selectivity.[4,5] Focusing on the model catalysts, the six sub-units of a large coffin-shaped ZSM-5 crystal each contain either straight or sinusoidal channel pores, which are perpendicular to each other along the long axis of the crystal. Taking either parent, steamed at 500 $^{\circ}\text{C}$ or 700 $^{\circ}\text{C}$ ZSM-5 crystals, multiple laser line wavelengths in combination with a confocal fluorescence microscope showed that by analyzing the polarization plane of the emitting fluorescence, the orientation of the restricted oligomer molecules can be distinguished, and hence the pores they occupy. The confocal ability of the fluorescence microscope allows a 3-D chemical map to be formed, clearly depicting the shape-selective nature of zeolite crystals.

Using the same batch of parent and steamed large ZSM-5 crystals, Ristanović *et al.* have taken fluorescence microscopy to its ultimate sensitivity limit, performing quantitative 3-D imaging of single catalytic turnovers during the oligomerization of furfuryl alcohol.[6] *Single molecule fluorescence microscopy* is widely used in the life sciences, but in this case it was uniquely used to show that depending on the surface porosity and degree of dealumination, ZSM-5 crystals operate at significantly different single turnover

kinetics (at varying spatial regions) with nanometer resolution. It was observed that mild steaming (i.e., at 500 °C) obtained a higher surface reactivity than parent crystals, with up to 4 times higher local turnover rates. This was confirmed by *Time-Of-Flight-Secondary-Ion-Mass-Spectrometry* (TOF-SIMS) to be attributed to the 3-D distribution of Al, influencing surface diffusion barriers. Severe steaming (i.e., at 700 °C) obtains a drastically reduced turnover rate (2 orders of magnitude lower), due to the substantial dealumination of the material (hence lower Brønsted acid site number). This advanced technique is not limited to model systems, as it was previously applied to larger-scale systems with smaller zeolite domains, in the form of FCC particles. [7]

These advanced lab-based micro-spectroscopic techniques are paving the way to efficiently obtain significant detail into zeolite catalytic properties, without excessive pre-treatment of the sample prior to analysis and allows realistic operation conditions.

Synchrotron-based micro-spectroscopy

The recent developments of 3rd and 4th generation synchrotron sources offer a means to study zeolitic materials with improved spectral brightness, detector sensitivity, as well more advanced focusing optics. [8] This allows imaging of materials with a significantly increased photon flux (compared to conventional methods) with high spatiotemporal resolution from IR to X-ray regions.

Vibrational spectroscopy techniques allow the identification of the molecular structures, composition and interactions present within a sample. The use of *synchrotron IR* micro-spectroscopy coupled with multiplex *Coherent Anti-Stokes Raman Scattering* (CARS), offers a novel tool to analyze catalytic properties of zeolites, by achieving a 2-4 fold improvement in the spatiotemporal resolution over conventional IR and Raman micro-spectroscopy. Kox *et al.* utilized this unique technique to follow *in situ* the oligomerization of 2-chlorothiophene in large H-ZSM-5 crystals, in order to reveal the interaction of reactant (CARS) and formed molecular species (IR) within the zeolite pores. [9] CARS allows the added benefit of performing 2-D/3-D chemical mapping, with intrinsic lateral resolution (x, y) of ~400 nm and a depth-resolution (z) of 1 mm. By analyzing the distribution of the =C-H stretching vibration (3115 cm^{-1}) at varying x, y, z positions within the ZSM-5 crystal impregnated with 2-chlorothiophene, gradients of reactant concentration were found. An increase in concentration towards the middle of the crystal was noted (2.5 times more than the outer regions), most likely due to capillary forces induced by the micropore structure, or evaporation of reactant from the surface of the crystal by local laser heating. In an additional experiment, IR-microscopy was employed to study the formation of intermediate/product species upon heat treatment. Firstly, polarization dependency experiments showed that bands attributed to ring stretching vibrations of aromatic reaction products ($1401, 1506, 1550\text{ cm}^{-1}$) were highly influenced by the polarization angle. This backs up earlier studies by Sprung *et al.* that elongated molecules are entrapped/aligned within the straight channels of the ZSM-5 crystal. Mapping of the reactant (1412 cm^{-1}) and elongated product (1401 cm^{-1}) species at different reaction times depicts the decreasing intensity of the reactant as the reaction proceeds. Furthermore, the edge region contains significantly less reactant and product. This corroborates well with CARS experiments, showing the synergy of both techniques.

X-ray-based micro-spectroscopic techniques also offer a valuable method to analyze zeolites, due to their highly penetrating nature, as well their energy tunability to study features such as oxidation/coordination states, chemical compositions, and crystallinity, among others. Aramburo *et al.* provide a good example of applying soft X-rays to study a single zeolite particle. [10] *Scanning Transmission X-ray Microscopy*

(STXM) utilizes chemical sensitivity using a Fresnel zone plate, to focus the X-ray beam onto a nm-size area of the sample, raster-scanning in a specific focal plane and recording the transmitted X-ray intensity. This technique was used on both calcined and steamed (i.e., at 700 °C) H-ZSM-5 particles to chemically map at the aluminum *k*-edge, in order to determine the distribution and coordination environments of aluminum in 2-D/3-D. At a spatial resolution of 30 nm and a field of view of 3 x 3 μm , STXM images were recorded at three different energies to allow measurements of 4-fold and 6-fold aluminum. In the case of the calcined particle, 89 % 4-fold aluminum was homogeneously distributed and 11 % 6-fold aluminum was present at random isolated regions, confirming no aluminum zoning. In contrast, the steamed ZSM-5 particle depicts not only the presence of two different types of 4-fold and 5-fold aluminum, but also a higher overall coordination number (no aluminum zoning).

In situ STXM and tomography, coupled with ^{27}Al and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, were applied by van der Bij *et al.* to determine if three industrial type zeolites, MOR, FAU and FER were able to form an aluminum-phosphate binder after hydrothermal treatment and reaction with phosphoric acid. [11] Unlike the FER framework topology, MOR and FAU both formed an AlO(OH) extra-framework (EF) aluminum phase after dealumination. This was due to the EF Al being trapped within the pores of the FER framework. Upon reaction with phosphoric acid, the AlO(OH) readily reacts to form an AlPO₄ phase. Whether AlPO₄ is present outside or inside the channels of the zeolite, determines whether it forms AlPO₄ islands, or remains amorphous, respectively. Therefore, in order to form an AlPO₄ phase within a zeolite structure, the following parameters should be taken into account: Si/Al ratio, pore dimensions and accessibility, as well as stability of the aluminum atoms in the framework.

Meirer *et al.* have recently applied the use of hard X-ray nano-tomography using Transmission X-ray microscopy (TXM) for the first time to correlate differences in pore structure/connectivity with metal deposition in Fluid Catalytic Cracking (FCC) particles at varying stages of life cycles.[12] TXM allows us to study sub-30 nm with 2-D resolution, but by stitching together multiple fields of view (i.e. 30 x 30 μm^2) at varying angles, a 3-D reconstruction can be made.[13] FCC particles are 40-70 μm spheres that contain a mixture of zeolite active phase, matrix and filler. As these particles crack long-chain feedstock molecules (of crude oil) into smaller, valuable molecules, metals accumulate and influence the activity and selectivity of the catalyst particles. The 3-D distribution of Ni and Fe in a fresh particle and those with varying degrees of deactivation showed that they are mainly present at the near-surface layer of the particle (most concentrated in the early stages of life cycle). This effectively impedes entry of reactant molecules to the macropores of the matrix surrounding the zeolite crystals, hence reducing catalytic activity overtime.

Conclusions

The advanced lab- and synchrotron-based methods discussed in this article have provided new insights into the catalytic properties of zeolites that have previously been lacking with conventional 'standard' bulk characterization techniques. Not only are we now able to couple structural and chemical properties of a fresh zeolite material in a spatially resolved manner, but we are also able to monitor, in a time-resolved manner, their reactivity and deactivation during a catalytic process. Resolving spatiotemporal physicochemical information on a variety of length scales, offers a plethora of

opportunities in understanding and developing zeolites further, which will eventually enhance process efficiency.

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12. Modeling of zeolites: from the unit cell to the crystal

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Introduction

Molecular simulation offers a new dimension, complementary to experimental techniques and pen-and-paper theoretical models, to the study of numerous physical and chemical phenomena in gas, liquid, and solid phases. Since its emergence in the 1950s, and its popularization in the next decades, it has seen ever-growing use in the research community in physics, chemistry, materials science and biology. The uninterrupted development and publication of novel methods, combined with the exponential increase in available computational power (thanks to Moore's law), have widely expanded the range of problems that can be addressed through modeling.

Various computational techniques have reached the status of being relatively "routine" computations, at least for well-known systems, and are now considered an integral part of the researcher's toolbox just as, e.g., X-ray diffraction and NMR spectroscopy. Among those, we can cite Density Functional Theory calculations and Grand Canonical Monte Carlo simulations. It is possible to become a *user* of these tools with relatively little training, relying either on commercial or academic software with user-friendly interfaces. However, as with any technique, one should always take great care in checking the validity of the tools for the system at hand, as well as in interpreting the results obtained.

Here, we give an overview of some of the computational chemistry methods commonly used in the field of nanoporous materials in general, and zeolites in particular. It is by no means a systematic review (though some can be found in the existing literature), but rather an introduction to the topic of molecular simulation in zeolite science.

Adsorption

As in all nanoporous materials, adsorption of molecular fluids and fluid mixtures is both one of the most common tools for the characterization of zeolites and one of their most sought-after properties for industrial applications. As such, a very large body of theoretical work has focused on the molecular modeling of gas and liquid adsorption in zeolitic materials, in order to shed light into the microscopic root of the behaviors observed experimentally (i.e., decrypting the adsorption mechanism behind a measured isotherm) and also to predict co-adsorption and separation properties in fluid mixtures.

The standard (and well-established) technique for molecular simulation of adsorption thermodynamics in rigid nanoporous materials is the Monte Carlo simulation method in the Grand Canonical ensemble, also known as Grand Canonical Monte Carlo (GCMC). [1,2,3] This approach, schematized in Figure 1, models the adsorption of molecular fluids or mixtures inside a rigid zeolite (system of fixed volume V), for given values of the temperature (T) and chemical potential of the bulk fluid (μ) or fluid mixtures components (μ_1, μ_2, \dots). These simulation conditions are close to the thermodynamic conditions during experimental adsorption measurements, where the temperature and pressure P_{fluid} of the external fluid typically are controlled. Notably, the experimental

pressure of the bulk fluid (P_{fluid}) can be related to its chemical potential (μ), used in the GCMC simulations, through an equation of state.

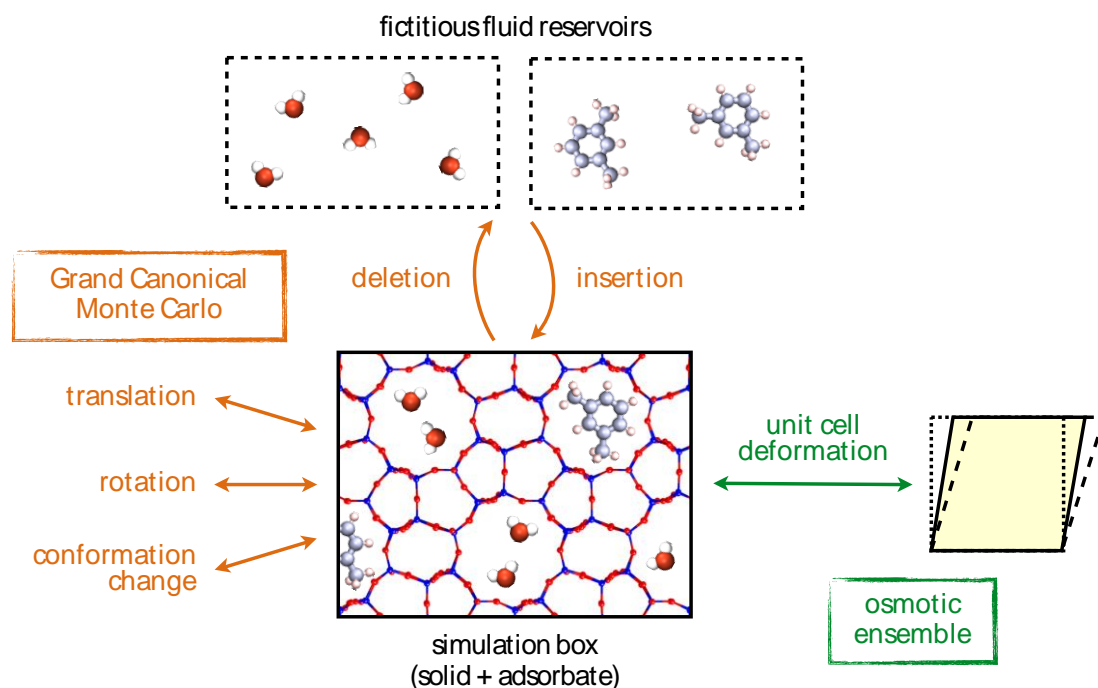


Figure 1. Schematic diagram of the Monte Carlo simulation of adsorption in a porous host, in the Grand Canonical thermodynamic ensemble (in orange) and in the osmotic ensemble (allowing deformation of the material, in green). Reproduced with permission from Ref. [4], Copyright 2016, with permission from Elsevier.

Grand Canonical Monte Carlo simulations allow the calculation of equilibrium thermodynamic quantities, such as the average number of adsorbed molecules, or absolute adsorption uptake $\langle N \rangle$, the isosteric heat of adsorption q_{st} , and the Henry's constant K . Such macroscopic observables can be compared to experimental data, and used directly in the comparison of different materials or as input to the numerical simulation of industrial processes, e.g. fixed-bed adsorption columns. In addition, GCMC simulations provide detailed structural information, including density distributions of adsorbed molecules, yielding valuable insight into the adsorption mechanism and driving forces at the atomistic scale. Moreover, as hinted above, GCMC simulations can directly probe coadsorption, i.e. the adsorption of fluid mixtures, as well as that of pure components. This is of particular interest, in particular in the computational prediction of fluid separation properties, which can be difficult and time-consuming experimentally, in particular due to the large number of control parameters (temperature, pressure, mixture composition).

A key factor in the realization of high-quality GCMC simulations is the description of the interactions between fluid molecules and the zeolite (framework and cations). These interactions are typically described by so-called *force fields* or *classical interaction potentials*, and break down the host–guest and guest–guest interactions into physically relevant terms with simple analytical expressions, including Coulombic interactions, long-range dispersion, short-range interatomic repulsion, polarizability, etc. These force fields need to be optimized for each specific system and property studied, by comparison either to experimental data or reference quantum chemistry calculations. It should be stressed that the choice of force field, as input to the molecular simulation method, controls the quality of the results obtained and needs to be carefully considered. A large

number of force fields for various zeolites have been made proposed and validated in the literature in the last 25 years.

Finally, it should be noted that Monte Carlo simulations in the Grand Canonical ensemble, although considered the golden standard in the simulation of adsorption in zeolites, assume that the zeolitic framework is rigid. This approximation is very reasonable when it comes to the thermodynamics of adsorption in most zeolites, where framework flexibility is limited. It is not universally valid, however, as some zeolites show adsorption-induced structural transitions (as do some more flexible nanoporous materials, such as metal–organic frameworks). Extension of the GCMC technique to flexible materials, taking into account the material's deformation in the osmotic ensemble (see Figure 1), has been recently implemented in some Monte Carlo simulation codes. [5,6]

Dynamics of adsorbate and transport properties

Monte Carlo simulations provide both thermodynamic characterization on the adsorption process, and structural information on the adsorbed phase (such as location of adsorbed species). However, by its very nature it does not provide any results on the dynamics of the adsorbed phase. Yet, dynamic properties of adsorbates play a key role in separation processes and reactions, as even the zeolite with the largest thermodynamic separation properties is useless if diffusion of guest molecules is too slow. There is thus a need of being able to model the dynamics of adsorbates and their transport properties. The “gold standard” technique for this is Molecular Dynamics (MD), [2,7,8] which is a direct simulation of the physical movements of the atoms in a given system over time. It can thus be used to study both structural and dynamical properties of nanoporous materials.

Observables quantities that can be calculated from molecular dynamics simulations include many dynamical properties. At the smallest time and length scale, one can characterize framework and guest deformation (if flexible molecular models are used), as well as the orientational dynamics of the guest species. From dynamics at larger time and length scales, one can characterize the translational dynamics, i.e. the diffusion of guest molecules in the pores of the material. The determination of diffusivities in zeolites, either from experiments or calculations, is key to understanding the transport within their pore systems. In particular, it can be linked to the permeability coefficient of zeolite membranes, a crucial quantity for many membrane-based applications. Moreover, molecular dynamics simulations can provide valuable microscopic insight into the observed diffusivities of confined fluids and mixtures, by detailed analysis of the trajectories of individual molecules over time.

Molecular dynamics, like Monte Carlo simulations, typically require *force fields* model for the interatomic interactions in the system. However, contrary to the thermodynamic properties of adsorption, the influence of the zeolitic framework flexibility is actually very important in the dynamics of adsorbates. This is particularly the case in zeolites with small cages, or large cages connected by small windows. In such cases, where the dimensions of the zeolite pore spaces are close to the molecular diameter of the adsorbed fluid, the detailed atomic motion of the framework vibrations influences significantly the diffusion and transport of guest molecules. As such, studies of diffusion and transport in small-pore zeolites are typically done with flexible frameworks, using intramolecular zeolite force fields.

Finally, we note that it is also possible to perform molecular dynamics simulations based on quantum chemistry evaluation of the interatomic forces (in the Density

Functional Theory approach), rather than relying on *ad hoc* optimized classical force fields. While much less used in the literature than force field-based MD, the continuous increase in computational power available has led to more frequent use of this computationally demanding technique, often called *ab initio* MD or first principles MD. This is particularly useful to study detailed atomic motions at short time scales, such as vibrational and orientational properties.

Catalysis

Catalysis is one of the most important applications of zeolitic materials, and thus catalytic processes in zeolites have been extensively studied from a theoretical point of view. This analysis of reactivity requires the modeling of the breaking and formation of chemical bonds, electron transfers as well as change in the electronic environment and oxidation states of atom. Therefore, it needs to be modeled at the quantum mechanical level, which can be performed at different levels of theory: the most popular methods with the necessary accuracy to predict chemical reactivity are post-Hartree–Fock methods and calculations based on Density Functional Theory (DFT).

Another choice to be made for the quantum chemical modeling of reactivity in zeolites is that of the size of the system studied. For zeolites with small enough unit cells, it is possible to use a “solid state” approach, where the full unit cell of the crystalline solid is represented, with periodic boundary conditions. However, for larger systems, the computational cost of a periodic calculation can be avoided by performing calculations on a subsystem, i.e. a carefully chosen cluster cut out from the zeolite structure around the region where the reaction occurs.

Quantum chemistry calculations, once set up, allow for both the structure and energetic characterization of catalytic cycles and reaction pathways. See refs. [9 and 10] for reviews on this topic, and refs. [11 and 12] for research papers (out of the large body of literature on this topic) exemplifying the quantum chemical modeling of zeolite catalysis. First, for each possible structure, conformation or state of interest (reactant, products, and intermediaries), one needs to build an input structure: this can be hand-built from chemical intuition, extracted from earlier work or obtained from classical (MD or MC) simulations. Then, these initial structures will be *relaxed* in a process of energy minimization, until local energy minima are found. Both the resulting structures themselves, as well as their energies, are of interest. Finally, a full mapping of the reaction pathways can be performed by searching for transition states between these structures. This allows for the determination of activation energies, and thus kinetic parameters such as reaction rate constants.

It should be noted that, while quantum chemical calculations only allow to calculate the relative energies of molecular and crystalline structures, it can also be used to estimate their relative entropies. For relatively rigid structures (with no soft vibration modes), the vibrational entropy of all structures is approximated in the (quasi-)harmonic approximation. It can thus be calculated from vibration frequencies (or phonon frequencies, for a solid), themselves computed in quantum chemistry calculations through the second derivatives of the energy with respect to the atomic coordinates. This allows for a rough estimation of relative entropies, and thus relative free energies of the states of interest (reactants, products, intermediaries and transition states) at a given temperature.

Structure prediction and feasibility

While more than 200 zeolite frameworks have been observed in natural or synthesized zeolitic materials, and more are discovered every year, this is only a very small number compared to the infinite number of mathematically generated edge-sharing tetrahedra networks. Moreover, most framework types can only be obtained for specific ranges of chemical composition; for example, less than a quarter of that number (46 out of 206, at time of writing) can be experimentally obtained as pure silica compounds. It is thus not surprising that the question of computationally predicting zeolite structures has been the focus of a lot of effort from the research community, as has the issue of evaluating the experimental “feasibility” of predicted structures (whether they can be obtained in given experimental conditions). The ultimate goal here would be for theoreticians to be able to guide the design and synthesis of novel zeolites with targeted properties: being able to suggest synthesis conditions (solvent, templates, temperature, etc.) for materials with specific pore sizes or catalytic activity. This remains today,

The first step in predicting zeolite structures and feasibility is the enumeration of a large number of four-connected net topologies, and their scoring - i.e., the assignment of rough “figures of merit” to each structure, associated to their relevance as zeolitic framework. Such figures of merit are typically based either on geometric criteria (bond angles, ring sizes, etc.) or relative energies (obtained using classical force fields). Using this approach, Deem et al. generated 2.6 million unique hypothetical zeolite frameworks, including ~500 000 with reasonably low energy. [13] This is still much larger than the total number of known zeolitic frameworks, calling for better feasibility criteria to discriminate between these hypothetical structures. As can be expected, the energetics of the zeolitic frameworks has been one of the key factors investigated, and in particular the link between framework topology, geometric properties (e.g. strained rings), chemical composition and relative stability. [14,15,16] Some studies have focused on the matching between the zeolite framework and templating agents. [17] Other feasibility criteria have also been proposed, such as the framework flexibility [18] or mechanical properties. [19] However, the question of feasibility of zeolitic frameworks remains, for the most part, an entirely open question to date. [20]

More than the unit cell...

Most of the discussion in this introduction to modeling of zeolites relies on the representation of the solid either as an infinite periodic crystal, for adsorption and diffusion studies, or as a cluster of atoms representative of the active site in a catalytic process. It should however be noted that the understanding the behavior of zeolites at interfaces, such as grain boundaries or external crystal surfaces, is still largely an unsolved challenge. It involves the determination of the nature of external surface structures, [21] as a function of the synthesis protocol and thermodynamic conditions. It also typically requires the modeling of several crystal facets, who can have markedly different structure and properties. Finally, the particularly reactive nature of the external surface sites makes it in most cases necessary for those to be treated at the quantum chemical level, making the modeling of zeolite surfaces a very computationally expensive issue.

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13. Nanoporous materials in adsorptive separation science & technology

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Introduction

The separation step in any process is vital as it helps to define product yield and purity. Separation process can account for up to 40% of capital expenditure (capex) and 60% of operational expenditure (opex). For gases and liquids, various separation technologies are used and these include processes using distillation, absorption and adsorption. For adsorption-based separation, nanoporous solids are used including active carbons, silica, alumina and zeolites. These approaches have potential benefits in terms of energy saving. [1]

As there is a need to reduce both the cost the environmental footprint of processes, there is still much room to optimize the separation step. Indeed, one example is that of CO₂ capture using amine solutions, which, whilst very selectively capturing this greenhouse gas, can suffer from problems including corrosion and toxicity. A further problem with this process is associated with the large cost of regeneration, which is carried out by heating the amine solution to above 100°C, with the inefficiencies of heating a significant amount of water which does not take part in the capture process. A second example is that of propylene or ethylene recovery from propane or ethane respectively. These are probably the most energy intensive commercial separation processes using distillation with up to 200 stages and often at sub-ambient temperatures. Separation processes using adsorption could provide elegant solutions to these and other problems.

Adsorption

We know the phenomenon of adsorption as the increase in concentration of a fluid close to surfaces. [2] As we increase the pressure (or partial pressure ...) of a gas we can encounter adsorption at active sites (cations, hydroxyls ...), monolayer and multilayer formation, filling of micropores, as well as capillary condensation. In the laboratory, an understanding of the adsorption phenomena is most often used for the characterization of powders and porous solids. Indeed, the adsorption of nitrogen or argon at cryogenic temperatures is used to gain information about the accessible surface area of the solid as well as information about any pore volume, size and in some cases, pore shape. [3]

Separation

In adsorption based separation processes, we may exploit the fact that some molecules may adsorb at a surface more strongly than others and we can estimate the extent of these interactions by measuring or calculating the enthalpies of adsorption. We can also exploit the possibility for steric hindrance and even size exclusion, and in these cases adsorption kinetics are of great interest to measure. Furthermore, in some cases, we can use the fact that molecules may have a 'good fit' inside the porosity leading to entropy effects.

Pressure Swing Adsorption (PSA)

Of the various separation processes, Pressure Swing Adsorption (PSA) has the advantage of ease of applicability under various conditions of temperature. One generally considers PSA of interest when the concentration of the fluid to be recovered is above a few percent. [4] In this process, the gas mixture is adsorbed in an adsorbent column at pressures above atmospheric. The adsorbent regeneration then occurs by rinsing at a lower working pressure, which can be as low as 1 bar. Several beds can be used with each working at different stages of the process (e.g. pressurization, adsorption, rinse, blowdown, purge ...) in order to allow for continuous gas production. The first, and most well known cycle, using several beds, was patented by Charles Skarstrom for oxygen enrichment. [5] A variation to PSA is Vacuum Swing Adsorption (VSA) where the lower working pressure is below atmospheric. Hybrid vacuum-pressure swing adsorption systems also exist.

Temperature Swing Adsorption (TSA)

Temperature Swing Adsorption (TSA), as its name implies, employs a variation in temperature where adsorption/separation occurs at the lower working temperature and adsorbent regeneration occurs at higher temperatures. This upper working temperature is often achieved using a hot purge gas or stream. TSA is a relatively slow process compared to PSA. Whilst adsorption steps of a few seconds can be achieved using PSA, several hours may be required for TSA. However, gas pressurization in PSA may be less cost effective than using intelligent heat management to obtain the hot purging gas in TSA. On the other hand, the short cycles that can be used in PSA processes mean that adsorbents do not necessarily need to have very high capacities. The long adsorption times used in TSA mean that this process is adapted to mixtures in which the component to recover is low in concentration.

Towards faster regeneration methods

One of the problems of temperature swing adsorption is that the regeneration step is relatively slow. This is leading to research into methods to increase the rate of regeneration. One method is known as Electric Swing Adsorption (ESA) [6] where the regeneration step is performed by increasing the temperature of the adsorbent using the Joule effect of passing electricity through a conductor. One can equally use microwave heating for the regeneration, which again is seen to increase the time needed for adsorbent regeneration. [7]

Materials

Adsorption based separation processes traditionally use active carbons, silica, alumina and zeolites. Whilst much research is being devoted to the use of functionalized mesoporous silica or metal-organic frameworks, to the best of the author's knowledge, only a few pilot scale schemes have been studied.

Zeolites in separation

The main zeolite structures used in separations are the same as those used in many catalytic processes. The LTA structure (NaA, CaA, KA) can be used in drying, CO₂ recovery from natural gas, O₂ recovery from air, as well as a linear /paraffin hydrocarbon separation. The FAU structure, especially BaX, is extensively used in xylene

separations. NaX can use for hydrogen purification and CaX is used for mercaptan removal from natural gas. Silicalite (MFI) is used for the removal of organics from water whereas ZSM-5 can again be found in xylene separations.

Shaping

In all adsorption-based process, shaping is critical. In PSA or TSA, materials can be found in the shape of spherical beads or cylindrical extrudates. The shaping allows the micron sized zeolite crystals to be agglomerated into millimeter-sized pellets, which are more practical for the separation process. For this agglomeration typically clays, alumina, silica or a mixture of these inorganic binders are used in the range of 10-20 weight %. Critical points are the mechanical strength of the pellet along with the possibility to gain optimal mass transfer properties. The binder should ideally not influence the adsorption properties of the adsorbent. This shaping process is an art in itself and it is not simple to gain insight into some of the 'secrets' involved.

Depending of the final application, the active materials can be immobilized on the surface of other types of support. These can include paper like filters, on metal heat exchangers or in honeycomb type monoliths. In these cases, the aggregation of the zeolite to the surface is critical.

Equally critical for shaping is the crystal size and shape with often the wish for small crystals. However, as the crystal size decreases, adsorption on the external surface can be of importance, especially when this external surface contains defect sites.

Zeolites in membranes

A further separation process in which zeolites can be used involves membranes in which the feed is flowed across one side, potentially under pressure and a sweep gas flows on the other side of the membrane. Zeolites are also used in pervaporation studies in which liquid mixtures can be separated. [8] This operation differs from PSA or TSA in that it is a continuous process and does not involve transient steps. Membrane operation is potentially cheaper and easier to operate than PSA or TSA as no moving parts are required. From a materials standpoint, the operational performance of a membrane is dependent on the selectivity and permeability. These factors can be compared with the factors such as capacity, selectivity and kinetics in PSA or TSA. Industrial scale gas separations using membranes are not common although interesting results have been obtained with small pore zeolites (SOD, CHA, DDR) and the zeolite SAPO-34 for CO₂ recovery from CH₄. [9] Large scale commercial pervaporation used for organic molecule dehydration is made with LTA. For this application, these zeolite membranes have higher selectivities and permeabilities than polymeric membranes.

In general, zeolite membranes are generally attractive in terms of separation performance and stability (chemical, thermal). However, this is offset by significant fabrication costs and in some cases, production reproducibility. In a recent review on the subject [10] the authors argue that advances in this area will be a hand in hand improvement in membrane support and active layer along with better adhesion between these elements. The tendency to decrease active layer thickness is clear with, in some cases, the use of further coating to aid the healing of defects.

Membranes can be supported on other porous materials such as macroporous alumina and again this porous support should not influence the membrane properties. Freestanding membranes also exist. Recent research is focusing on mixed matrix membranes in which the active materials (zeolite) is embedded in a resin or polymer. The advantage of the mixed matrix membrane idea lies in the combination of the ease of polymer film processing with the high selectivity and permeability of the zeolite.

Laboratory scale evaluation of nanoporous materials for separations

Turning back to laboratory scale evaluation of novel zeolites and other nanoporous materials for adsorptive separations there is a problem of scale. Whilst process engineers require often kilogram quantities of material, synthesis chemists are often preparing milligram quantities of new sample. It is impossible to relate measurements of pore volume or surface area, obtained during many synthesis studies, to process scale parameters. However, it is relatively simple to carry out single gas adsorption experiments at temperatures and in the pressure range used in processes using commercially available equipment. From these isotherms, it is possible to predict properties relevant to the separation process. Parameters such as working capacity and selectivity can be obtained from this data. Isotherms obtained at several temperatures can be used to estimate adsorption enthalpies or alternatively direct measurement of these quantities can be obtained by microcalorimetry. Adsorption/desorption kinetics are more difficult to accurately estimate. Quasi-elastic neutron scattering or Pulsed-Field Gradient NMR gain insight into diffusion with the pores, however for the process, diffusion between the in the bed and between pellets can equally be of importance. Thus for a laboratory scale comparison between materials, various comparisons have been suggested. These include simple ratios of Henry constants [11] or selectivities to the more elaborate PSA selection parameter, [12] Adsorbent Performance Indicator [13] or Adiabatic Separation Factor. For membranes, parameters such as selectivity and permeability/permeance can be obtained at the laboratory scale with a relatively small amount of material.

Concluding remarks

Understanding adsorption phenomena in zeolites and zeotypes can require a multi-disciplinary approach often coupling the adsorption with complementary approaches such as calorimetry to gain the adsorption heats, and diffraction to follow the structure of the solid and/or adsorbed phase. Spectroscopy can be used to gain information about local interactions and variable temperature IR can be equally used to gain information about the adsorption enthalpies. All of these experimental methods can be accompanied by theoretical approaches using computer modeling structures and molecular simulation of the adsorption and diffusion processes. These approaches can be a very good inputs to for the development of structure property relationships, which are starting to be developed for applications in gas storage.

In summary, there are still a large number of strategic areas where separations using adsorption with zeolites, zeotypes or other nanoporous materials could lead to significant progress or breakthroughs. However, the young synthesis chemist making novel materials, often on quite a small scale, needs to keep in the back of their mind that a number of significant hurdles lie ahead prior to testing by process engineers. However, initial laboratory scale evaluations and comparisons are possible and these can give very clear ideas concerning future directions for materials design.

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14. New zeolite-based catalytic processes

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Introduction

The already significant contributions of zeolites in many segments of the chemical industry are documented in numerous reviews and books. [1-3] Zeolites are used as heterogeneous catalysts and adsorbents, the latter often combined with catalytic processes. Their impact is felt by two types of innovations:

Breakthroughs: FCC (Fluid Catalytic Cracking) is the best example where a zeolite-based (Y type of the FAU family) catalyst swiftly displaced, around 1964, the previous generations (amorphous silica-alumina). The new catalysts yielding far more gasoline, the effect was spectacular as the US FCC capacity did not need to increase while serving a growing market. [1]

Incremental improvements: Again in FCC, many improvements of zeolite Y (crystal quality, efficiency of the synthesis, post-synthesis treatments...) led to today's catalysts, far superior to the original brought to market over 50 years ago.

The case of FCC is very illustrative since the combination of a breakthrough innovation followed by a sustained stream of incremental improvements met all the challenges of this difficult but key process. Over the years, FAU-based FCC catalysts proved always better than any other zeolite catalyst; and the story is not over yet...

This short introduction cannot be another review of zeolite-based processes since space is very limited, but also because identifying new zeolite-based processes is in fact very challenging. While new processes are advertised and some of their characteristics are openly available, the core of these processes, *i.e.* the zeolite used and its detailed properties are often well-kept secrets. Even a careful survey of the patent literature helps little in identifying the precise nature of the specific zeolite (framework type, chemical composition, particle size and shape...) in use. Moreover, improved catalysts are often loaded in existing units, as drop-in solutions, further increasing the difficulty of noticing that a new catalyst generation is commercialized.

Two types of complementary activities take place in the preparation of zeolitic materials:

Synthesis of new structures: this avenue has over the years been very successful; more than 230 framework types are so far recognized by the IZA' Structure Commission and more are in the pipeline as the potential is immense. [4]

Zeolite crystal engineering: many existing zeolites can be produced with very tight specifications on their properties such as particle size and shape, chemical composition (framework and extra-framework), additional mesoporosity, *in-situ* growth on a support....

About a dozen zeolite framework types (AEL, BEA, CHA, EUO, FAU, FER, LTA, LTL, MFI, MOR, MTT, MTW, MWW, TON...) out of 230 are thought to be in commercial use; it is only 5% of the currently available structures. It should not be wrongly concluded that the search for new structures is vain; some are inherently unstable and will find no use in industry, but emerging needs may require one of the currently "exotic" structures.

The creativity of some chemists to produce new structures (BEA, MFI...) combined with the ability of others to design catalysts with the right properties explains that a few structures can be tailored to meet the requirements of quite different processes (eg. FAU in FCC, Hydrocracking and separation processes...).

We will briefly review some recent/emerging applications of 3 framework types (CHA, MOR, MWW) and highlight the reasons for their successful commercial deployment.

Emerging applications of zeolites

CHA (SSZ-13 & SAPO-34)

The CHA structure is commercially used both as an aluminosilicate (SSZ-13) and a silicoaluminophosphate (SAPO-34) for different reasons.

Cu loaded SSZ-13 is currently the best ammonia selective catalytic reduction (NH₃-SCR) catalyst for NO_x. [5] Cu-SSZ-13 displays a very high NO_x conversion and N₂ selectivity together with exceptionally high hydrothermal stability at high temperatures. Moreover, it provides the best environment for the Cu active sites (location either in 6 or 8 member rings), Figure 1. Their exact nature and location under reaction conditions is still debated (complex interplay between redox and acidic sites) and the detailed mechanism is not yet fully understood.

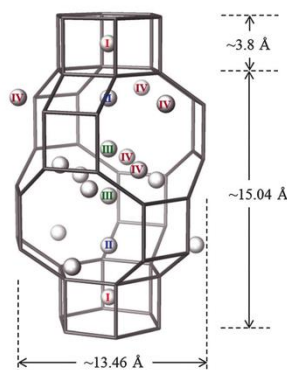


Figure 1. CHA cage with the various cation positions (Reproduced from ref. 5 with permission of the RSC).

Another success story of CHA is the use of SAPO-34 in the Methanol to Olefins reaction (MTO). MTO is currently deployed commercially in China on a grand scale since 2010. Two processes, one developed by the Dalian Institute of Chemical Physics (DICP) [6] and the other by UOP LLC [7] contribute to meet the need of light olefins in China. The CHA cage made of Si, Al and P tetrahedral framework cations is unique in building an inorganic-organic hybrid catalytic site during an induction period and releasing selectively lower olefins (ethylene and propylene mostly) in a steady-state from an “hydrocarbon-pool” before deactivation and rejuvenation in a fluid bed reactor, Figure 2. [8]

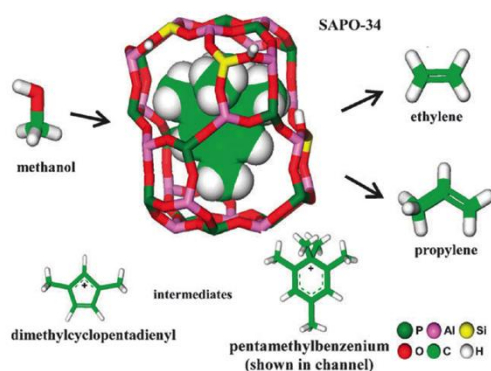


Figure 2. MTO reaction on SAPO-34 (Reproduced from ref. 8 with permission of the RSC)

Such a reaction is a stunning example of the building of an active site during the early stages of the reaction, often referred to as “catalysis by coke deposits” and already encountered with zeolitic [9] and non-zeolitic [10] catalysts.

MOR (H-Mordenite and UZM-14)

Some of the early applications of MOR were as bifunctional catalysts, Pt/H-MOR, for light naphtha (pentane and hexane) and C₈ aromatics (xylenes and ethylbenzene) hydroisomerization. In light naphtha hydroisomerization, MOR is dealuminated in such a way to promote enhanced acidity and add mesoporosity to lower diffusion limitations. [11] In xylene and ethylbenzene isomerization, the number and location of acid sites is adjusted by a selective neutralization of the side pocket acidity by Na⁺ exchange, leaving acid sites only in the main channels. Such a treatment blocks most bimolecular reactions and increases dramatically p-xylene yields. [12, 13]

More recently, refinements of the MOR properties allowed dramatic improvement in the: *i*) transalkylation of toluene with C₉₋₁₀ alkyl aromatics to produce xylenes (UOP’s Tatoray process), *ii*) carbonylation of methanol and dimethyl ether to produce acetic acid and methyl acetate. Using the so-called “Charge Density Mismatch” methodology, UOP produced high quality nanosized MOR crystals with increased accessibility along the pore openings and displaying superior performances (activity and stability) in the transalkylation of toluene with C₉₋₁₀ alkyl benzenes (lower value aromatics) to xylene (high value aromatics). [14] This is a typical example of an incremental improvement of a catalyst that can swiftly replace a less performing one, a so-called drop-in solution.

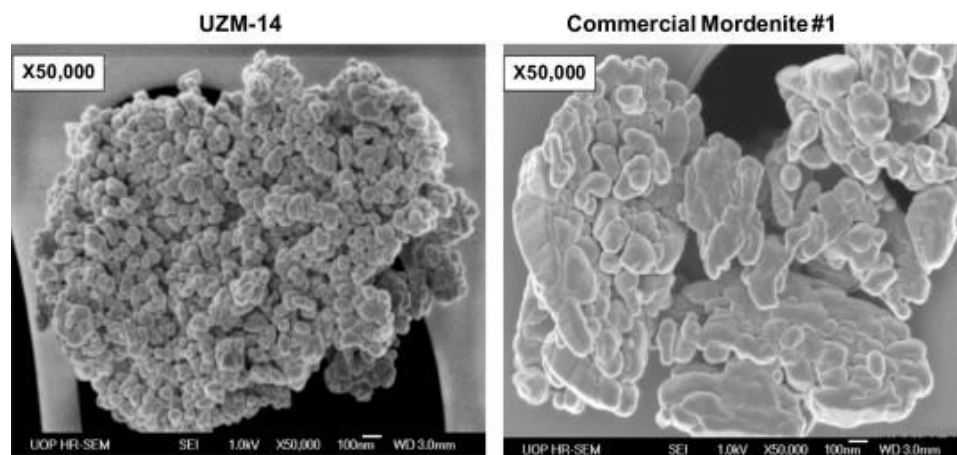


Figure 3. UZM-14 size and morphology compared to a commercially available Mordenite (Reproduced from ref. 14 with permission of Elsevier).

In the carbonylation of methanol and dimethyl ether, the replacement of corrosive homogeneous catalysts (Rh or Ir organometallic complexes combined with halide promoters) by a MOR-based catalyst greatly reduces the investment in the reactor (no need for exotic metals such as Zr) and downstream processing (distillation of non-corrosive mixtures). A process named SaaBre is currently developed by BP and a 1 million metric tons per year unit is considered for a petrochemical investment in Oman. [15] Here, elegant and fundamental studies (spectroscopy, kinetic studies and molecular modelling) indicate that the MOR catalytic sites are tailored at the nanometer level. The groups of Iglesia [16], and Corma [17], working with BP, unraveled the design rules of such a catalyst, namely that the active sites are located in the side-pockets (8 MR) of MOR and that secondary reactions leading to deactivation take place in the main channels (12 MR). So, a reverse strategy than in the design of C₈ aromatics isomerization, *vide supra*. The Brønsted sites in the side pockets are promptly methoxylated by methanol or dimethyl ether. The orientation of these methoxy groups (T3–O33 position), deep inside the side-pockets allows the perfect fitting of a linear transition state after their attack by a CO and further stabilized by framework oxygens. Bulkier nucleophiles are prevented from attacking any molecules inside the side pockets. On the contrary, at the rim of the side pockets/main channels (T4–O44 position), hydrocarbons can be produced due to lesser steric constraints and these lead to deactivation; here the hydrocarbon pool mechanism, so useful in MTO, leads to a fast deactivation by rapidly blocking the one-dimensional porosity of MOR main channels.

In order to avoid such excessive side reactions, a shortening of the diffusion pathlength for the product molecules could be beneficial; moving to nanosized MOR crystals indeed improves further the catalytic performances. [18]

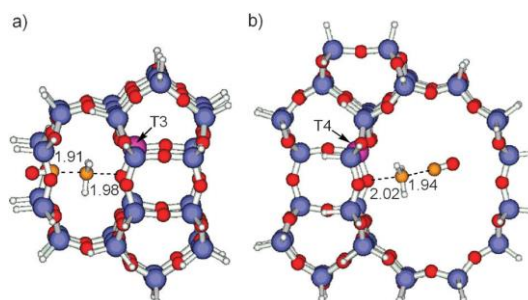


Figure 4. Methoxy groups a) inside the MOR side pockets, b) at the interface between main channels and side pockets (Reproduced from ref. 17 with permission of the RSC).

MWW (MCM-22)

Cumene is an important molecule in petrochemistry and was first produced by the alkylation of benzene with propylene on very corrosive AlCl_3 or H_3PO_4 supported on SiO_2 . High silica zeolites displaced these catalysts due to their superior yields, better selectivities and longer cycle times. [1,19,20] Although many zeolite structures (BEA, MOR, MWW, USY...) are used as catalysts in this reaction, one deserves a particular attention, MWW. This zeolite displays the usual microporosity found in many zeolites but its external surface is dotted with pockets (diameter: 0.71 nm) promoting benzene alkylation with propylene in an open catalytic nest providing an easy escape route for the product, cumene, therefore avoiding undesired multiple alkylations and other side reactions.

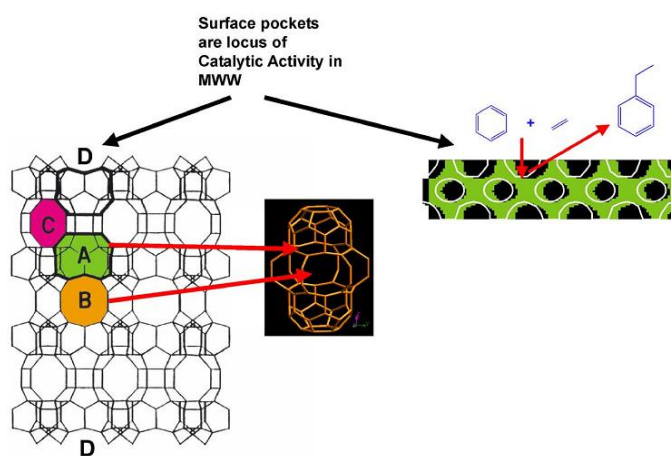


Figure 5. Structural features of MWW: i) 12-ring cavity (A) accessible through a 10-ring aperture (B), ii) 10-ring channel system (C), iii) 12-ring surface pockets (D) (Reproduced from ref. 20 with permission of Elsevier).

The reaction also takes place in the liquid phase easing the cleaning of the surface resulting in an extended stability of the catalysts. In fact, all the desirable reactions take place on the outer surface of the MWW crystals and the microporosity is not participating in the desired reaction. Corma *et al.* showed that delaminating such a zeolite, leads to ITQ-2, a material with an even higher external surface and a superior catalyst in the dealkylation of 1,3,5-triisopropylbenzene. [21]

Conclusions and perspectives

This short overview points to an ever greater need to master the properties of zeolites at ever finer levels: particle size, shape, chemical composition, hierarchization (during

synthesis and postsynthesis treatments) up to the precise location of framework Al, *i.e.* active sites. The amazing flexibility of zeolite chemistry and the remarkable creativity of researchers led to multiple uses of a small fraction of the structures available. Again, it does not imply that searching for new structures is useless; on the contrary, the discovery of many new synthetic structures over the years (MFI, BEA, TON, MTT, MWW...) also met industrial needs for cleaner processes. These two approaches are not mutually exclusive but very complementary.

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VI. Synthesis recipes

ABW

Li-A (BW)

Si(50), Al(50)

Contributed by Poul Norby

Verified by J. MacDougall and D. Vaughan

Type Material $\text{Li}_4[\text{Al}_4\text{Si}_4\text{O}_{16}] : 4 \text{H}_2\text{O}^{\text{a}}$

Method P. Norby, A. Norlund Christensen, I. G. Krogh Andersen [1]

Batch Composition $\text{NaAlSiO}_4 : 4.3 \text{LiCl} : 154 \text{H}_2\text{O}^{\text{b}}$

Source Materials

distilled water

lithium chloride (LiCl) (Merck, analytical grade)

sodium Zeolite A (Na-LTA) (Union Carbide, $\text{NaAlSiO}_4 \cdot 2.5\text{H}_2\text{O}$)

Batch Preparation (for 6.9 g product)

- (1) [150 mL water + 10g LiCl], stir until dissolved
- (2) [(1) + 10 g Na-LTA], mix until uniform slurry

Crystallization

Vessel: Teflon-lined autoclave^c

Time: 72 hours

Temperature: 250 °C^d

Agitation: none

Product Recovery

- (1) Cool to ambient temperature
- (2) Filter
- (3) Wash until chloride-free
- (4) Dry at 110 °C
- (5) Yield: close to 100%

Product Characterization

XRD: ABW, no other crystalline phases or amorphous material detected ^{e,f}

Elemental Analysis: $\text{Li}_{1.02}\text{Na}_{0.004}\text{AlSiO}_4 \cdot 1.1 \text{H}_2\text{O}$ ^{g,h}

Crystal Size and Habit: small elongated flat needles

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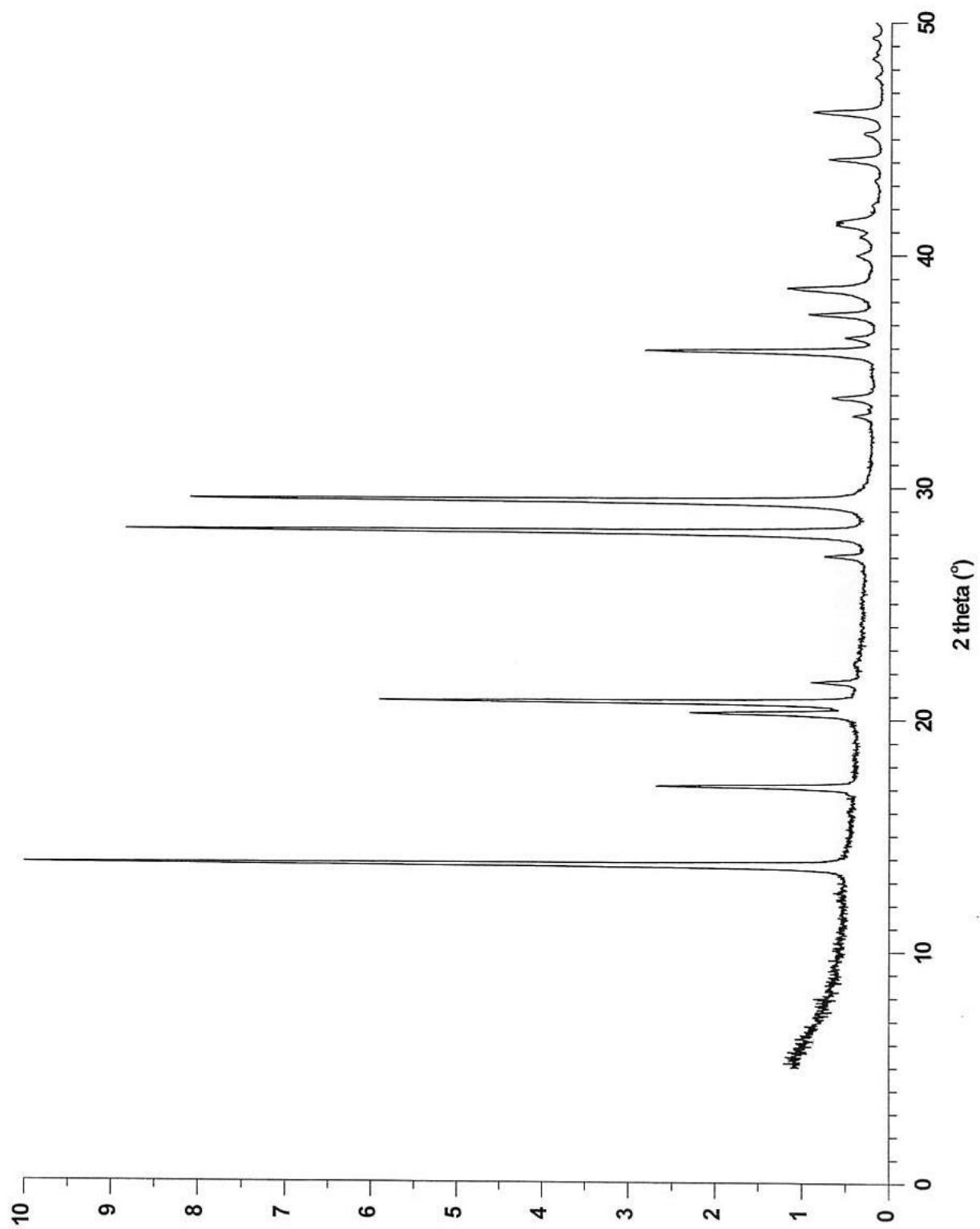
Notes

- a. Of the aluminosilicate ABW type analogues, only the hydrated Li-form and the anhydrous Rb-, Cs-, and Tl-forms may be directly synthesized. [2]
- b. Addition of small amounts of potassium fluoride are reported to have a marked mineralizing effect. [3]
- c. In a gold-lined steel autoclave, the reaction was performed at 285°C in 72 hours.
- d. Good results have been obtained by crystallization at 200°C for 93 hours.
- e. At temperatures above 350°C a -eucryptite is formed. Li_2SiO_3 may occur. [1]
- f. Upon dehydration of zeolite Li-A(BW) the framework topology is retained, but the 8-ring channel is considerably narrowed. The lithium cation coordinates across the channel, preventing rehydration of the material even when submerged in water. However, by hydrothermal treatment at temperatures above 110°C, rehydration to the original zeolite is possible.
- g. The Si/Al ratios of ABW type are close to 1. Though Li-A(BW) may be synthesized from oxide compositions with Si/Al ratios from 0.5 to 7, there is no evidence of variation in the Si/Al ratio of the product. [3]
- h. Reversible dehydration of Li-A(BW) is possible to a limited extent. [4] The anhydrous ABW-types do not show any sorption of water at ambient conditions.
- i. In one experiment (sodium bromosodalite and LiBr, hydrothermal 260°C, 72 h), single crystals large enough for single crystal diffraction were obtained (0.1 x 0.05 x 0.01 mm) [1,5]

ABW

Li-A (BW)

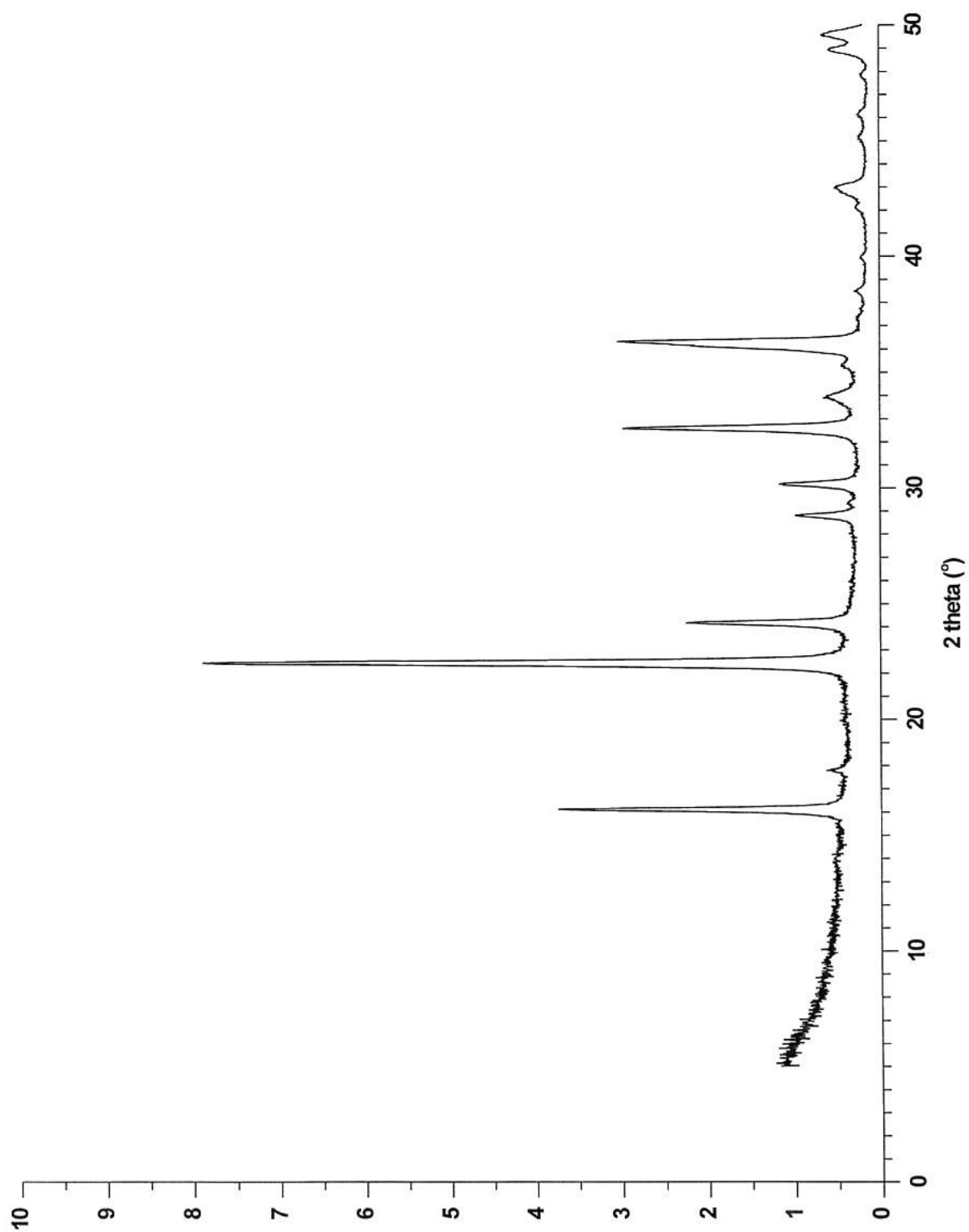
Si(50), Al(50)



ABW

Li-A (BW) (calcined)

Si(50), Al(50)



AEI

AlPO₄-18

Al(50), P(50)

Contributed by Rune Wendelbo

Verified by S. Kaliaguine, E. Dumitnu and C. Round

Type Material [Al₂₄P₂₄O₉₆]

Method S. T. Wilson, E. M. Flanigen [1, 2]

Batch Composition Al₂O₃ : P₂O₅ : (TEA)₂O : 60 H₂O : 6 i-C₃H₇OH
(TEA tetraethylammonium)

Source Materials distilled

water phosphoric acid

(85%)

aluminum isopropoxide (Jansen, 98+ %)

tetraethylammonium hydroxide (Aldrich, 40% (TEAOH)^a)

Batch Preparation (for 15.8 g dry product)

- (1) [36.3 g water + 15.0 g phosphoric acid + 27.2 g aluminum isopropoxide], add diluted phosphoric acid to the aluminum isopropoxide in a 250 mL polypropylene bottle and shake vigorously for one minute
- (2) [(1) + 49 g (TEAOH solution)], shake to produce a uniform gel. Transfer to the autoclave

Crystallization

Vessel: 200 mL Teflon-lined stainless steel autoclave (Berghof)

Incubation: 6 hours at room temperature

Time: 69 hours ^b

Temperature: 215°C ^b

Agitation: gentle ^c

Product Recovery

- (1) Recover solid product by centrifugation ^d
- (2) Wash once with distilled water; recover product by centrifugation ^d
- (3) Dry overnight at 100°C
- (4) Calcine for 4 h at 550°C in flowing dry air
- (5) Store under nitrogen. Yield near 100%

Product Characterization

XRD: fully crystalline AEI; competing phase: AFI ^e

Elemental Analysis: 24.26% Al, 20.59% P, 0.20% Si ^f

Crystal size and habit: square platelets 0.2-8 μm x 0.1 μm thick ^g

References

- [1] S. T. Wilson, E. M. Flanigen, US Patent 4310440 (1982)
- [2] R Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad, Appl. Catal. A General 142 (1996) L197

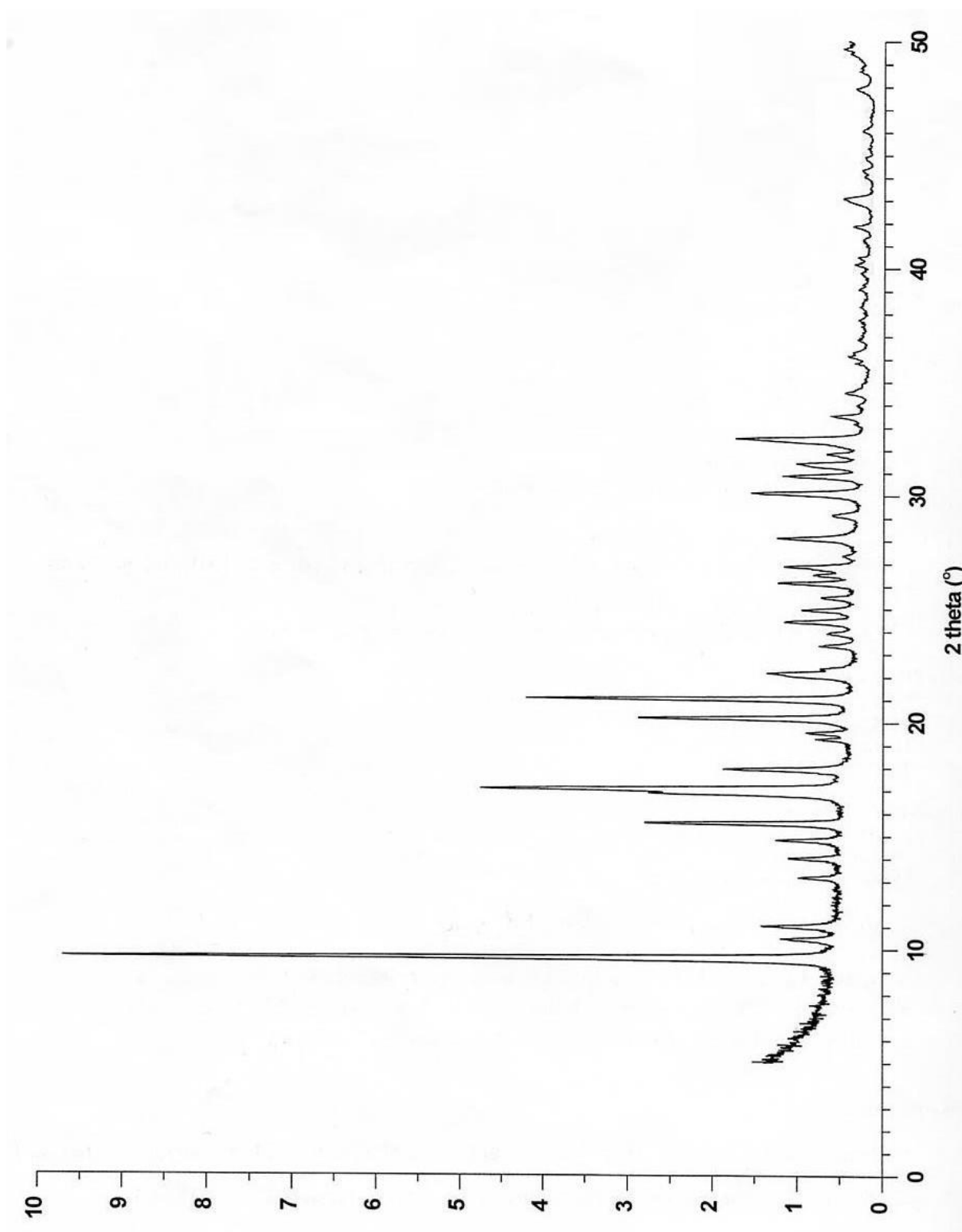
Notes

- a. This product is now traded as 35% TEAOH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum K^+ and Na^+ concentrations.
- b. The synthesis temperature can probably be reduced to $200^{\circ}C$ and the time reduced substantially, but this has not been tested.
- c. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
- d. Filtration leads to loss of fine material or goes very slowly depending on the filter.
- e. AFI appears as a contaminant.
- f. A Cameca microprobe was used averaging 5 points each $50 \times 50 \mu m$. The analysis was done on "as synthesized material".
- g. Micropore volume 0.28 mL/g (by N_2 adsorption).

AEI

AlPO₄-18

Al(50), P(50)



Contributed by Moussa Zaarour and Svetlana Mintova

Verified by E.-P. Poh, H. Awala, L. Tosheva

Type Material: [Al₂₄P₂₄O₉₆]

Method: M. Vilaseca, S. Mintova, V. Valtchev, T. H. Metzger, T. Bein [1]
H. van Heyden, S. Mintova, T. Bein [2]

Batch Composition: 1 Al₂O₃ : 3.16 P₂O₅ : 3.16 (TEA)₂O : 186 H₂O.

Source Materials

Aluminum isopropoxide (98 wt.%, Aldrich)
Tetraethylammoniumhydroxide (35 wt.%, Aldrich)
Phosphoric acid (85 wt.%, Aldrich)
Distilled water

Batch Preparation

- (1) 7.76 g Aluminium isopropoxide + 50.52 g tetraethylammoniumhydroxide + 28.69 g H₂O], stir vigorously for 1 h
- (2) Add 13.84 g phosphoric acid very slowly in dropwise to (1), stir 2h^a
- (3) Age for 24 h at room temperature

Crystallization

Vessel: polypropylene (PP) bottles
Temperature: 100°C
Time: 48 h

Product Recovery

- (1) Centrifugation (20 000 rpm, 1h)^b
- (2) Filter and redisperse in water using ultrasonication
- (3) Stable colloidal suspension

Product Characterization

DLS: monodomial particle size distribution, radius~ 90 nm
XRD: AEI-type
SEM: elongated crystals with length/width aspect ratio of 2
N₂ adsorption: BET = 600 m²*g⁻¹, Pore volume = 0.38 mL.g⁻¹

Reference

- [1] M. Vilaseca, S. Mintova, V. Valtchev, T. H. Metzger, T. Bein, J. Mater. Chem.13 (2003) 1526
- [2] H. van Heyden, S. Mintova, T. Bein, J. Mater. Chem. 16 (2006) 514

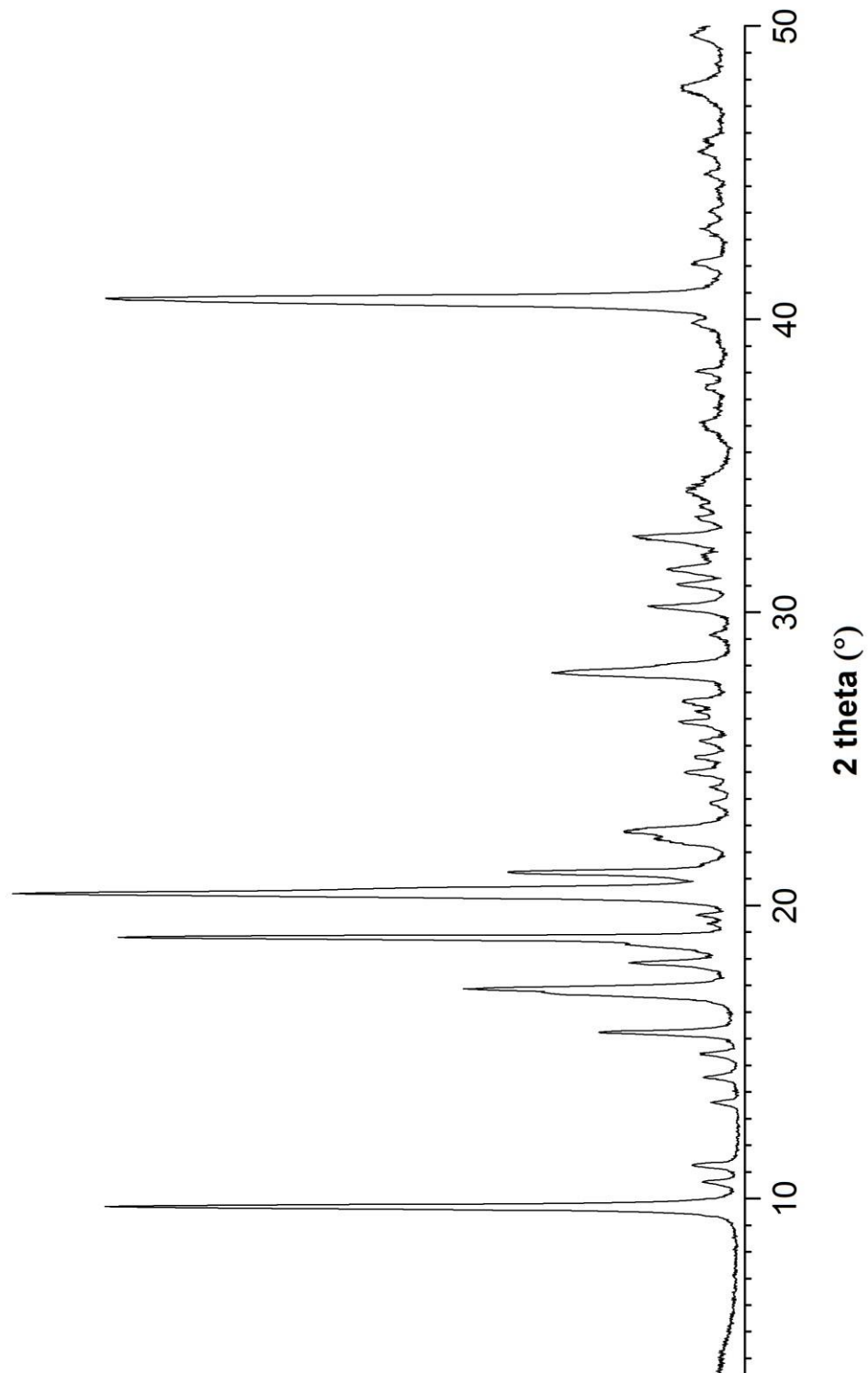
Notes

- a. Clear suspension is obtained
- b. Processes (1) then (2) were repeated three times

AEI

Nanosized AlPO_4 -18

Al(50), P(50)



AEI

SAPO-18 (DPEA method)

Al(49), P(42), Si(9)

Contributed by Jiesheng Chen and John M. Thomas

Verified by S. Schunk, J. López Nieto and D. Akolekar

Type Material [Al₂₄P₂₀Si₄O₉₆] : mR: nH₂O (R = N,N-diisopropylethylamine)^b

Method J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow [1]

Batch Composition 0.40 SiO₂ : Al₂O₃ : 0.90 P₂O₅ : 50 H₂O : 1.60 R

Source Materials

distilled water

phosphoric acid (Aldrich, 85% H₃PO₄)

aluminum hydroxide hydrate (Aldrich, Ca. 55% Al₂O₃)

Aerosil (Degussa, 99% SiO₂)

N,N-diisopropylethylamine (Aldrich, 99% C₈H₁₉N)

Batch Preparation (for 2 g product)

- [1] [19.4 g water + 3.48 g phosphoric acid + 4.64 g aluminum hydroxide hydrate], stir until homogeneous
- [2] [(1) + 0.60 g Aerosil], stir until homogeneous
- [3] [(2) + 5.10 g N,N-diisopropylethylamine], stir until homogeneous

Crystallization

Vessel: PTFE-lined stainless steel autoclave

Temperature: 160 °C

Time: 8 days

Agitation: none

Product Recovery

- (1) Filter; wash with distilled water
- (2) Dry at 50 °C in air
- (3) Yield: 60% based on Al₂O₃

Product Characterization

XRD: ° Characteristic strong reflections at d = 9.1 and 5.1 Å for as-synthesized materials;

competing phase is AFI when P₂O₅/Al₂O₃ > 1.2 or R/P₂O₅ < 1.2

Elemental Analysis (exclusive of R and H₂): 0.35 SiO₂ : Al₂O₃ : 0.87 P₂O₅

Crystal Size and Habit: small cubes less than 2 μm in diameter

References

- [1] J. Chen, P. A. Wright, J. M. Thomas, S. Natarajan, L. Marchese, S. M. Bradley, G. Sankar, C. R. A. Catlow, J. Phys. Chem. 98 (1994) 10216
- [2] A. Simmen, L. B. McCusker, Ch. Baerlocher, W. M. Meier, Zeolites 11(1991) 654

- [3] S. T. Wilson, B. M. Lok, C. A. Messina, T. R Cannan, E. M. Hanigen, J. Am. Chem. Soc. 104 (1982) 1146
- [4] H. He, J. Klinowski, J. Phys. Chem. 97 (1993) 10385

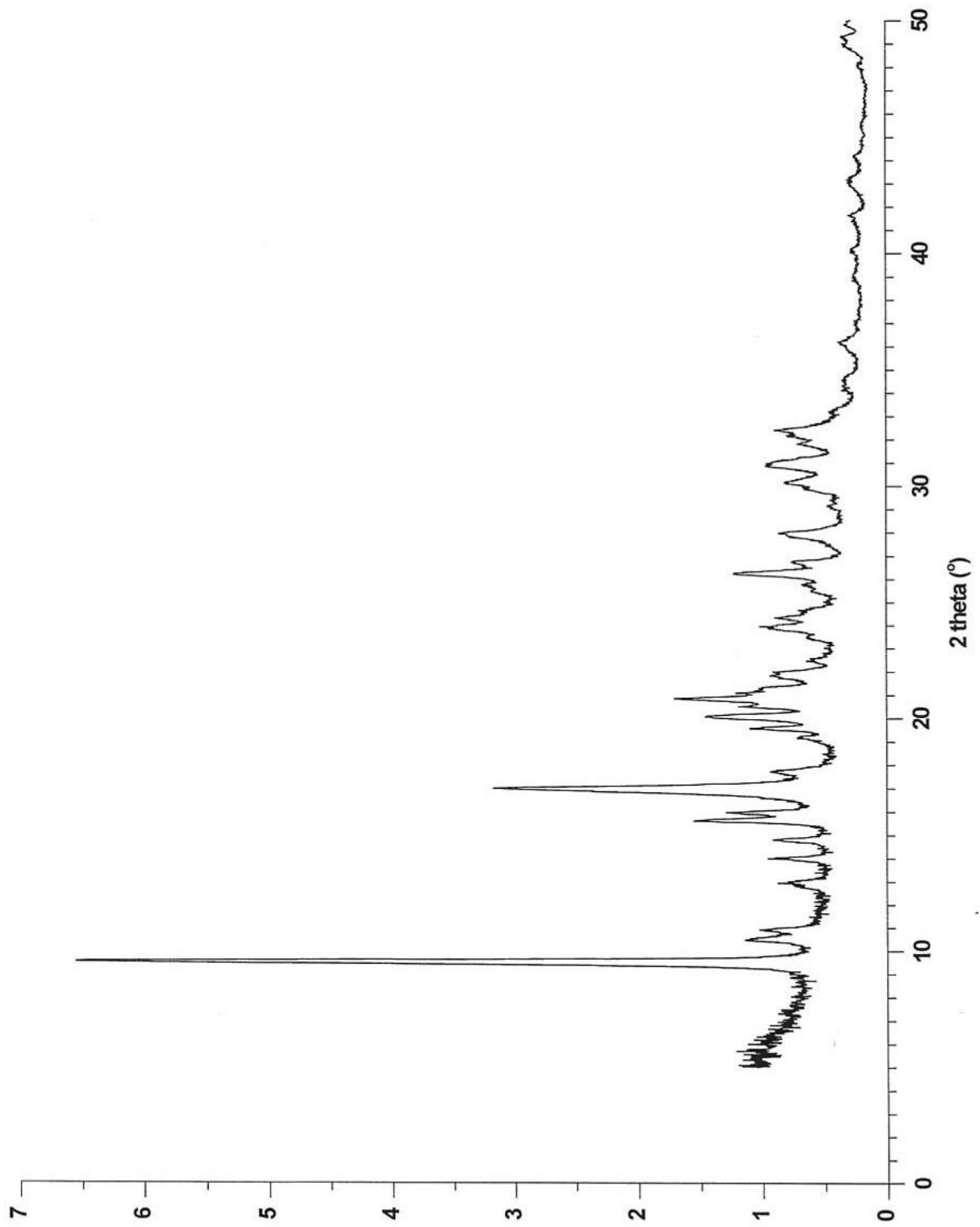
Notes

- a. Preparation for SAPO-18 only is given. For AIPO₄-18 [2], no Aerosil is added, and the amounts of reactants should be changed to give gel composition Al₂O₃ : P₂O₅ : 50 H₂O : 1.80 R
- b. AIPO₄-18 was originally prepared by using tetraethylammonium hydroxide (TEA-OH) as the template in the presence of HCl. It is not possible to prepare SAPO-18 using (TEA)-OH. [3, 4]
- c. The XRD patterns of the AEI materials are very sensitive to water molecules present in the channels of the structure.
- d. Crystals are typically cubic; crystal size increases to a certain degree as the amount of silica in the reaction mixture increases.

AEI

SAPO-18 (DPEA method)

Al(49), P(42), Si(9)



AEI

SAPO-18 (TEA method)

P(50), Al(48), Si(02)

Contributed by Rune Wendelbo

Verified by E Dumitriu and C. Round

Type Material [Al_{23.2}SiO_{0.8}P₂₄O₉₆]^b

Method: R Wendelbo, D. Akporiaye, A. Andersen, I. M. Dahl, H. B. Mostad [1]

Batch Composition Al₂O₃ : 0.98 P₂O₅ : 0.015 HCl : 0.075 SiO₂ : (TEA)₂O : 70 H₂O : 2.8 i-C₃H₇OH^c (TEA = tetraethylammonium)

Source Materials

distilled water

aluminum isopropoxide (Jansen, 98+%)

phosphoric acid (85%)

hydrochloric acid (37%)

silica sol (DuPont Ludox LS-30, 30% SiO₂)

tetraethylammonium hydroxide (Aldrich, 40 % (TEA)OH)^d

Batch Preparation: (for 13.8 g dry product)

- (1) [108 g water + 81.6 g aluminum isopropoxide], mix in a one-liter poly-propylene bottle and shake for 1 minute
- (2) [(1) + 45 g phosphoric acid], shake for 1 minute then cool under running tap water
- (3) [(2) + 0.6 g hydrochloric acid], shake bottle^e
- (4) [(3) + 3.0 g silica sol], shake bottle. filter gel for 10 minutes (water suction). About 100 g filtrate is removed and discarded. Transfer one-third of filter cake gel to a 250 mL plastic bottle
- (5) [One-third (4) + 49 g tetraethylammonium hydroxide solution], shake

Crystallization

Vessel: 200 mL stainless steel, Teflon-lined autoclave (Berghof)

Incubation: 12 hours at room temperature

Time: 120 hours

Temp: 215°C

Agitation: gentle^f

Product Recovery

- (1) Recover solid product by centrifugation.^g
- (2) Wash once with distilled water; recover product by centrifugation^g
- (3) Dry overnight at 100°C
- (4) Calcine for 4 hours at 550°C in flowing, dry air
- (5) Store under nitrogen. Yield near 100%

Product Characterization

XRD: fully crystalline AEI; competing phase AFI and CHA^h

Elemental Analyses: 0.84% Si, 19.9% Al, 26.6% Pⁱ

Crystal size and habit: square platelets, 0.1-2.0 μm x 0.1 μm thick^j

Reference

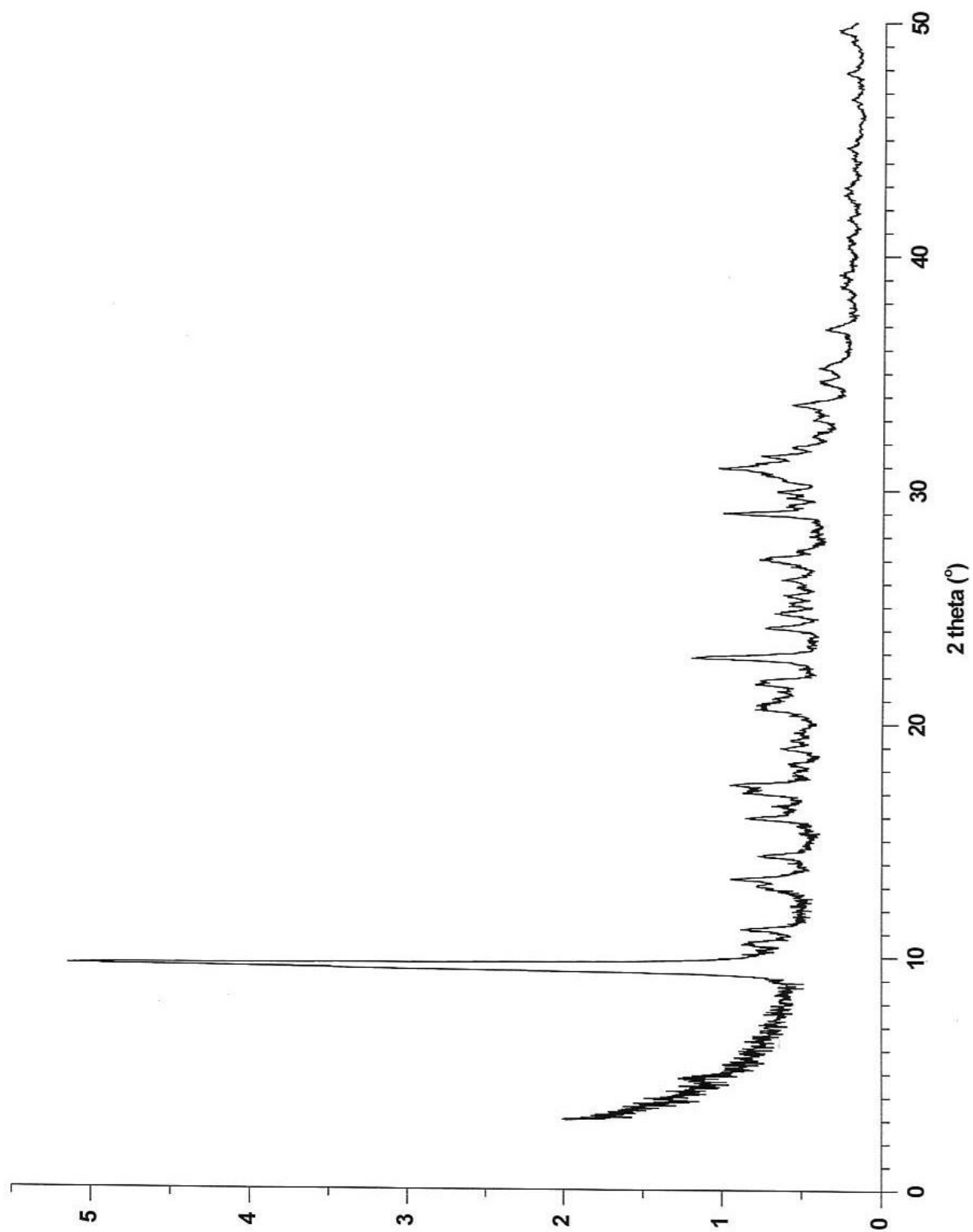
- [1] R Wendelbo, D. Akporiaye, A. Andersen, I. M Dahl, H. B. Mostad, *Appi. Catal. A: General* 142 (1996) L197

Notes

- a. Mg AIPO-18 and Zn APO-18 were synthesized like SAPO-18 by using Mg and Zn nitrates in place of colloidal silica in equivalent amounts on a molar basis. The Mg and Zn nitrates were dissolved in the phosphoric acid 20 m prior to mixing with the other reagents. Products showed 0.14 Mg and 0.10 Zn (nmol/g).
- b. Based on Si content; excess P is unexplained.
- c. It is assumed that water, HCl and isopropanol are lost in equal proportions and no other components are lost in gel filtration.
- d. This product is now traded as 35% (TEA)OH solution. I would use the same volume of the 35% solution, since the synthesis is not sensitive to a variation of the template concentration of this order. It is important that the (TEA)OH source have minimum K⁺ and Na⁺ concentrations.
- e. Addition of HCl has previously been found to allow better control of Si substitution in SAPO-34 and has been used in this case for the same purpose.
- f. Standing autoclaves in a heated block on a "shaking table" rotated at about 60 rpm.
- g. Filtration leads to loss of fine material or goes very slowly depending on the filter.
- h. At lower water content, AFI appears as a contaminant; at higher water content, CHA appears.
- i. Analysis by XRF.
- j. Micropore volume 0.25 mL/g (by N₂ sorption)

AEI

SAPO-18 (TEA method) P(50), Al(48), Si(02)



AEL

AlPO₄-11

Al(50), P(50)

Contributed by Kristin Vinje

Verified by J. Campelo and J. Kornatowski

Type Material [Al₂₀P₂₀O₂₀] : wH₂O

Method R Szostak, B. Duncan, R. Aiello, A. Nastro, K. Vinje, K. P. Lillerud [1]

Batch Composition 1.0 Al₂O₃ : 1.25 P₂O₅ : 2.37 DPA : 1.80 HF : 156 H₂O (DPA = di-n-propylamine)

Source Materials

deionized water

aluminum hydroxide (Aldrich 23918-6, 50-57.5% Al₂O₃)^a

phosphoric acid (Fisher, 85% H₃PO₄)

di-n-propylamine (DPA)(Kodak, 100%)

hydrofluoric acid (Fisher, 48% HF)

Batch Preparation (for 4 g dry product)

- (1) [20.0 g water + 7.8 g aluminum hydroxide] stir well
- (2) [(1) + 14.4 g phosphoric acid]; add acid dropwise and stir until effervescence is completed
- (3) [(2) + 100 g water]; dilute and stir
- (4) [(3) + 12.0 g DPA]; add amine dropwise and stir
- (5) [(4) + 10.0 g water 3.75 g hydrofluoric acid]: stir for two hours^b

Crystallization

Vessel: Teflon-lined steel autoclave

Temperature: 145°C

Time: 18 hours

Agitation: none

Product Recovery

- (1) Cool autoclave rapidly.
- (2) Filter immediately to recover solids and wash.
- (3) Dry overnight at room temperature.
- (4) Yield: ~70%^c

Product Characterization

XRD: AEL only crystalline phase: no other crystalline phases or amorphous material detected

Elemental Analysis: (atomic %): 15.5 Al, 13.9 P, Al/P = 1.1^d

Crystal Habit: Bow-tie crystals constructed of long needles (or needles ~ 1 mm long)^c

Reference

- [1] R. Szostak, B. Duncan, R Aiello, A. Nastro, K. Vinje, K. P. Lillerud, in *Synthesis of Microporous Materials*, M. Occelli, H. Robson, (eds.), Van Nostrand Reinhold, New York (1992), pp 240-7

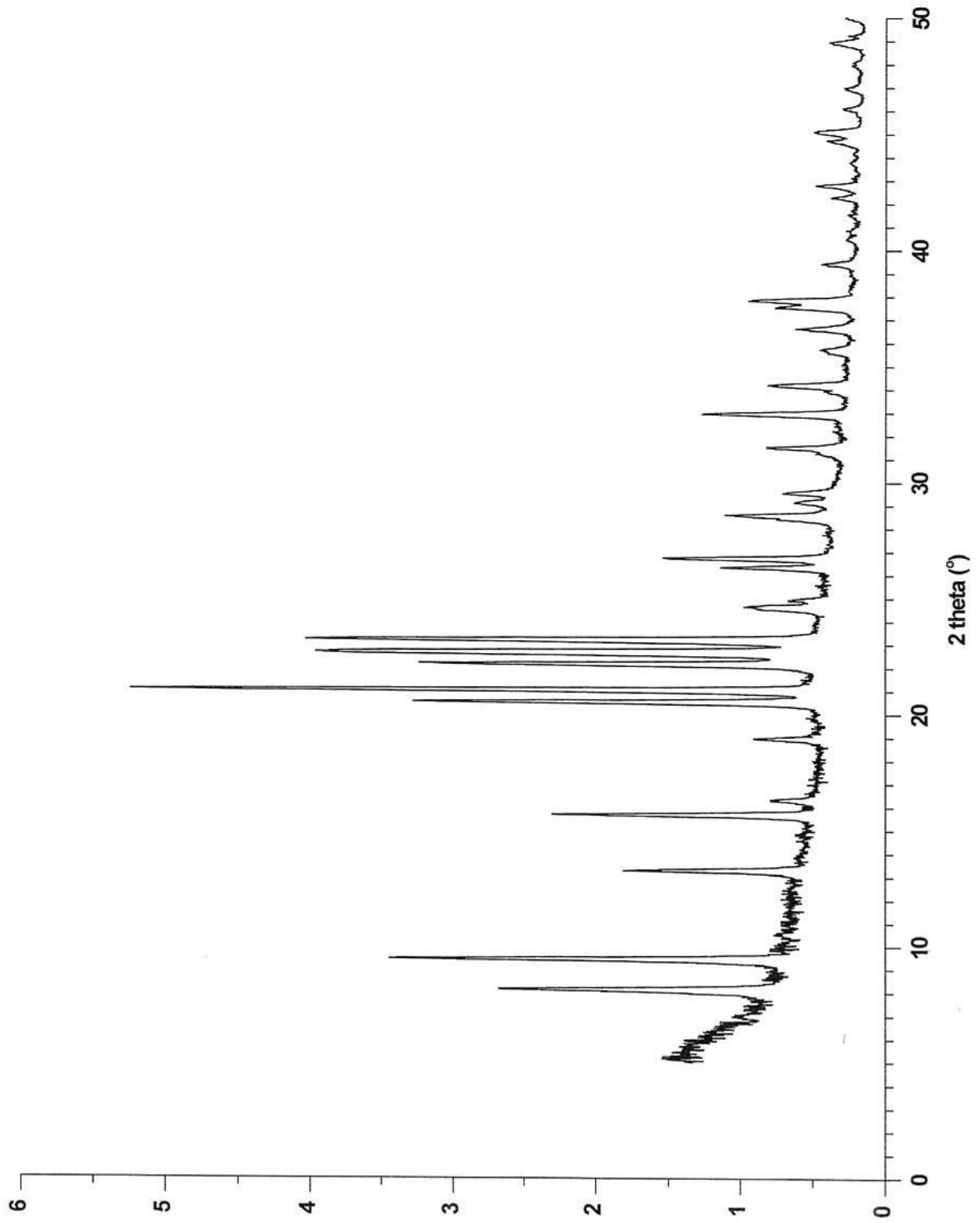
Notes

- a. Consistently good results have been obtained using the Aldrich Al-source, but difficulties were encountered using other aluminum sources.
- b. Should produce a clear solution; initial pH = 5.5, final pH = 6.0
- c. After 18 hours the yield increases to 50-75% at the expense of the crystal size with smaller 5 to 10 μm crystals resulting.
- d. Determined on a CAMECA SX 100 Microbeam.

AEL

AlPO₄-11

Al(50), P(50)



AET

AlPO₄-8

Al(50), P(50)

Contributed by Louwanda Lakiss

Verified by E.-P. Ng, J. Yu, M. Rangus, D. Fan

Type Material: [Al₃₆P₃₆O₁₄₄]

Method: J. O. Perez, N.K. Mcguire, A. Clearfield [1]

Batch Composition: 1 Al₂O₃ : 1 P₂O₅ : 1 DPA : 45 H₂O (DPA = di-*n*-propylamine)

Source Materials

hydrated pseudoboehmite alumina (Catapal B-alumina, Vista Chem. Co.; 74% Al₂O₃, 26% H₂O)
phosphoric acid (Fisher Reagent grade, 85%)
di-*n*-propylamine, *n*-Pr₂NH
distilled water

Batch Preparation

- (1) [13.8 g pseudoboehmite + 41.1 g water] stir the slurry for 10-15 min
- (2) [23.1 g 85% H₃PO₄ + 27.4 g water + (1)] under continuous stirring^a
- (3) gel is obtained and aged for 10 h at room temperature
- (4) [(3) + 10.1 g of DPA] stir and add DPA dropwise; continue stirring for 20-30 min

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 125° C
Time: 20-25 hours
Agitation: No

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at 50 °C

Product Characterization

XRD: AET; competing phases: no

References

- [1] J. O. Perez, N K. Mcguire, A. Clearfield, Catal. Lett. 8 (1991) 145

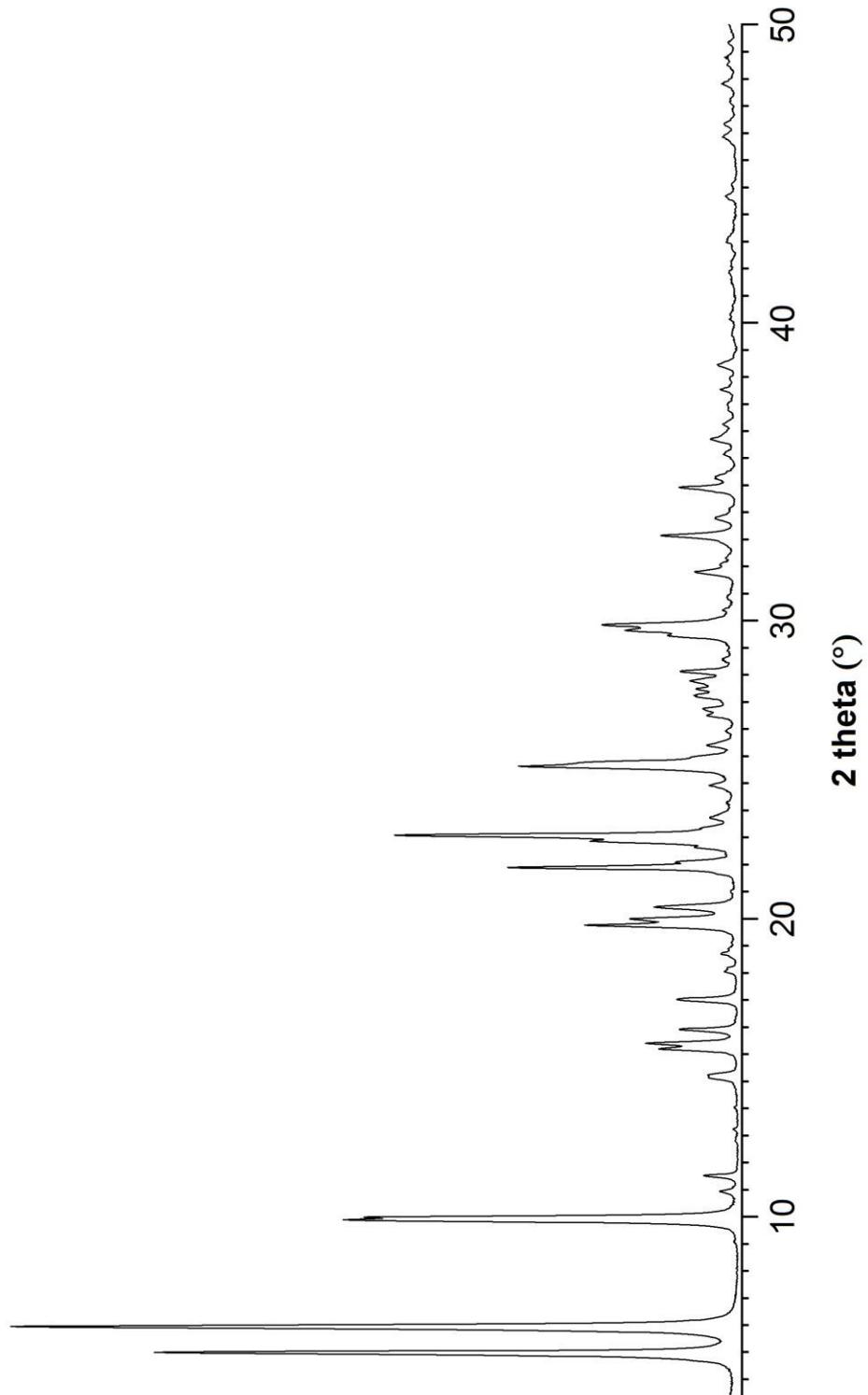
Notes

- a. phosphoric acid solution should be added in the pseudoboehmite slurry in increments of 7 mL with a 2 min interval between additions

AET

AlPO₄-8

Al(50), P(50)



AFI

AIPO₄-5

Al(50), P(50)

Contributed by Juergen Caro and Irma Girnus

Verified by S. Cresswell, B. Weckhuysen and G. Schulz-Ekloff

Type Material Al₁₂P₁₂O₄₈

Method I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro [1] ^a

Batch Composition Al₂O₃ : 1.3 P₂O₅ : 1.6 TEA : 1.3 HF : 425 H₂O : 6 C₃H₇OH ^b

Source Materials

deionized water

orthophosphoric acid (Merck, 85 wt% H₃PO₄)

triethylamine (TriEA), (Riedel de Haen, (C₂H₅)₃N) ^c

aluminum triisopropylate (Merck, Al(C₃H₇O)₃) ^d

hydrofluoric acid (Merck, 40 wt% HF in water)

Batch Preparation (for 3 g product)

- (1) [7 g water + 3.84 g of phosphoric acid], mix
- (2) [(1) + 2.07 g TriEA], add TriEA dropwise and mix
- (3) [(2) + 5.23 g aluminum isopropylate], add in small amounts at 0°C with intense stirring then stir the mixture at room temperature for 2 hours
- (4) [(0.83 g hydrofluoric acid + 89.2 g water], mix
- (5) [(3) + (4)], stir for 2 hours

Crystallization

Vessel: 150 mL Teflon-lined steel autoclave

Temperature: 180°C (preheated oven)

Time: 6 hours ^f

Agitation: none

Product Recovery

- (1) Decant the supernatant liquid and discard
- (2) Wash the precipitate four times with 100 mL deionized water
- (3) Calcine in air at 600°C until product is colorless (white) ^g
- (4) Yield: near 100% on Al₂O₃

Product Characterization

XRD: Characteristic strong reflections at d = 11.90, 5.93, 4.48, 4.24, 3.96, and 3.42 Å; competing phases (if present): tridymite

Elemental Analysis: 42.9 wt% P₂O₅, 30.5 wt% Al₂O₃ (P/Al = 1.00)

Crystal size and Habit: Hexagonal columns up to 50 μm ^h

References

- [1] I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro, Zeolites 15 (1995) 33

- [2] S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, E. M. Flanigen, *J. Am. Chem. Soc.* 104 (1982) 1146
- [3] J. M. Bennett, J. P. Cohen, E. M. Flanigen, J. J. Pluth, J. V. Smith, *ACS Symp. Series 218*, Am. Chem. Soc., Washington, D. C., 1983, p. 109
- [4] S. Oju, W. Pang, H. Kessler, J.-L. Guth, *Zeolites* 9 (1989) 440
- [5] A. S. T. Chiang, C.-K. Lee, Z. H. Chang, *Zeolites* 11 (1991) 380
- [6] G. Finger, J. Richter-Mendau, M. Bulow, J. Kornatowski, *Zeolites* 11(1991) 443
- [7] D. Demuth, G. D. Stucky, K. K. Unger, F. Schüth, *Micropor. Mater.* 3 (1994) 473
- [8] I. Girnus, K. Hoffmann, F. Marlow, G. Döring, J. Caro, *Micropor. Mater.* 2 (1994) 537

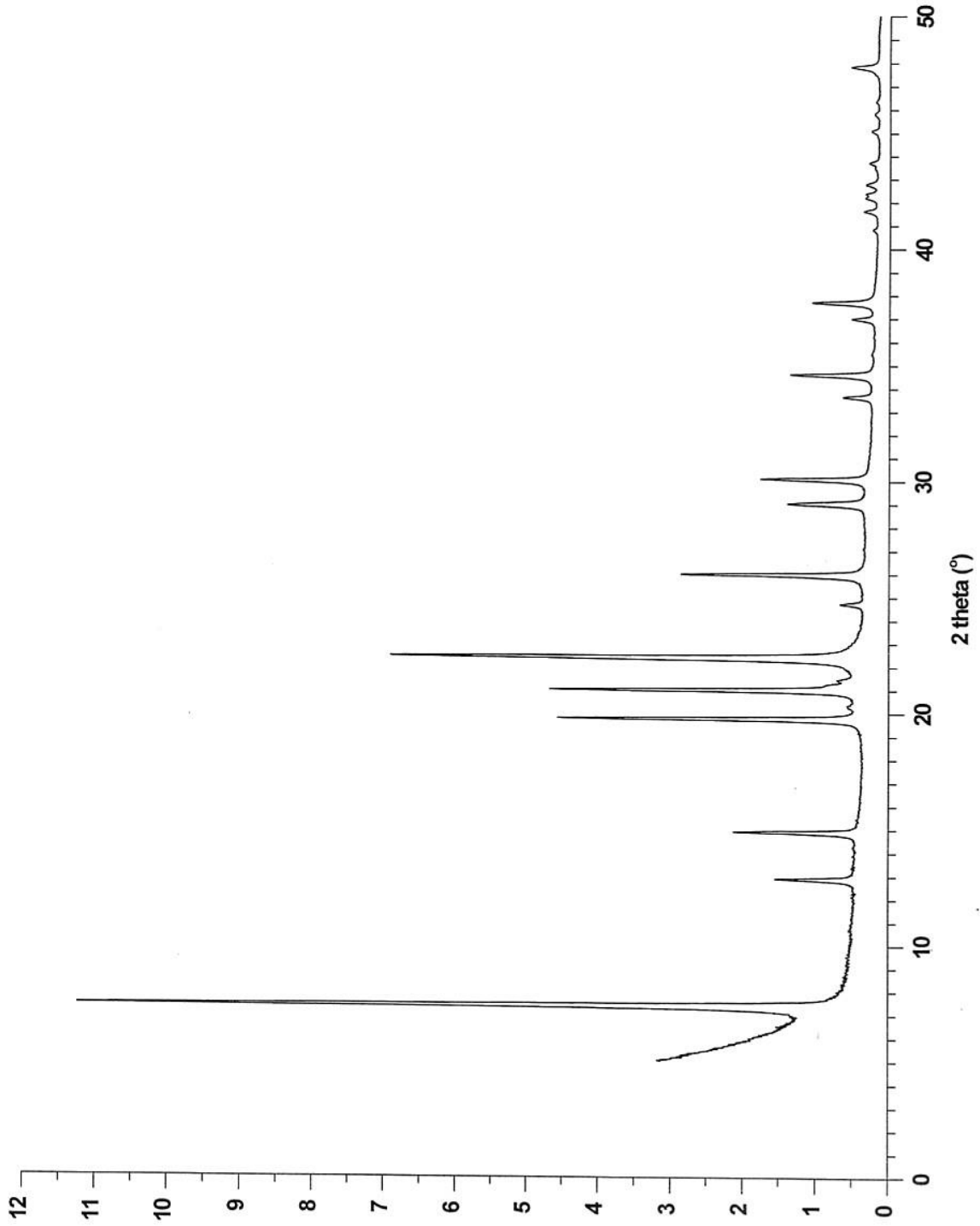
Notes

- a. The decisive difference of this synthesis from that of Wilson and Flanigen [2,3] is the use of HF as proposed by Kessler and Guth [4]. However, crystallization proceeds also in the absence of HF, but less favorably.
- b. Because Al triisopropylate is used as Al source, a fixed amount of 3 isopropyl alcohol molecules per Al is always present in the gel.
- c. The AlPO₄-5 phase can be prepared with numerous templates. Good results are also reported using tripropylamine [3-5].
- d. Other Al sources as pseudoboehmite [2, 3] and Al hydroxide [6] also give good and large crystals.
- e. For microwave heating, full Teflon autoclaves.
- f. For microwave oven (heating rate 4 grd/sec), 15 minutes at 180°C.
- g. If the product remains brown or gray after 4 hours at 600°C, this can be taken as a hint that free diffusion in the one-dimensional pores is blocked (by stacking faults or by non-framework material) thus preventing oxygen from entering and oxidation products from leaving the pores. By going to 900°C, the material can be made "white," but the uptake capacity remains low.
- h. Crystals up to 50 µm in length in the direction of the hexagonal columns are easily obtained; in optimized synthesis, Crystals up to 500 µm are observed. Incorporation of Si [7] or Co [8] gives larger and better crystals. Numerous compositional variants are known.

AFI

AlPO₄-5

Al(50), P(50)



AFI

SAPO-5

Al(49),P(35),Si(16)

Contributed by David Young

Verified by R. Borade and S. Schunk

Type Material [Al_{11.8}P_{9.4}Si_{3.8}O₄₈] : rR : wH₂O

Method D. Young, M. F. Davis [1] ^a

Batch Composition 0.15 cHA : 0.25 [(CH₃)₂CHO]₃Al : 0.25 H₃PO₄ : 13 H₂O 0.5 SiO₂

Source Materials

deionized water

aluminum isopropoxide (Aldrich, 98+%)

phosphoric acid (Aldrich A.C.S. grade, 85% H₃PO₄)

cyclohexylamine (cHA)(Aldrich, 99+%)

silica sol (Dupont Ludox AS-40, 40% SiO₂)

Batch Preparation (for 1 g product) ^b

- (1) [4 g water + 1.44 g aluminum isopropoxide]; make slurry
- (2) [1.2 g water + 0.81 g phosphoric acid]; mix
- (3) [(1) + (2)]; add diluted phosphoric acid dropwise to the aluminum isopropoxide slurry. Stir and age the gel for one hour to ensure homogeneity
- (4) [(3) + 0.42 g cHA]; add cHA dropwise. A viscous gel results. Stir and age for 90 minutes
- (5) [(4) + 2.13 g silica sol]; check to see that gel (4) is homogeneous, then add silica sol and stir for 10 minutes ^c

Crystallization

Vessel: 15 mL Teflon-lined autoclave ^d

Temperature: 200°C ^e

Time: 3 hours ^f

Agitation: none

Product Recovery

- (1) Remove reactor from the oven and quench cool
- (2) Transfer product from the liner to a beaker with a wash bottle ^g
- (3) Slurry with 50 mL deionized water. Allow the SAPO-5 crystallites to settle and decant off the suspended impurities. Repeat twice
- (4) Filter off product on a Buechner funnel. Wash copiously with water. Air dry
- (5) Yield: 1 g (Approximately 85% with respect to phosphoric acid)

Product Characterization

XRD: high purity SAPO-5 free from amorphous or crystalline impurities (SAPO-44) ^d

Elemental Analysis: Al_{0.49}P_{0.35}Si_{0.16}O₂ ^h

Crystal size and habit: spherical or hexagonal aggregates, average size of 20 μm

References

- [1] D. Young, M. E. Davis, *Zeolites* 11 (1991) 277
- [2] S. T. Wilson, B. M. Lok, E. M. Flanigen, US Patent 4 310 440 (1982)
- [3] J. A. Martens, C. Janssens, P. J. Grobet, H. K. Beyer, P. A. Jacobs, *Stud. Surf. Sci. Catal.* 49A (1989) 215

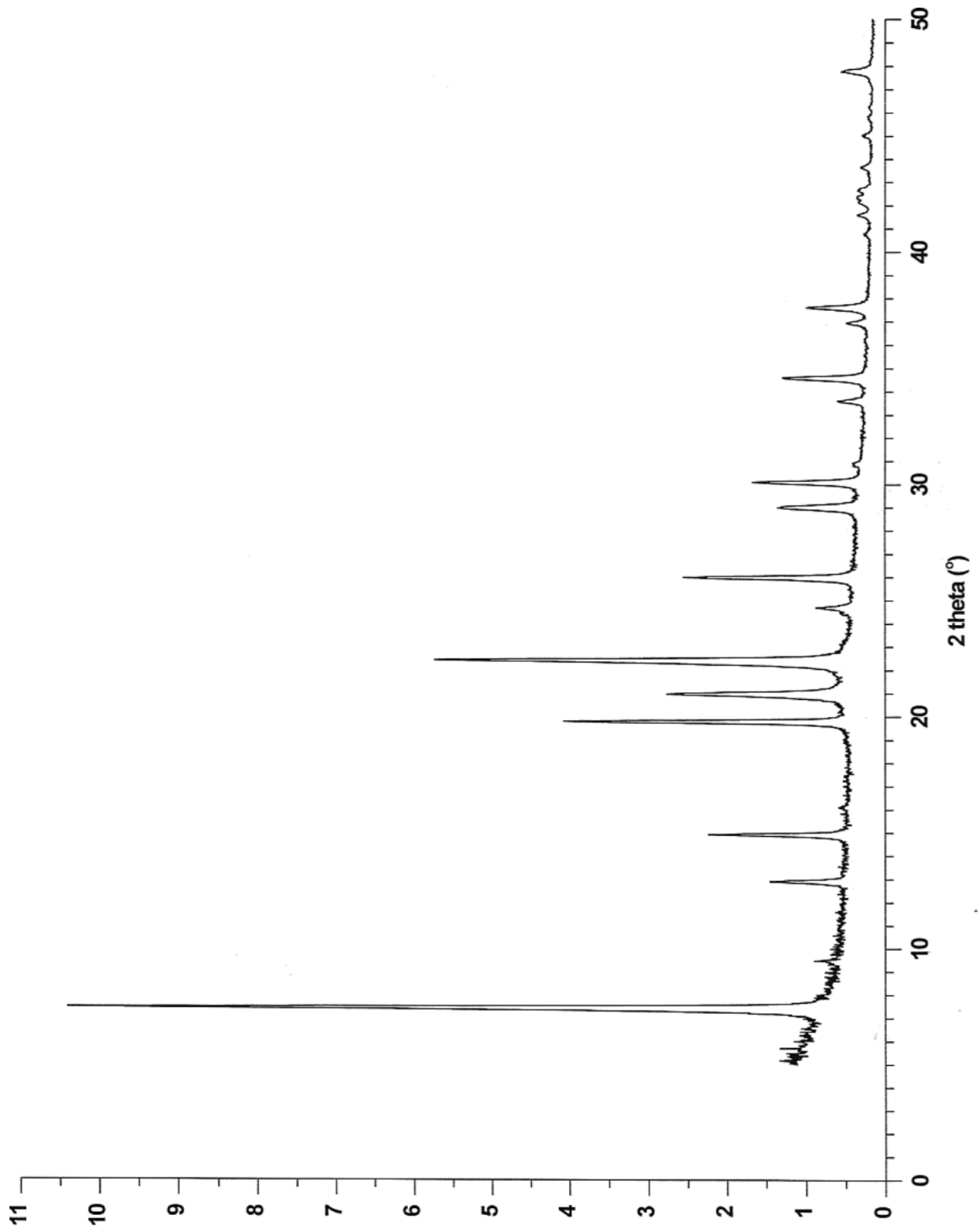
Notes

- a. Developed from S. T. Wilson, et al., [2] and from J. A. Martens, et al., [3]
- b. When handling small quantities of polar liquids, the use of glassware which has been pretreated with dichlorodimethylsilane is recommended. This ensures a clean transfer of reagents.
- c. Failure to mix the reagents in this order will result in different products, i.e., the silicoaluminophosphate analogue of quartz/berlinite.
- d. Due to the rapid crystallization of the SAPO-5 product and its propensity to transform to SAPO-44 upon synthesis over-run, small reactors with a narrow aspect ratio are recommended. This synthesis is recommended for a 15 mL capacity reactor. It can be scaled up, but the gel should be split between small reactors. Even with 45 mL reactors, impure product will result.
- e. Place autoclave on a rack in a forced convection oven at 200°C.
- f. A four-hour synthesis time results in SAPO-44 impurities: a two-hour reaction yields an amorphous gel. Deliberate over-run of one week will yield an excellent SAPO-44.
- g. The pH of the synthesis mother liquor will peak at close to 10, which coincides with the crystallization of the SAPO-5.
- h. This indicates that the main mode of T-atom substitution is silicon for phosphorous. However, surface analysis reveals significant silicon enrichment with strong evidence for silica islanding by Si-O-Si substitution for Al-O-P. ^{29}Si NMR: P-substitution peak at -90 ppm and Si-O-Si peak at -110 ppm.

AFI

SAPO-5

Al(49), P(35), Si(16)



AFI

CoAPO-5

P(51), Al(45), Co(4)

Contributed by Myriam Uytterhoeven and An Verberckmoes

Verified by S. Ashtekar, P. Norby, J. Jänchen and H. van Breukelen

Type Material [CoAl₁₁P₁₂O₄₈]: wH₂O (w = 0.1 to 0.2)

Method M. G. Uytterhoeven, R. A. Schoonheydt [1, 2]

Batch Composition 0.7 TriEA : (Co_{0.08}Al_{0.92}P)₄: 20 H₂O

Source Materials

water (doubly distilled)
phosphoric acid (Janssen Chimica, 85% H₃PO₄)
cobalt nitrate, Co(NO₃)₂ · 6 H₂O (Janssen Chimica)
pseudoboehmite (Catapal, Vista, 70% Al₂O₃)
triethylamine (TriEA) (Janssen Chimica 99%)

Batch Preparation (for 27 g product)

- (1) [62.6 g water + 23.06 g phosphoric acid], mix; chill to 0°C
- (2) [(1) + 4.66 g cobalt nitrate], stir until dissolved
- (3) [(2) + 13.4 g pseudoboehmite], add alumina under continuous stirring
- (4) [(3) + 14.3 g TriEA], add amine under continuous stirring;^a stir for one additional hour. Initial pH ~3

Crystallization

Vessel: stirred, Teflon-lined autoclave
Temperature: 200°C
Time: 24 hours
Agitation: Stirring is essential.^b Autoclaves were "tumbled" (end-over-end) in the oven

Product Recovery

- (1) Filter and wash with distilled water; dry at room temperature
- (2) Yield: near 100% on T-atom basis

Product Characterization

XRD: pure AFI, CHA impurity when present is evidenced by a line at 9.5_i(2q)^c
Elemental Analysis: 0.10 TriEA. (Co_{0.086}Al_{0.892}P_{1.000}O₄) · 0.13 H₂O^d
Crystal Size and Habit: agglomerates formed by hexagonal platelets, regularly shaped (spherical or diabolo-shaped) with dia. = 55 μm^{e,f}

References

- [1] M. G. Uytterhoeven, R. A. Schoonheydt, *Micropor. Mater.* 3 (1994) 265
- [2] M. G. Uytterhoeven, R. A. Schoonheydt, *Proc. Ninth Int. Zeo. Conf.*, R von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, Boston, 1993, p. 329

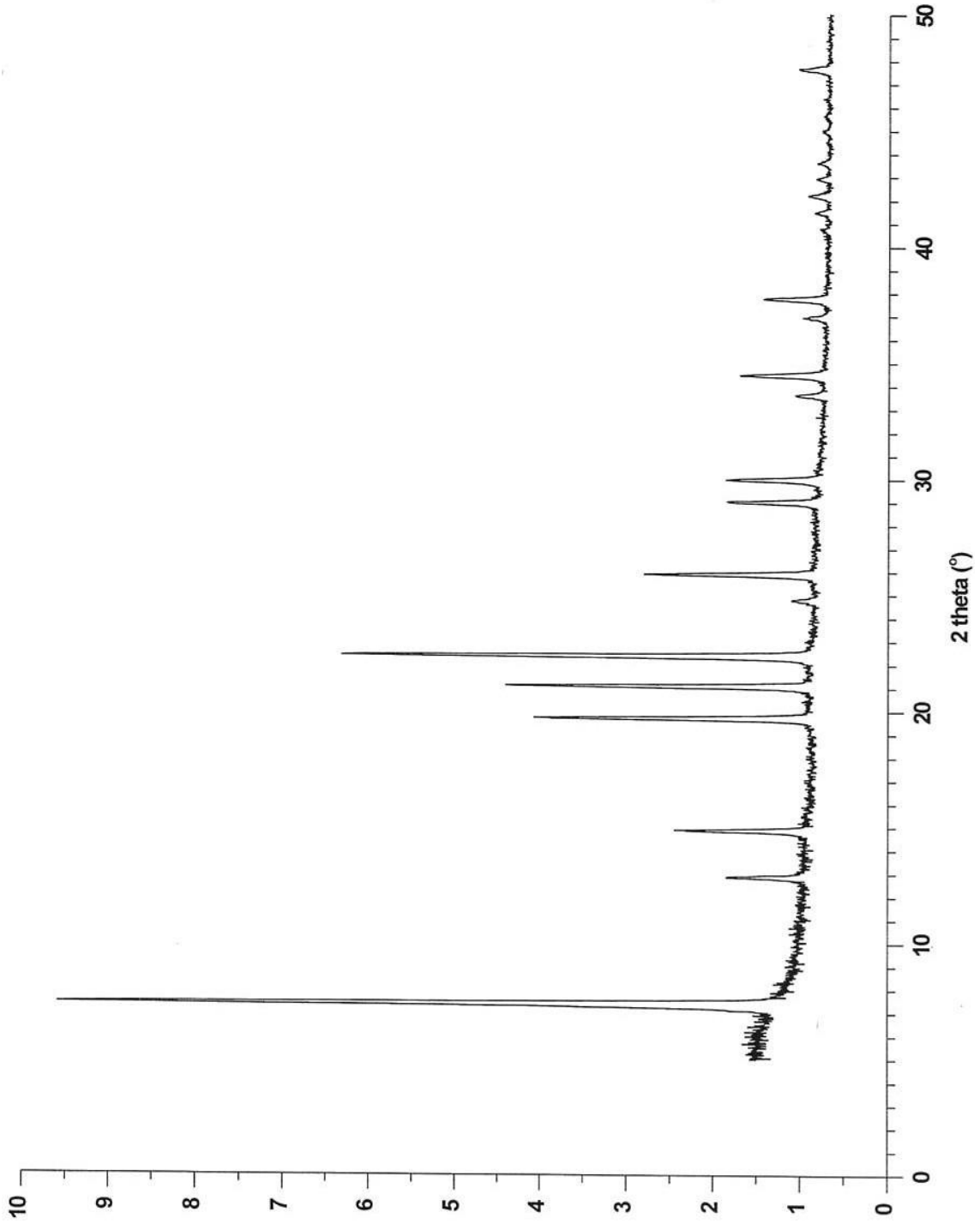
Notes

- a. TriEA addition causes an exothermic reaction; the preparation should be performed at 0 °C and TriEA added drop by drop under careful temperature control.
- b. Under static conditions, co-crystallization of CHA is more probable.
- c. The co-crystallization of CHA can be suppressed by reducing the amine content and/or decreasing the cobalt content. The latter requires an increase of the Al content so that $[Al + Co = P]$.
- d. On T-atom basis, the product composition is almost equal to the gel composition. $Al + Co = P$ should be approximately achieved.
- e. SEM is suited to distinguish between AFT and much smaller CHA crystals.
- f. At low cobalt content (e.g., $Co_{0.02}Al_{0.98}P_{1.00}$), single crystals are formed, shaped as hexagonal bars. Twinning can occur. Increasing cobalt content causes agglomeration giving larger, regular agglomerates. At high cobalt content (for example, $Co_{0.08}Al_{0.92}P_{1.00}$) single crystal formation can be achieved by increasing dilution and increasing template content, although the latter favors the co-crystallization of CHA.

AFI

CoAPO-5

P(51), Al(45), Co(4)



AFI

SSZ-24

Si(100)

Contributed by S. I. Zones and L T. Yuen

Verified by A. Bell, C. Gittleman, A. Cheetham, R Lobo and D. Shantz

Type Material (SiO₂)₂₄. aRN⁺ a = 0.96 ± 0.24 (RN⁺ = trimethyl-1-adamantammonium)

Method R. A. Van Nordstrand, D. S. Santilli, S. I. Zones [1]

Batch Composition 5 K₂O : 15 RN⁺:100 SiO₂ : 4400 H₂O

Source Materials

deionized water

RN⁺ (see above) 0.72 Molar [2]

potassium hydroxide (Baker reagent, 87.8% KOH)

fumed silica (Cab-O-Sil M5, 97% SiO₂, 3% H₂O)

Batch Preparation (for 3.5 g product)

- (1) [38.32 g water + 13.90 g (0.72M RN⁺) + 0.44 g potassium hydroxide], mix until dissolved
- (2) [(1) + 4.00 g fumed silica], mix in the Teflon liner of a 125 mL Parr stainless steel reactor ^a

Crystallization

Vessel: Parr 125 mL reactor (Teflon-lined) heated in a Blue M oven

Temperature: 150 °C

Time: 7 days ^{b,c}

Agitation: none

Product Recovery

- (1) Upon cooling to room temperature, the product should be settled to the bottom of the reactor liner; pH with a calibrated probe should be 11.50-11.70
- (2) Filter to recover solids (medium grade glass-frit funnel)
- (3) Wash product with approximately 100 mL 0.01N KOH solution ^d
- (4) Wash with approximately 1 liter water
- (5) Air dry overnight while pulling a vacuum through the frit
- (6) Yield: 3.52 g; 79% yield based on SiO₂

Product Characterization

XRD: AFI only crystalline phase

Elemental Analysis: RN⁺ is approximately 10 wt% and alkali cation is usually less than 0.5 wt%. The remaining material is SiO₂ [3]

Crystal Size and Habit: Typically, hexagonal rods composed of identical hexagonal plates on top of each other. The rods are usually about 10 μm long

References

- [1] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones in Molecular Sieve Science, ACS Symp. Ser. 368. W. H. Flank, T. E Whyte, (eds.), Am. Chem. Soc., Washington, D. C., 1988, pp. 236-245
- [2] S. I. Zones, US Patent 4665 110 (1987)
- [3] I. Petrovic, A. Navrotsky, M. E.. Davis, S. I. Zones, Chem. Mater. 5 (1993) 1805
- [4] R. A. Van Nordstrand, D. S. Santilli, S. I. Zones, in Synthesis of Microporous Materials, Vol. 1, M. L Ocelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992. pp. 373-383

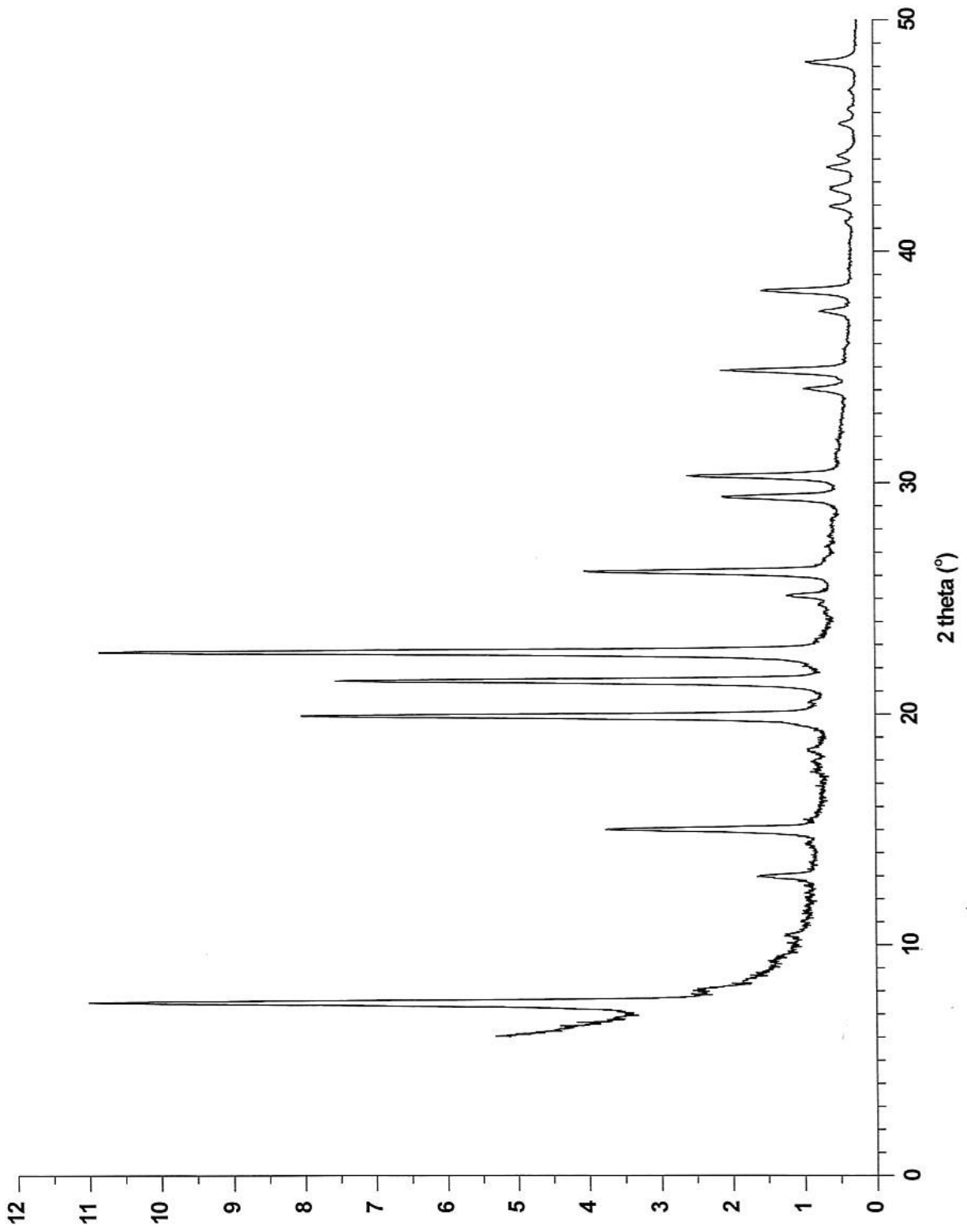
Notes

- a. High speed stirring of this preparation leads to SSZ-23 formation [1].
- b. The reaction can be accelerated by seeding after some initial material has been made.
- c. The synthesis of the borosilicate [4] requires only one day; the crystals are smaller.
- d. The alkaline wash helps to prevent unreacted silica from coming out of solution during washing and causing pore.

AFI

SSZ-24

Si(100)



AFO

Nanosized AIPO-41

Al(50), P(50)

Contributed by Gerardo Majano

Verified by V. Georgieva, L. Tosheva, K. L. Wong

Type Material: [Al₁₀P₁₀O₄₀]

Method: G. Majano, K. Raltchev, A. Vicente and S. Mintova [1]

Batch Composition: 0.7 Al₂O₃ : 1.3 P₂O₅ : 0.2 TPeAOH : 2.8 DPA : 25 EtOH : 25 H₂O

Source Materials

aluminium isopropoxide (AIP, >98%, Aldrich)
tetrapentylammonium hydroxide (TPeAOH, 20% in water, Aldrich)
n-dipropylamine (DPA, 99%, Aldrich)
absolute ethanol (EtOH, AnalR NORMAPUR)
phosphoric acid (85%, Aldrich)
distilled water (H₂O)

Batch Preparation

- (1) [2.64 g AIP + 2.59 g DPA + 2.86 g TPeAOH + 10.45g EtOH +1.31 g H₂O] stir the mixture for 30 min
- (2) [(1) + 3.08 g H₃PO₄] add dropwise under stirring (1 drop/5 s, 500 rpm)

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 180° C
Time: 24 hours
Agitation: 16 hours

Product Recovery

- (1) Centrifugation (20 000 rpm, 1h)
- (2) Redisperse in water using ultrasonication; solid product and colloidal suspensions are preserved.

Product Characterization

XRD: AFO; competing phase: no
Crystal size and habit: rectangular morphology, with dimension between 80 and 500 nm.

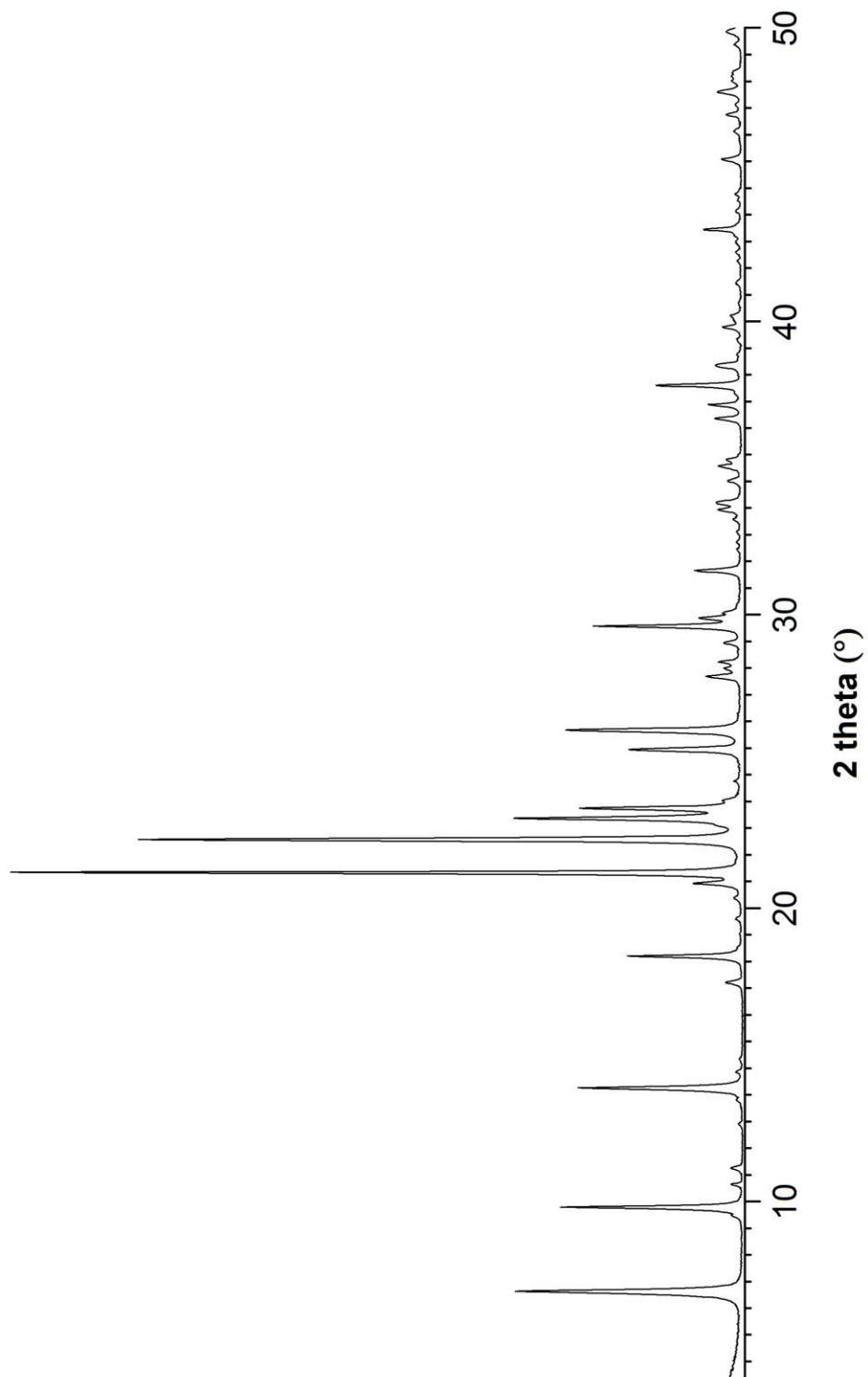
References

- [1] G. Majano, K. Raltchev, A. Vicente and S. Mintova, *Nanoscale* 7 (2015) 5787

AFO

Nanosized AlPO_4 -41

Al(50), P(50)



AFO

SAPO-41

Al(51), P(46), Si(3)

Contributed by A. M. Prakash and D. K. Chakrabarty

Verified by P. Mériaudeau, J. Pérez-Pariente and J. Rodriguez

Type material [(Al_{20.4}P_{18.4}Si_{1.2}) O₈₀] · mR · nH₂O (R = Di-n-propylamine)

Method A. M. Prakash, S. V. V. Chilukuri, R. P. Bagwe, S. Ashtekar, D. K. Chakrabarty [1]

Batch Composition 1.0 Al₂O₃ : 1.3 P₂O₅ : 0.1 SiO₂^a : 4.0 R^b : 58.2 H₂O^c

Source Materials

deionized water
orthophosphoric acid (Merck, 85%)
pseudoboehmite (Vista; Catapal-B, assumed 70 wt% Al₂O₃)
fumed silica (Degussa, Aerosil-200)
di-n-propylamine (Merck, 99%)

Batch Preparation (for 16 g product)

- (1) [23.06 g phosphoric acid + 25 g water], mix together
- (2) [(1) + 14.57 g pseudoboehmite], add slowly over a period of 3.5 hours and continue stirring for 1.5 hours
- (3) [0.60 g silica + 25 g water], mix together to form a slurry
- (4) [(2) + (3)], add silica slurry over a period of 30 minutes and continue stirring for 1 hour
- (5) [(4) + 40 g water], mix together
- (6) [(5) + 40.88 g di-n-propylamine], add dropwise to gel and continue stirring for 30 minutes
- (7) Adjust pH of the gel to 7.7 by slowly adding 4 mL of phosphoric acid diluted in 6 g water and stir the final gel for 30 minutes to ensure homogeneity

Crystallization

Vessel: 500 mL stainless steel autoclave
Temperature: 180°C
Time: 11 days

Product Recovery

- (1) Decant the mother liquor
- (2) Slurry with deionized water. Allow the crystallites to settle and decant the water
- (3) Repeat step (2) three times
- (4) Filter off product and wash again with water
- (5) Dry at 100°C overnight
- (6) Yield: 65% based on alumina

Product characterization

XRD: SAPO-41 [1]^d Orthorhombic; $a = 9.7 \text{ \AA}$, $b = 25.5 \text{ \AA}$, $c = 8.4 \text{ \AA}$, competing phases: SAPO-11 and SAPO-31 at low template concentration and SAPO-46 at high silica concentration [1, 2]

Elemental Analysis (exclusive of R and H₂O): 1.00 Al₂O₃ : 0.90 P₂O₅ : 0.11 SiO₂
Crystal size and habit: 5-10 μm crystals of rectangular morphology

References

- [1] A. M. Prakash, S. V. V. Chilukuri, R. B. Bagwe, S. Ashtekar, D. K. Chakrabarty, *Micropor. Mater.* 6 (1996), 89
- [2] P. Mériaudeau, V. A. Tuan, V. T. Nghiem, S. Y. Lai, L. Hung, C. Naccache, *J. Catal.* 169 (1997) 55

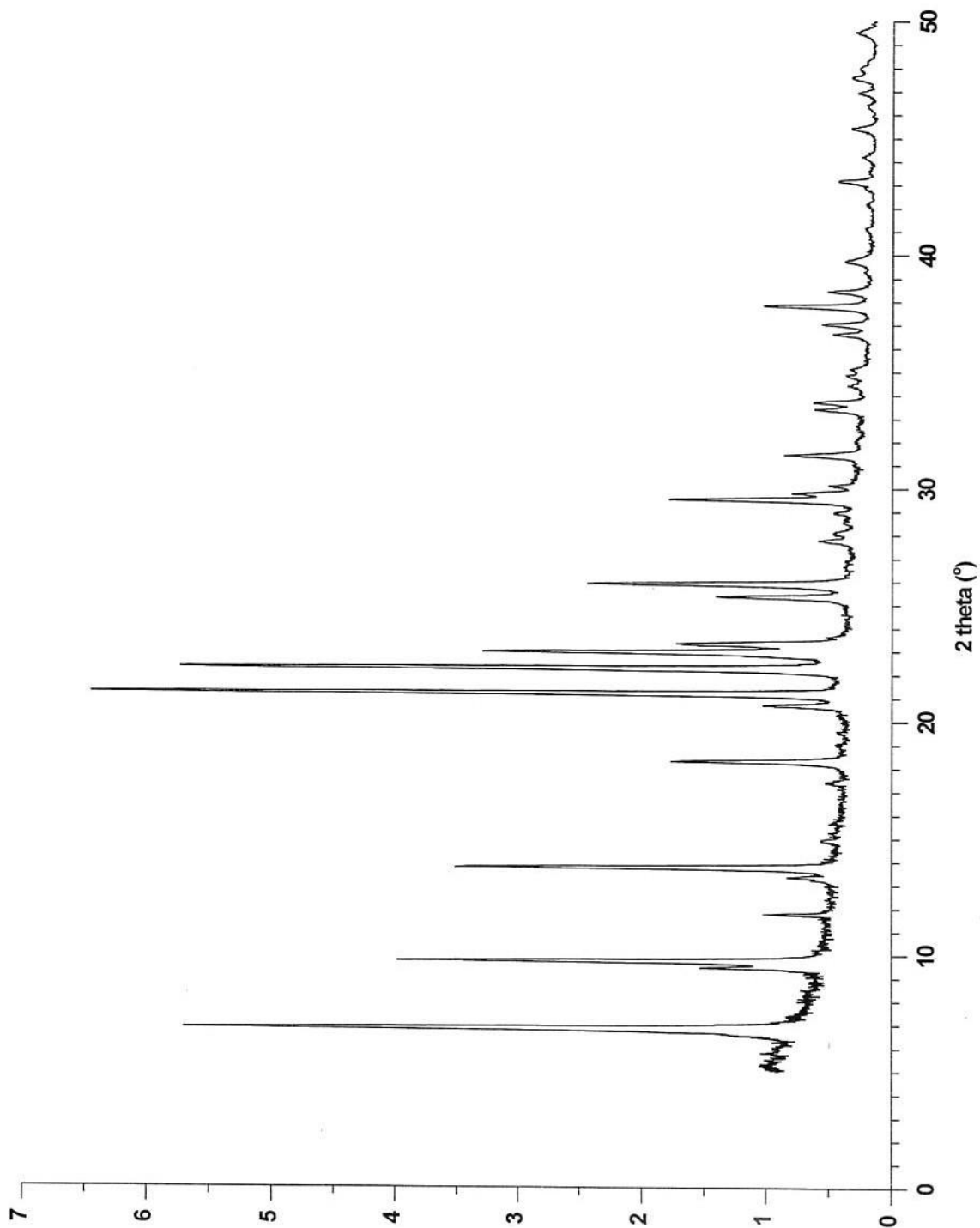
Notes

- a. In this synthesis pure phase SAPO-41 crystallizes only at low SiO₂ concentration in the gel. High concentration of silica generally leads to phases such as SAPO-11, SAPO-31, SAPO-46 depending on template concentration, temperature and period of crystallization.
- b. Template concentration should be high ($3 \text{ mol} < R < 4 \text{ mol}$) for obtaining pure SAPO-41. Lower template concentration leads to SAPO-11 and SAPO-31 depending on silica concentration.
- c. H₂O included water from pseudoboehmite, phosphoric acid and added water.
- d. Extra low-intensity lines between 9-18 degrees (2θ) have not been identified. They may indicate a lower symmetry due to retained template. However, a competing phase cannot be ruled out.

AFO

SAPO-41

Al(51), P(46), Si(3)



AFS

MAPO-46

P(50),Al(40),Mg(10)

Contributed by Deepak B. Akolekar

Verified by H. Tian and A. Prakash

Type Material $\text{Mg}_{5.54}\text{Al}_{22.4}\text{P}_{28.06}\text{O}_{112} \cdot 8.1 \text{ R} \cdot 11.0 \text{ H}_2\text{O}$ (R = di-n-propylamine)

Method D. B. Akolekar, S. Kaliaguine [1]

Batch Composition 2 R: 0.30 MgO : 0.85 Al₂O₃ : 1.0 P₂O₅ : 50 H₂O

Source Materials

deionized water
orthophosphoric acid (85%, Aldrich)
pseudoboehmite (Vista Chemical Co., 71.8% Al₂O₃)
magnesium oxide (99.9%, Aldrich)
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 20 g dry, template-free product)

- (1) [65.0 g water + 25.16 g o-phosphoric acid + 13.18 g pseudo-boehmite], stir until homogeneous
- (2) [(1) + 1.32 g magnesium oxide + 32.0 g water], stir until homogeneous
- (3) [(2) + 29.9 mL n-.dipropylamine], stir until homogeneous (about 35 minutes) ^a

Crystallization

Vessel: PFFE-lined stainless steel autoclave (200 mL)
Temperature: 162 °C
Tune: 240 hours
Agitation: none

Product Recovery

- (1) Stir the total crystallization batch into 1.5 L deionized water. Allow to stand for a few minutes, then decant the top organic layer
- (2) Filter; wash with deionized water
- (3) Dry at 75 °C
- (4) Yield: > 60% based on Al₂O₃

Product Characterization

XRD: AFS, only crystalline product [2-4]; characteristic strong reflections at d = 11.43 and 4.12 Å
Elemental Analysis (H₂O and template-free): 0.396 MgO · 0.80 Al₂O₃ · 1.00 P₂O₅
Crystal Size and Habit: hexagonal rod-like, 0.8 x 8 μm

References

- [1] D. B. Akolekar, S. K. Kaliaguine, 1. Chem. Soc., Faraday Trans. 89 (1998) 4141
- [2] S. T. Wilson, E. M. Flanigen in ACS Symp. Ser. 398, M. L. Occelli, H. F. Robson (eds.), Am. Chem. Soc., Washington, D.C., 1989, p. 329

- [3] E. M. Flanigen, R L Patton, S. T. Wilson, Stud. Surf. Sci. Catal. 37 (1988) 13
[4] J. M. Bennett, B. K. Marcus, Stud. Surf. Sci. Catal. 37 (1988) 269

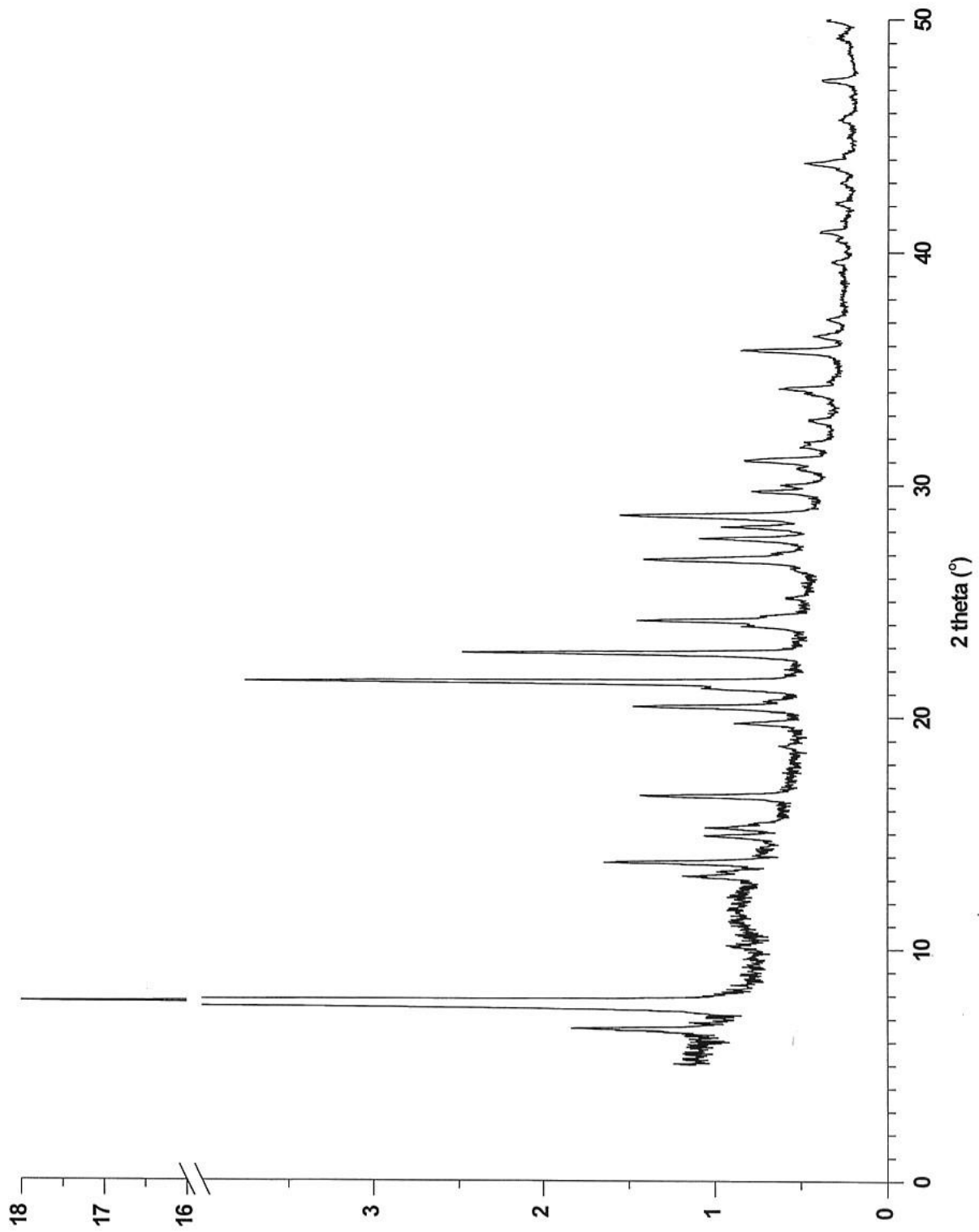
Note

- a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.

AFS

MAPO-46

P(50),Al(40),Mg(10)



ANA

Analcime

Si(68), Al(32)

Contributed by B. W. Garney

Verified by N. Evmiridis and F. Farzaneh

Type Material $\text{Na}_x[\text{Al}_x\text{Si}_{48-x}\text{O}_{96} : 16 \text{ H}_2\text{O}$ ($x = 15$ to 17)

Method Developed from J. F. Charnell [1], and A. Dyer, A. M. Yusof [2]

Batch Composition 4.5 Na_2O : Al_2O_3 : 4.5 SiO_2 : 3.0 H_2SO_4 : 380 H_2O : 6.1 triethanolamine ^a

Source Materials

demineralized water

aluminum sulfate [General Purpose Reagent, $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{ H}_2\text{O}$]

sodium metasilicate (Technical Grade, $\text{Na}_2\text{SiO}_3 \cdot 5 \text{ H}_2\text{O}$)

triethanolamine [General Purpose Reagent, $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$]

Batch Preparation (for approximately 7 g product) [3,4]

- (1) [55 g water + 9.8 g aluminum sulfate], stir until dissolved; filter through 0.7 micron glass microfibre filter
- (2) [36.5 g water + 14.9 g sodium metasilicate + 12.2 g triethanolamine], stir until dissolved; filter through 0.7 micron glass microfibre filter
- (3) [(1) + (2)], stir gently until gel thickens (do not over-stir)

Crystallization

Vessel: 150 mL Teflon-lined autoclave ^b

Time: 24 hours

Temperature: 200 °C (autoclave heated in the oven)

Agitation: none

Product Recovery

- (1) Cool to room temperature and filter to recover solids
- (2) Wash with distilled water until pH of filtrate < 10
- (3) De-agglomerate by adding 10 mL of 10% ethanol in water and immerse in a 150 watt ultrasonic bath for approximately 1 hour
- (4) Dry at 100 °C
- (5) Yield: approximately 90%

Product Characterization

XRD: ANA (only crystalline phase)

Elemental Analysis: 1.06 Na_2O : Al_2O_3 : 4.3 SiO_2 : 2 H_2O

H_2O (Wt. loss at 500 °C): 8.29% (± 0.20)

Na_2O : 14.6% (± 1.5)

Al_2O_3 : 22.7% (± 1.5)

SiO_2 : 57.3% (± 0.5)

Crystal Size and Habit: polycrystalline non-porous spherulites $\leq 180 \mu\text{m}$ dia. [2]

References

- [1] J. F. Charnell, J. Cryst. Growth 8 (1971) 291
- [2] A. Dyer, A. M. Yusof, Zeolites 7 (1987) 191
- [3] B. W. Garney, Fusion Technology 21 (1992) 604
- [4] B. W. Garney, UK Patent Application 9011151.9

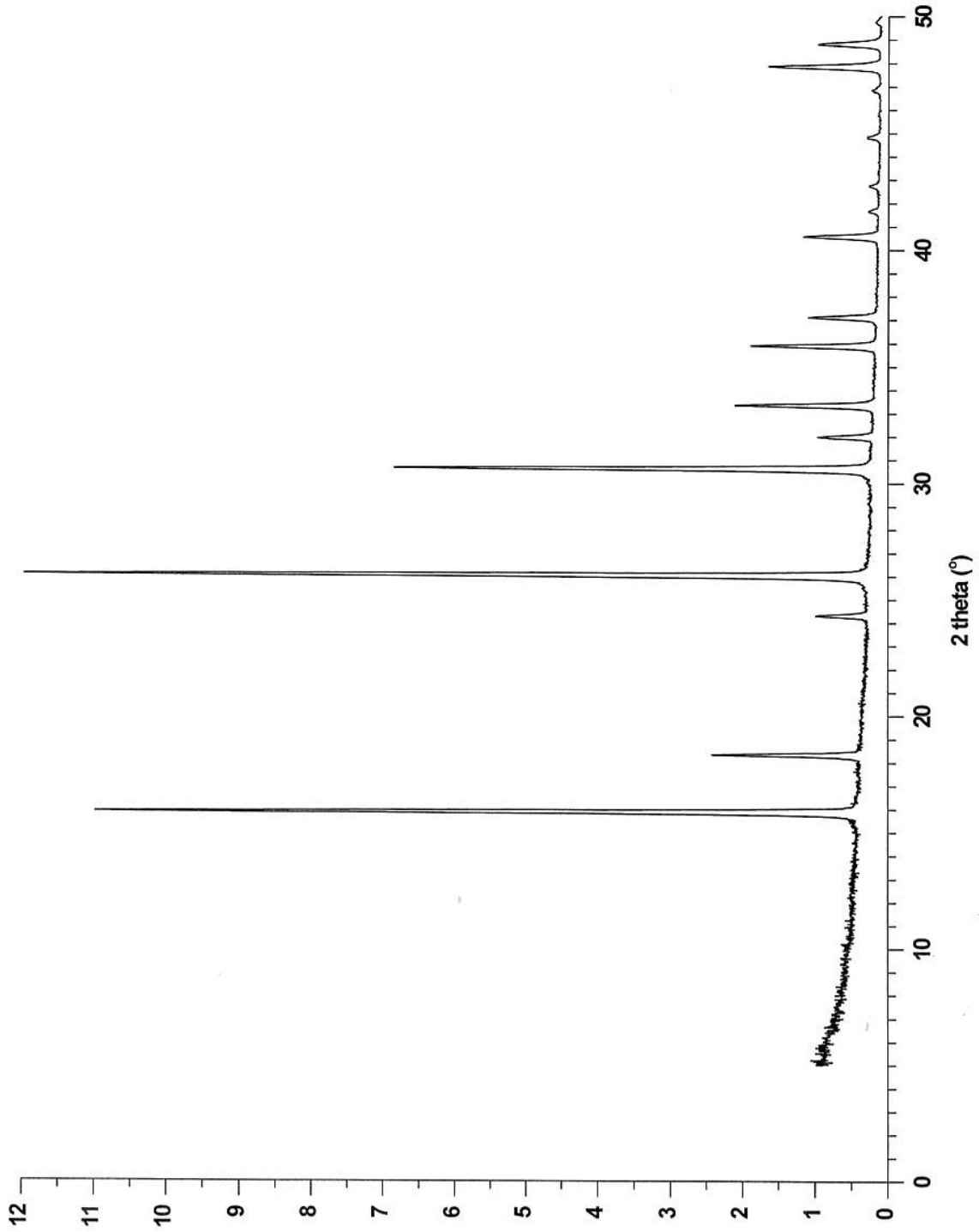
Notes

- a. This preparation gives the non-porous form of analcime. Replacing aluminum sulfate with an equivalent weight of sodium aluminate gives the porous form of analcime. Gel composition: 6.5 Na₂O : Al₂O₃ : 4.5 SiO₂ : 380 H₂O : 6.1 triethanolamine.
- b. The method of heating the gel is very important if large crystals are required. The largest crystals were obtained when the autoclave was placed in a laboratory oven where the heat flow was uniform all around the pot. Experiments using autoclaves which were heated by electrical jackets around the sides were not so successful.

ANA

Analcime

Si(68), Al(32)



AST

AlPO₄-16

Al(50), P(50)

Contributed by Joël Patarin

Verified by J. Shi and K. Balkus, by D. Akporiaye, and by T. Blasco

Type Material (Al₁₀P₁₀O₁₀)Q_{2.0}F_{1.6}: 3.0 H₂O^a (Q= quinucidine)

Method C. Schott-Darie, J. Patarin, P. Y. Le Goff, H. Kessler and E. Benazzi [1]

Batch Composition 1 P₂O₅ : 1 Al₂O₃ : 1 Q : 1 HF : 60 H₂O

Source Materials

distilled water
phosphoric acid (Fluka, 85% H₃PO₄)
aluminum isopropoxide (Aldrich, 98%)
quinuclidine C₇H₁₃N (Fluka, 97%)
hydrofluoric acid (Prolabo, 40%)

Batch Preparation^b (for 1.5 g of as-synthesized product)

- (1) [4.00 g water + 2.31 g phosphoric acid + 4.17 g aluminum isopropoxide], stir until homogenized
- (2) [6.15 g water + 1.14 g quinuclidine], stir until dissolved
- (3) [(1) + (2) + 0.50 g hydrofluoric acid], stir for 2 minutes. Gel pH= 7 to 7.5

Crystallization

Vessel: Teflon-lined stainless steel autoclave (50 cm³)
Temperature: 150°C
Time: 24 hours
Agitation: none
Final pH: approximately 8

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter or centrifuge
- (3) Wash until the pH of the filtrate is 5.5 to 6
- (4) Dry at 60-70°C overnight
- (5) Yield: 50% based on aluminum (as-synthesized product containing quinuclidine and some water)^d

Product Characterization

XRD: AST (only crystalline phase), Space group 14, a₀ = 9.3423(1) Å c₀ = 13.4760(2) Å^e
Elemental Analysis (wt%): Al₂O₃ = 32.8, P₂O₅ = 44.8, F = 1.9, (C₇H₁₃)N = 15.4, H₂O = 3.4
Crystal Size and Habit: tetrahedra, 0.5 to 3 μm

References

- [1] C. Schott-Daric, J. Patarin, P. Y. Le Goff, H. Kessler, E. Benazzi, *Micropor. Mater.* 3 (1994) 123
- [2] J. M. Bennett, R. M. Kirchner, *Zeolites* 11(1991) 502

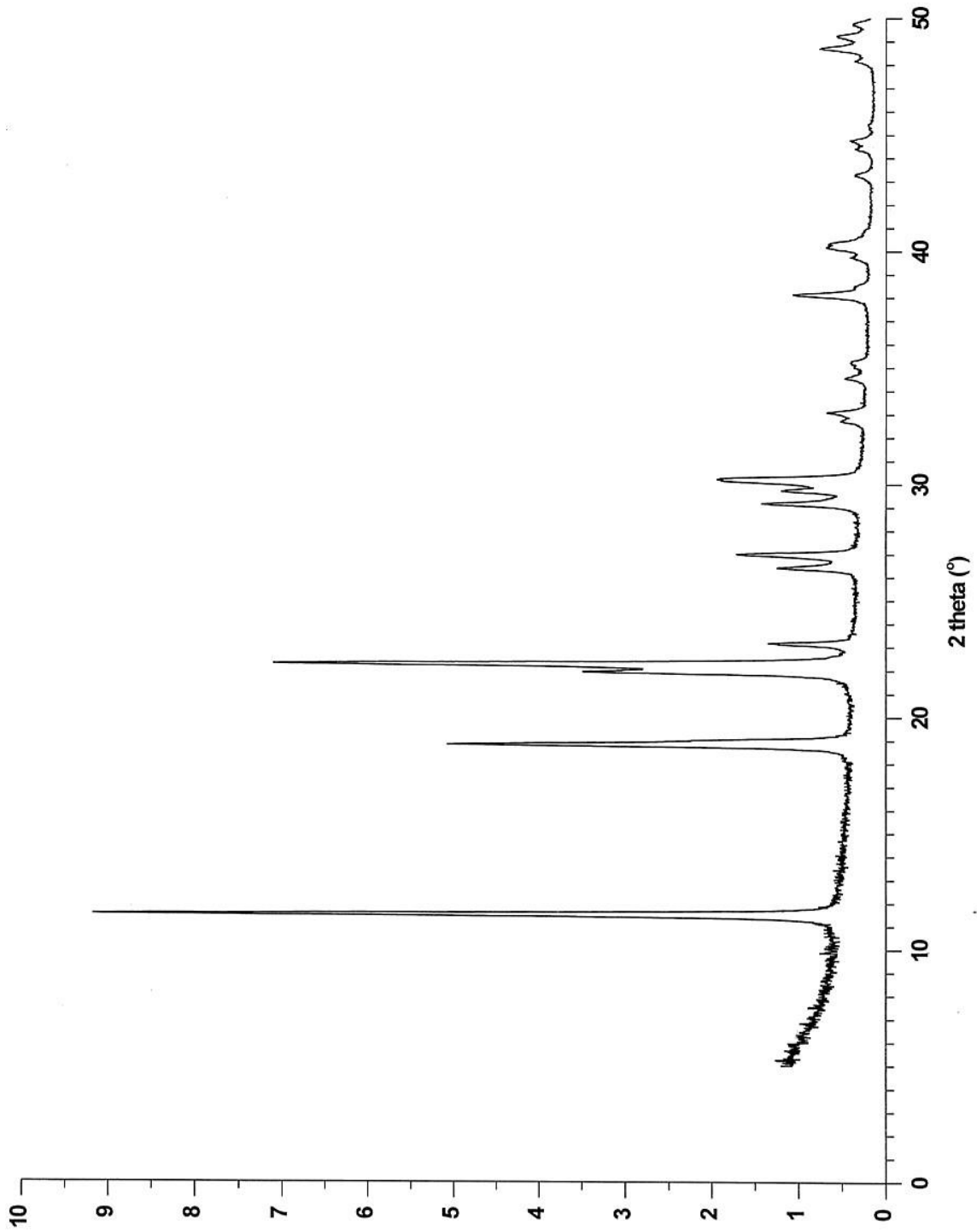
Notes

- a. The Q/F molar ratio is lower than 1. Part of the quinucidine is either not protonated or OH⁻ groups are present in order to get a neutral material.
- b. The starting mixture is prepared in a polyethylene vessel.
- c. The reaction is exothermic.
- d. After calcination (removal of the organic and fluoride species) the cubic form [2] of AlPO₄-16 is obtained.
- e. According to reference [1].

AST

AlPO4-16

Al(50), P(50)



ATN

MAPO-39

P(50), Al(40), Mg(9)

Contributed by Deepak Akolekar

Verified by P. Norby and by S. Sivasanker

Type Material $H_{1.6}[Mg_{1.6}Al_{64}P_8O_{32}]$

Method D. B. Akolekar, S. K. Kaliaguine [1]

Batch Composition 1.1 R : 0.40 MgO : 0.80 Al₂O₃ : 1.00 P₂O₅ : 41 H₂O (R = di-n-propylaniine)

Source Materials

deionized water
orthophosphoric acid (85%, Aldrich)
pseudoboehmite (Vista Chemical Co., 71.8% Al₂O₃)
magnesium oxide (99.9%, Aldrich)
n-dipropylamine (99%, Aldrich, 0.738 g/mL)

Batch Preparation (for 12 g dry, template-free product)

- (1) [70.0 g water + 32.3 g o-phosphoric acid + 15.91 g pseudoboehmite], stir until homogeneous
- (2) [(1) + 2.26 g magnesium oxide + 26 g water], stir until homogeneous
- (3) [(2) + 19.2 mL n-dipropylamine], stir until homogeneous (about 30 minutes) ^a

Crystallization

Vessel: PTFE-lined stainless steel autoclave (150 mL)
Temperature: 150 °C
Time: 114 hours
Agitation: none

Product Recovery

- (1) Stir the total crystallization batch into 1.5 L deionized water
- (2) Filter; wash with deionized water
- (3) Dry at 75 °C
- (4) Yield: > 70% based on Al₂O₃

Product Characterization

XRD ATN [2,3], characteristic strong reflections at $d = 4.19$ and 3.95\AA for as-synthesized material
Elemental Analysis: (exclusive of R and H₂O) (wt%): 6.31 MgO, 34.32 Al₂O₃, 59.37% P₂O₅
Crystal Size and Habit: small irregular platelike particles, 2.5 x 3.3 μm

References

- [1] D. B. Akolekar, S. K. Kaliaguine, Zeolites 14 (1994), 620

- [2] S. T. Wilson, E. M. Flanigen, in ACS Symp. Ser. 398, M. L. Occelli, H. F. Robson (eds.) Am. Chem. Soc., Washington, D.C., 1989, p. 329
- [3] L. B. McCusker, G. O. Brunner, A. F. Ojo, Acta Crystallogr. A46 (1990), C 59

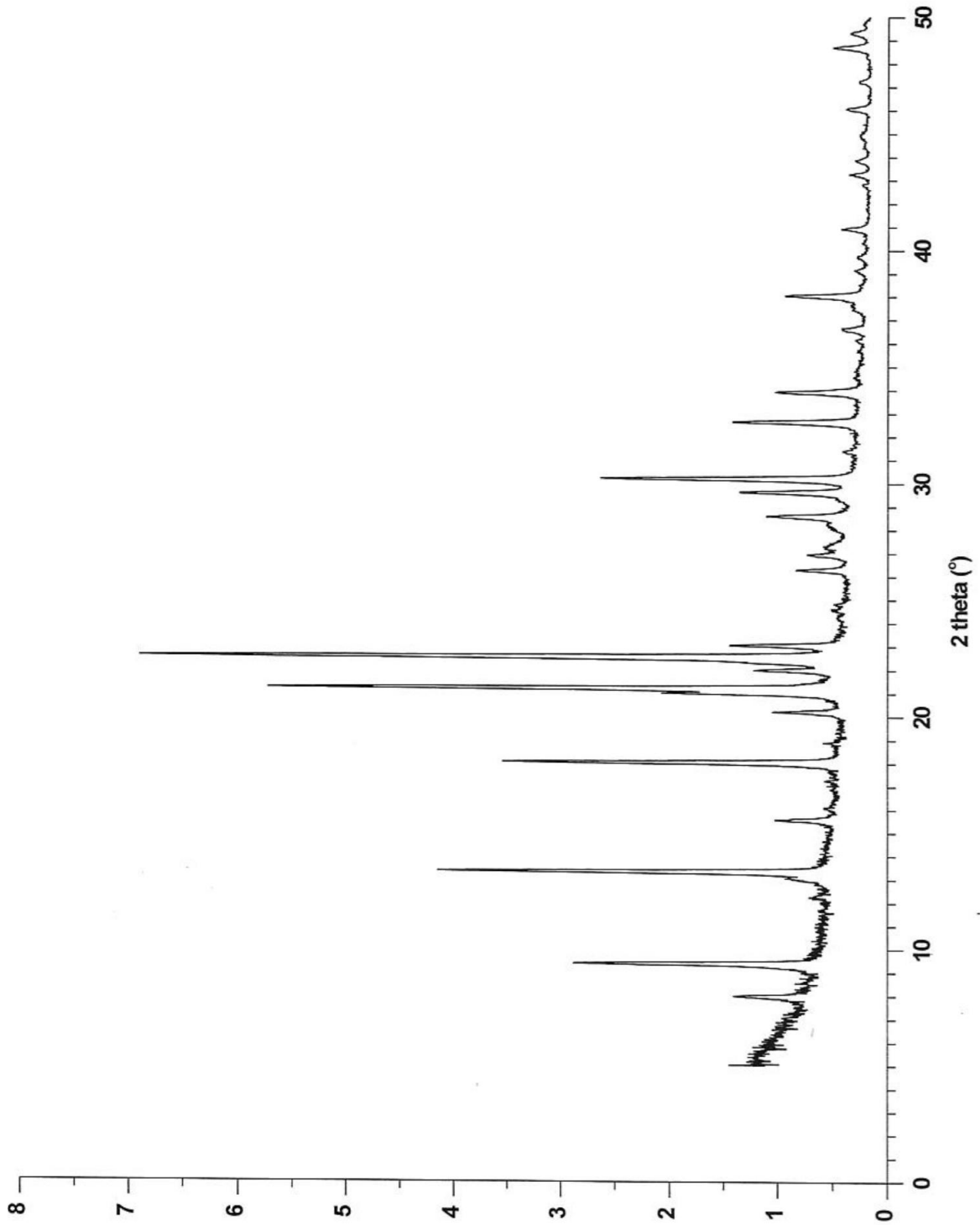
Note

- a. Uniform homogeneous gel formation is the important step for obtaining pure phase material.

ATN

MAPO-39

P(50), Al(40), Mg(9)



BEA

Beta

Si(93), Al(7)

Contributed by Joaquin Pérez-Pariente and Miguel Cambor

Verified by Shu-Hua Chien and Xianping Meng, and by D. Cardoso and S. Jahn

Type Material $\text{Na}_{0.92}\text{K}_{0.62}(\text{TEA})_{7.6}[\text{Al}_{4.53}\text{Si}_{59.47}\text{O}_{128}]^{\text{a}}$

Method M. A. Cambor, J. Pérez-Pariente [1]

Batch Composition 1.97 Na_2O : 1.00 K_2O : 12.5 $(\text{TEA})_{20}$: Al_2O_3 : 50 SiO_2 : 750 H_2O : 2.9 HCl ^b

Source Materials

deionized water

tetraethylammonium hydroxide (Alfa 40 wt% TEAOH, K < 1 ppm, Na < 3 ppm)

sodium chloride (reagent grade)

potassium chloride (reagent grade)

silica (Degussa Aerosil 200, 99+% SiO_2)

sodium hydroxide (Prolabo reagent grade, 98%)

sodium aluminate (Carlo Erba, 56 wt% Al_2O_3 , 37 wt% Na_2O)

Batch Preparation (for 20 g product)

- (1) [59.4 g water + 89.6 g TEAOH (40%) + 0.53 g sodium chloride + 1.44 g potassium chloride], stir until dissolved
- (2) [(1) + 29.54 g silica], stir until homogenized (10 minutes minimum)
- (3) [20.0 g water + 0.33 g sodium hydroxide + 1.79 g sodium aluminate], stir until dissolved
- (4) [(2) + (3)], stir for 10 minutes, (gives a thick gel)

Crystallization

Vessel: 60 mL stainless steel autoclaves with Teflon liners

Temperature: $135 \pm 1^\circ\text{C}$

Time: 15 to 20 hours

Agitation: autoclaves are rotated (60 rpm) ^c

Product Recovery

- (1) Quench autoclaves in cold water, product pH = 12.8 ± 0.1
- (2) Centrifuge (10,000 rpm), wash until pH ~9 and dry overnight (77°C)
- (3) Yield: 9.9 ± 0.2 g of solid / 100 g gel (~ 90% on Al)

Product Characterization

XRD: zeolite beta (no other phases)

Elemental Analysis (content per unit cell): $\text{Na}_{0.9}\text{K}_{0.62}(\text{TEA})_{7.6}[\text{Al}_{4.53}\text{Si}_{59.47}\text{O}_{128}]^{\text{d}}$
(Si/Al = 13.1 ± 0.1)

Crystal Size and Habit: The crystals are round-shaped. They do not show any particular crystal habit. Average crystal size is 0.20 μm , and the crystal size distribution is very narrow. (The size of ~90% of crystals is between 0.10-0.30 μm)

References

- [1] M. A. Cambor, J. Pérez-Pariente, Zeolites 11(1991) 202
- [2] M. A. Cambor, A. Mifsud, J. Pérez-Pariente, Zeolites 11(1991) 792

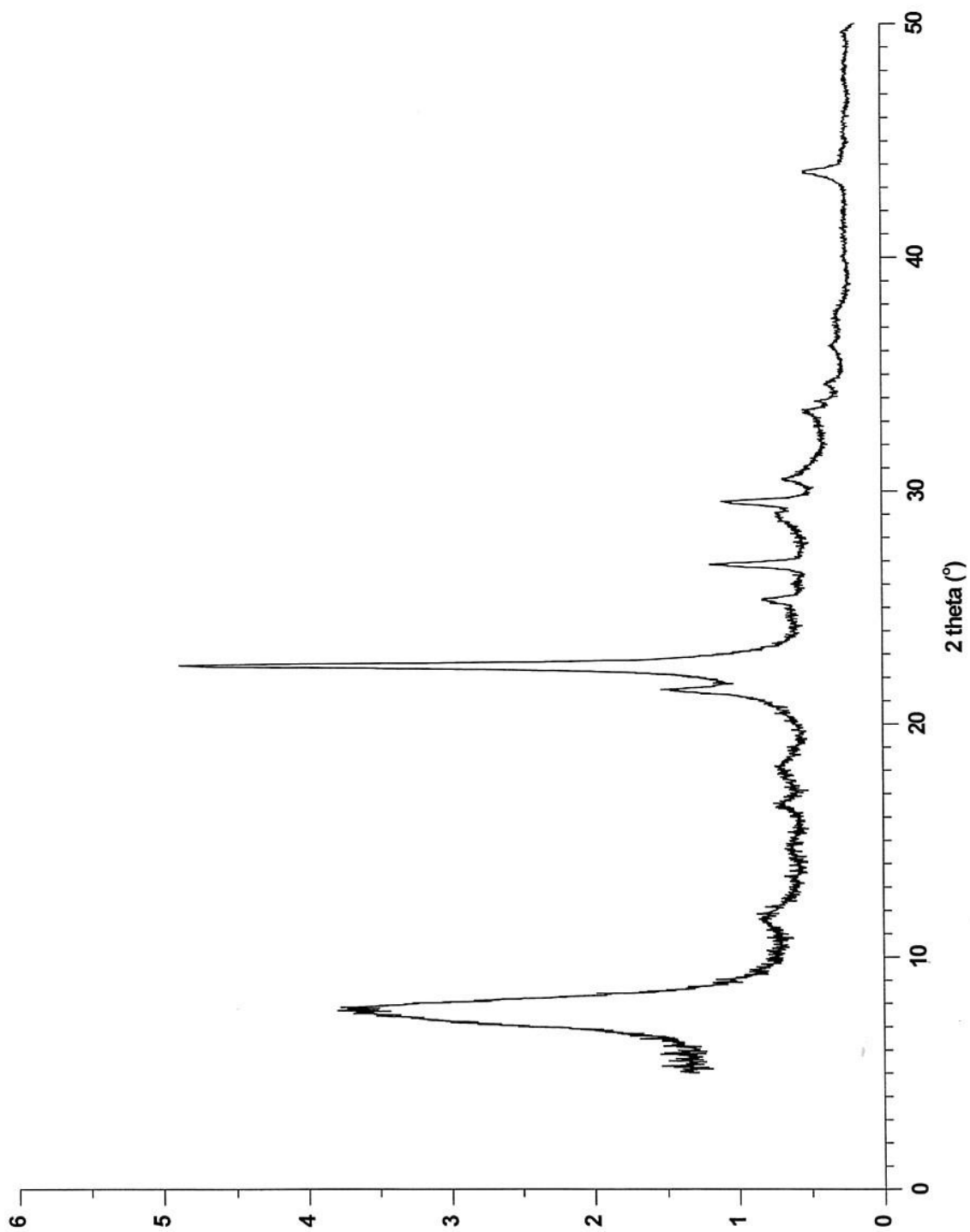
Notes

- a. Highly siliceous beta (Si/Al ~ 100 can be obtained by using tetraethyl-orthosilicate as silica source [2].
- b. $\text{OH}/\text{SiO}_2 = 0.56$
- c. In the specific synthesis conditions given in the recipe, the agitation has practically no influence on the properties of the product. However, by using different synthesis conditions, large differences in total crystallization time, average crystal size and crystal size distribution can be found between static and agitated synthesis.
- d. Excess cations assumed to be occluded TEAOH or TEA^+ compensating SiO-structure defects.

BEA

Beta

Si(93), Al(7)



BEA

Sn-Beta

Si(130), Sn(1)

Contributed by W. Fan and C.-C Chang

Verified by M. Zarrour, L. Tosheva

Type Material (SnO₂)(SiO₂)₁₃₀

Method Preparation of seed solution according to references [1-3]
Preparation of Sn-Beta according to references [3-5]

Batch Composition

Seed crystals: 1 SiO₂ : 0.01 Al₂O₃ : 0.36 TEAOH : 0.014 Na₂O : 13.2 H₂O

Sn-Beta crystallization gel:^a 1 SiO₂ : 0.008 SnO₂ : 7.5 H₂O : 0.54 TEAO₂ : 0.54 HF

Source Materials

deionized water (DI) tetraethylorthosilicate
(Alfa Aesar) silica sol, Ludox HS-30 (Aldrich)

tetraethylammonium hydroxide 35 wt.% (Alfa Aesar or SACHEM)

sodium hydroxide (Fisher)

aluminum isopropoxide (Aldrich)

tin (IV) chloride hydrate (Alfa Aesar)

nitric acid 70% (Fisher) hydrofluoric

acid 49% (Alfa Aesar) **Batch**

Preparation (for ~1 g product) I.

Preparation of seed crystals

- (1) Dissolve 0.1 g sodium hydroxide in 11.83 g tetraethylammonium hydroxide in a 50 mL polypropylene centrifuge tube under magnetic stirring.
- (2) Add 17.85g silica (Ludox HS-30) to the above solution dropwise under stirring, clear suspension is formed.
- (3) Cover and stir for 24 hours at room temperature.

II. Preparation of Sn-Beta

- (1) Add 11.43 g of tetraethylorthosilicate to 12.34 g of tetraethylammonium hydroxide solution in a 50 mL plastic beaker under magnetic stirring.
- (2) After stirred for 1 hour, a clear solution is formed.
- (3) Add 0.15 g of tin (IV) chloride hydrate (dissolved in 0.96 g DI) into the solution under stirring.
- (4) Keep stirring in a fumed hood at room temperature to evaporate ethanol (from hydrolysis of tetraethylorthosilicate) and water. The total weight loss to be 12.01 g.^b
- (5) Add 0.745 mL seed solution (0.175 g/mL, corresponding to 4 wt.% silica with respect to tetraethylorthosilicate) to the viscous clear solution, and mix by plastic spatula.
- (6) Add 1.034 mL hydrofluoric acid to the resulting solution, and mix by plastic spatula; dense gel is formed.

Crystallization

I. Crystallization of seed crystals

Vessel: Teflon-lined stainless steel autoclave

Temperature: 120° C

Time: 3 days

Agitation: no.

II. Crystallization of Sn-Beta (3 g of prepared gel)

Vessel: 50 mL Teflon-lined stainless steel autoclave

Temperature: 140° C

Time: 2 days

Agitation: 3 rpm (tumbling oven)

Product Recovery

I. Seed crystals

- (1) Remove reactor from oven and quench in tap water.
- (2) Milky slurry is obtained; centrifuge and wash product with ~200 mL DI until pH of supernatant is close to neutral.
- (3) Treat 2.5 mL of the seed crystals solution (0.2 g/mL) with 25 mL nitric acid in a stainless steel autoclave at 80 °C for 24 hr.^c
- (4) Remove reactor from oven and quench in tap water.
- (5) Centrifuge and wash product with DI until pH of supernatant is close to neutral.
- (6) Redisperse the seeds by sonication in an ultrasonic water bath for 1 hour.
- (7) Measure the seed concentration by drying 0.15 mL of the solution (weighted) in 80 °C overnight and weighing the obtained solids. The concentration of the crystal is 0.163 g per gram solution (or 0.175 g per mL solution).^d

II. Sn-Beta

- (1) Remove reactor from oven and quench in tap water.
- (2) White precipitate and solution are obtained; wash and recover the product by filtration with 1 L DI.
- (3) Dry at 80 °C in oven overnight.
- (4) Obtain 0.82 g dry product.
- (5) Calcination under air: 1 °C/min ramp to 550 °C and hold for 12 hr.

Product Characterization

XRD: *BEA

Elemental analysis: 130 SiO₂ : 1 SnO₂

Crystal size and habit:

Seeds: ~160 nm spherical crystals.

Sn-Beta: 0.5 to 1 μm in length and width, 0.1-0.2 μm in thickness, truncated bipyramidal crystals.

References

- [1] S. Mintova, V. Valtchev, T. Onfroy, C. Marichal, H. Knözinger and T. Bein, *Microporous Mesoporous Mater.* 90 (2006) 237
- [2] H. Y. Chen, J. Wydra, X. Y. Zhang, P. S. Lee, Z. P. Wang, W. Fan and M. Tsapatsis, *J. Am. Chem. Soc.* 133 (2011) 12390
- [3] C.-C. Chang, Z. Wang, P. Dornath, H. J. Cho and W. Fan, *RSC Adv.* 2 (2012) 10475
- [4] S S. Valencia and A. Corma, Stannosilicate molecular sieves, U.S. Patent 5,968,473, 1999

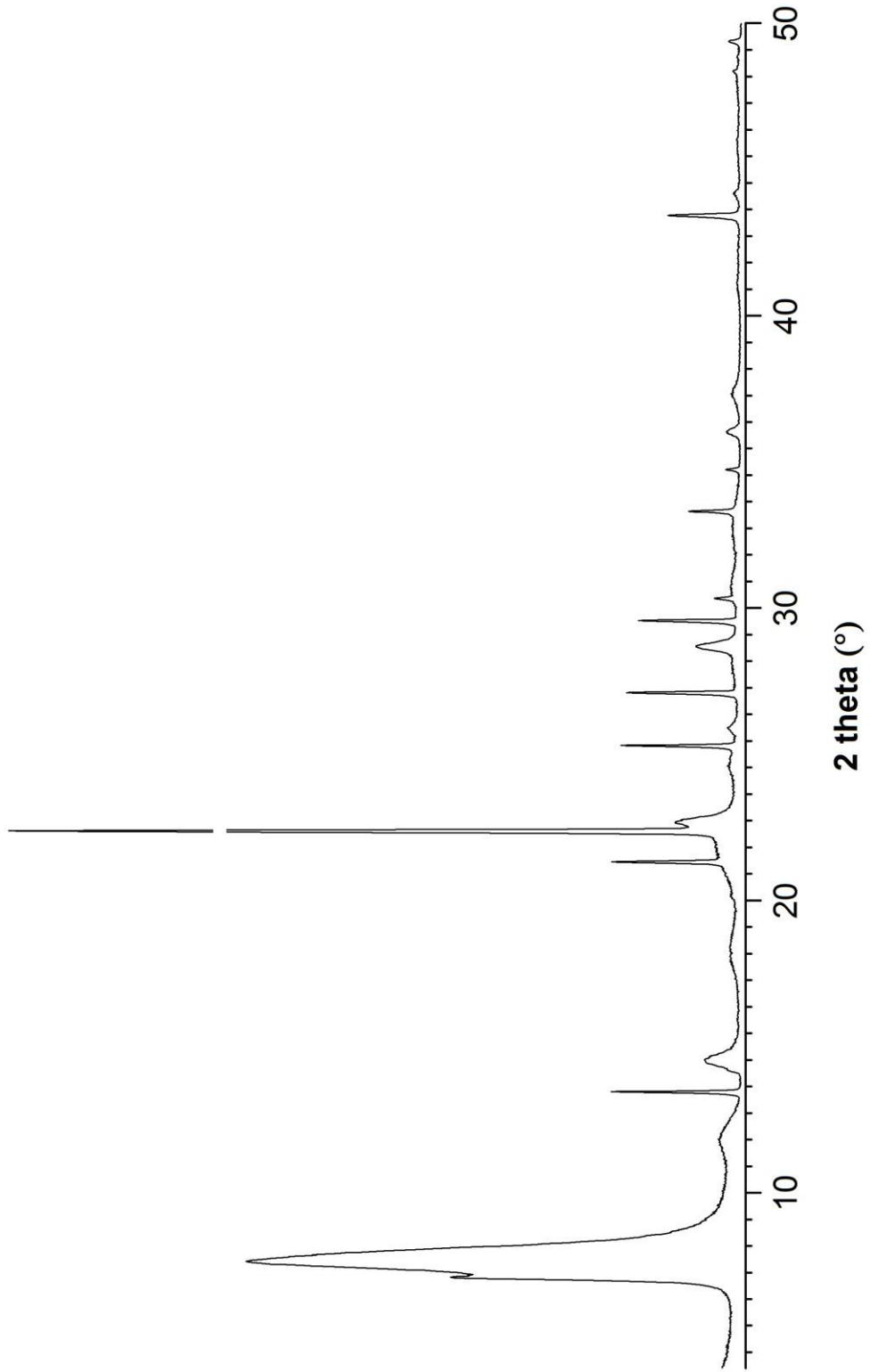
[5] A. Corma, L. T. Nemeth, M. Renz and S. Valencia, Nature 412 (2001) 423

Notes

- a. Not including seed crystals.
- b. The weight loss can be different depending on the concentration of seed crystal solution.
- c. The seed solution is not dried; after washing re-disperse in DI by sonication.
- d. The concentration of the seed solution can be different; adjust the amount of water to be evaporated accordingly.

Sn-Beta

Si(130), Sn(1)



BEA

[Ti,Al] Beta

Si(95), Ti(3), Al(2)

Contributed by Dilson Cardoso

Verified by M. Cambor and W. S. Ahn

Type Material (TEA) $1.5[\text{Ti}_{2.0}\text{Al}_{1.5}\text{Si}_{60.5}\text{O}_{128}]$ (TEA = tetraethylammonium)

Method S. Jahn, D. Cardoso [1,3], M. A. Cambor, A. Corma, J. Pérez-Pariente [2]

Batch Composition 0.033 TiO₂ : SiO₂ : 0.0026 Al₂O₃ : 0.269 (TEA)₂O : 15.5 H₂O

Source Materials

tetraethylammonium hydroxide (Aldrich, 35% TEA-OH aqueous solution)
tetraethylorthotitanate (Aldrich, 99%)
silica (Degussa Aerosil 380, 99+%)
aluminum nitrate (Al(NO₃)₃ 9 H₂O) deionized water

Batch Preparation (for ~1 g product)

- (1) [13.24 g tetraethylammonium hydroxide solution + 0.44 g tetraethylortho-titanate], mix in a glove box; stir for 10 minutes ^a
- (2) [(1) + 3.52 g silica], stir for 15 minutes
- (3) [0.11 g aluminum nitrate + 7.69 g water], stir until dissolved
- (4) [(3) + (2)], stir until homogenized (10 minutes minimum) ^b

Crystallization

Vessel: 50 mL stainless steel autoclave with Teflon liner
Time: 60-96 hours
Temperature: 140°C
Agitation: optional
Final pH: ~12.5

Product Recovery

- (1) Quench autoclave in cold water
- (2) Centrifuge (7000 rpm) and wash until pH is about 9
- (3) Dry overnight at 80°C
- (4) Yield: 3-4 g/100 g batch (about 90% based on Al, 40% on Ti and 25% on Si)

Product Characterization

XRD: zeolite beta (no other phases)
Elemental analyses: $\text{Ti}_{2.0}\text{Al}_{1.5}\text{Si}_{60.5}\text{O}_{128}$ (for material with 96 hours crystallization. As synthesized material contains TEA⁺ cations)
Crystal size and habit: round-shaped particles with average size 0.28 μm (for 96 hours crystallization) and a narrow size distribution

References

- [1] S. L Jahn, P. A. P. Nascente, D. Cardoso, Zeolites 19 (1997) 416
- [2] M. A. Cambor, A. Corma, J. Pérez-Pariente, Zeolites 13 (1993) 82

- [3] S. L. Jahn, D. Cardoso, in Proceedings of 12th International Zeolite Conference, Vol. III, M. M. J. Treacy, B. K. Marcus, M. F. Bisher, J. B. Higgins (eds.), Materials Research Soc., Warrendale, PA, USA (1998), pp 1885-1892

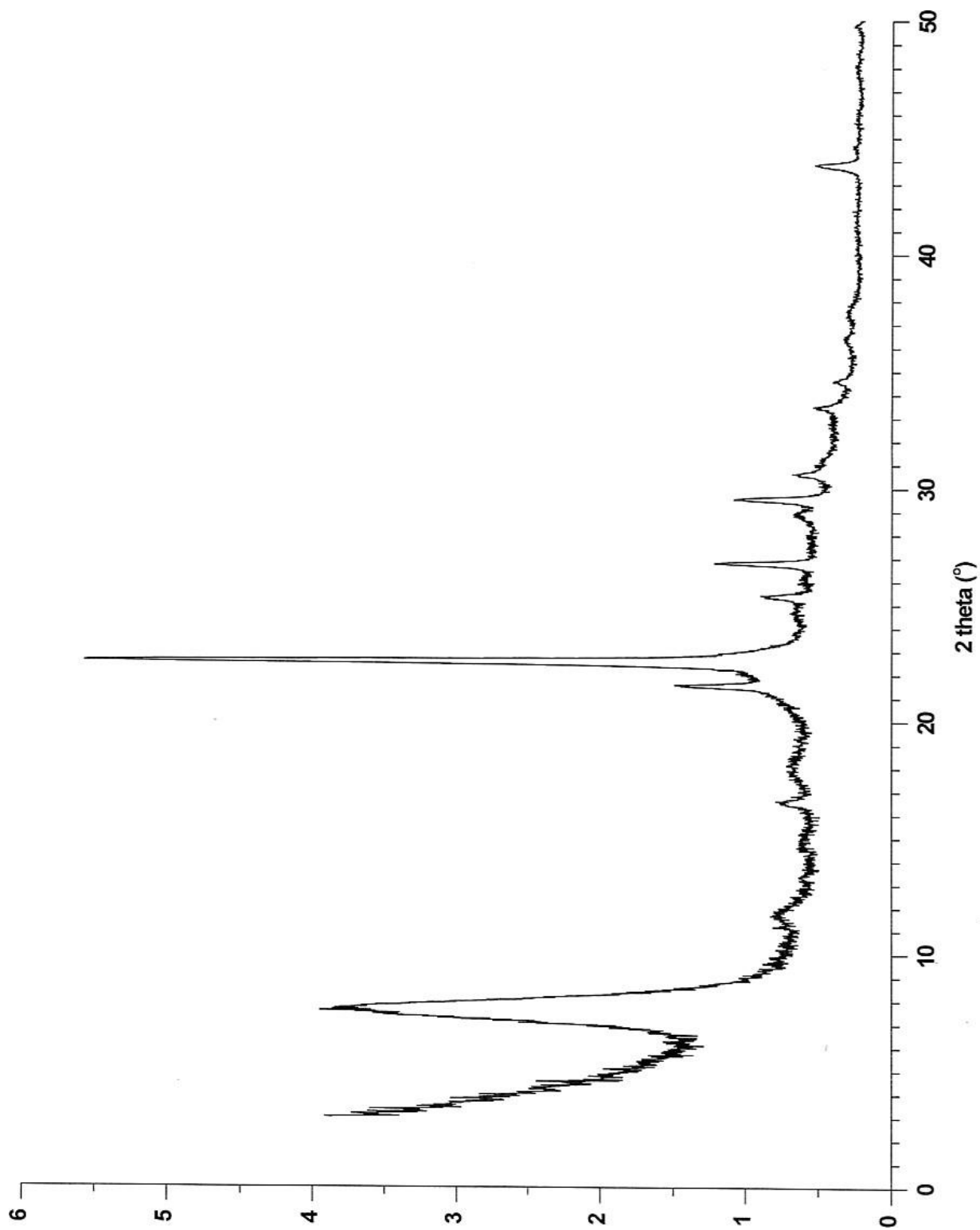
Notes

- a. Tetraethylorthotitanate hydrolyses very rapidly under normal atmospheric conditions forming extra framework TiO_2 . Using this Ti-source, the gel must be prepared in a glove box.
- b. If this equipment is not available, the gel can be prepared under normal atmosphere using a solution of tetraethylortho-titanate in isopropyl alcohol (TEOTi/iPrOH molar ratio of 1/10). This results in a small loss in solid yield.
- c. It is difficult to synthesize the beta structure in total absence of aluminum. This recipe employs the minimum content of this element (Si/Al ~400).
- d. The solid particles formed during synthesis are very small, and it is very difficult to filter them. Unfortunately, the appropriate method for purification is by centrifugation.

BEA

[Ti,Al] Beta

Si(95), Ti(3), Al(2)



Contributed by Manuel Moliner

Verified by B. Bellet, J.-L. Paillaud, V. Georgieva

Type Material: $(\text{SDA}^+)_{2.5} (\text{SiO}_2)_{20.6} (\text{GeO}_2)_{11.4} (\text{F}^-)_2 : w \text{ H}_2\text{O}$
(SDA = 1-benzyl-1,4-diazabicyclo [2.2.2]octane)^a

Method: A. Corma, M.T. Navarro, F. Rey, J. Rius, S. Valencia [1]

Batch Composition: 0.66 SiO₂ : 0.33 GeO₂ : 0.5 SDAOH : 0.5 HF : 8 H₂O

Source Materials

deionized water (DI)

1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich, 98%)

benzyl chloride (Aldrich, 99%)

ethyl acetate (Scharlab, 98%)

amberlite[®] IRN78, hydroxide form (Supelco)

germanium oxide (Aldrich, 99.99 %)

tetraethylorthosilicate (Aldrich, 99.99%)

hydrofluoric acid (Aldrich, 48% in water)

Batch Preparation (for 2.7 g dry product)

- (1) [10.23 g benzyl chloride + 13.7 g 1,4-diazabicyclo[2.2.2]octane + 150 g ethyl acetate], stir in a flask for 24 h, at room temperature.^a
- (2) recover solid (1) by filtration and wash with 250 g diethyl ether.
- (3) dry solid (2) in vacuum at room temperature for 5 h.
- (4) [solid (3)^b + 70 g Amberlite[®] + 75 g water], stir for 24h at room temperature, remove Amberlite[®] by filtration.
- (5) [31.25 g solution (4)^c + 1.74 g germanium oxide], stir until dissolved.
- (6) [solution (5) + 6.94 g tetraethylorthosilicate], stir 10 minutes.
- (7) [solution (6) + 1 g HF], stir until 23 g are evaporated (water + ethanol) for adjusting the gel composition

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 150° C

Time: 3 days

Agitation: no

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at 100°C
- (4) Yield: 2.7 g

Product Characterization

XRD: BEC;

Elemental analysis: 2 SiO₂: GeO₂^d

Crystal size and habit: rod like crystals with size below 1 μm

Reference

[1] A. Corma, M.T. Navarro, F. Rey, J. Rius, S. Valencia, *Angew. Chem. Ind. Ed.* 40 (2001) 2277

[2] G. Sastre, J.A. Vidal-Moya, T. Blasco, J. Rius, J.L. Jordá, M.T. Navarro, F. Rey, A. Corma, *Angew. Chem. Ind. Ed.* 41 (2002) 4722

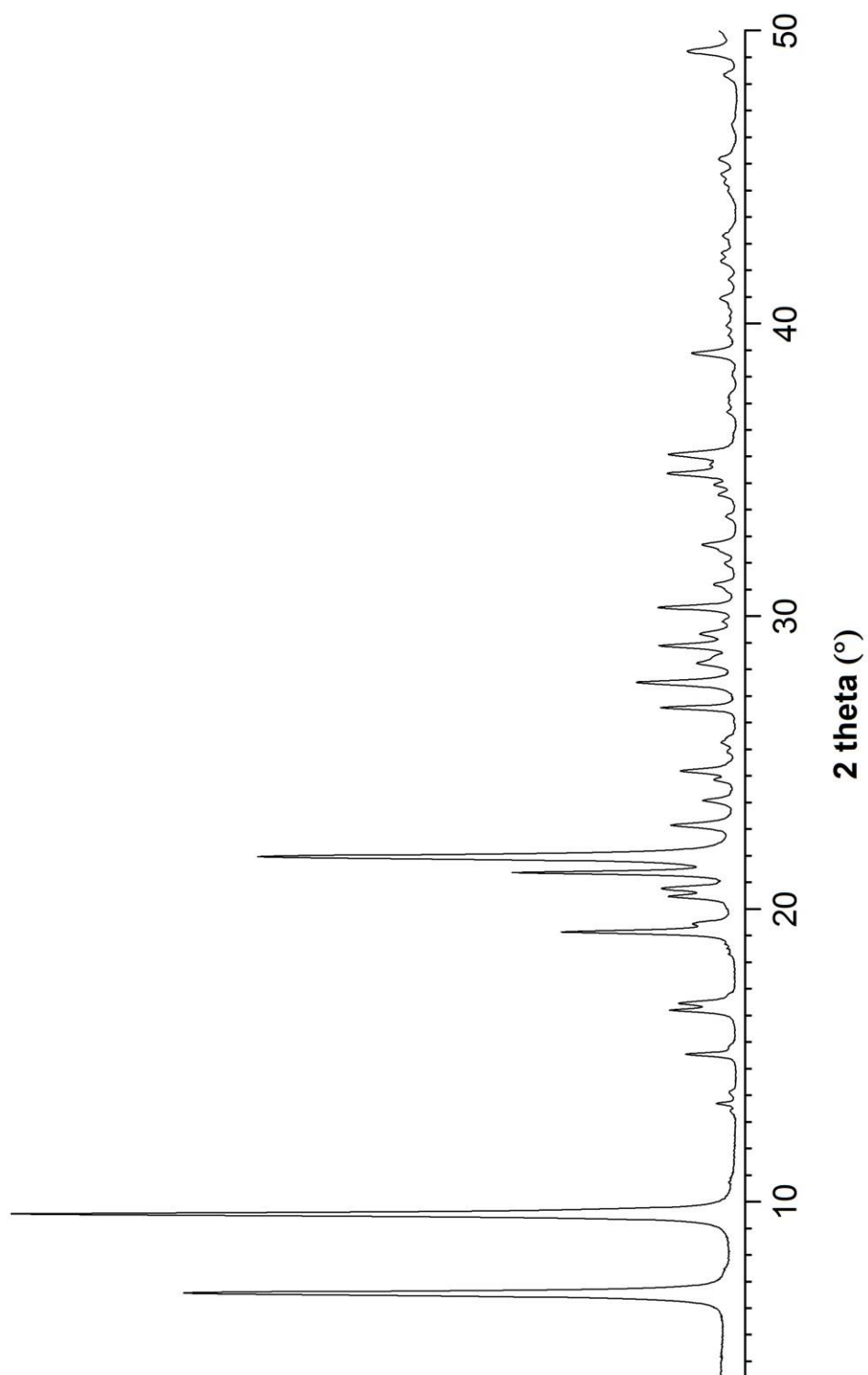
Notes

- a. SDA made in house
- b. 90 % yield of SDA
- c. [0.8M] SDAOH, titrated with HCl 0.1 N
- d. as-synthesized; organic content not specified

BEC

ITQ-17

Si(67), Ge(33)



CAN

Cancrinite

Si(50), Al(50)

Contributed by J.-Ch. Buhl

Verified by C. Williams and M. Bottale

Type Material $\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3 \cdot 4\text{H}_2\text{O}$

Method J.-Ch. Buhl [1]

Batch Composition 93 Na_2O : Al_2O_3 : 2 SiO_2 : 10 NaHCO_3 : 1386 $\text{H}_2\text{O}^{\text{a}}$

Source Materials

distilled water

sodium hydroxide (Merck pellets, analytical grade)

kaolin (Fluka)

sodium bicarbonate (Merck, analytical grade, NaHCO_3)

Batch Preparation (for 0.6 g product)

(1) [45 mL water + 14.4 g sodium hydroxide], stir until dissolved

(2) [(1) + 0.5 g kaolin + 1.7 g sodium bicarbonate], mix until uniform slurry

Crystallization

Vessel: Teflon-lined steel autoclave

Temperature: 200 °C

Time: 48 hours

Agitation: none

Product Recovery

(1) Cool to ambient temperature. Filter

(2) Wash free of NaOH residuals (approximately 150 mL water)

(3) Dry at 80 °C

(4) Yield: close to 100%

Product Characterization

XRD: CAN; small amounts of a disordered phase between CAN and SOD and amorphous material could be detected in the polycrystalline sample [1,2]

Elemental Analysis: $\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3 \cdot 4\text{H}_2\text{O}^{\text{b}}$

Crystal Size and Habit: small elongated needles

References

[1] J.-Ch. Buhl, *Thermochimica Acta* 178 (1991) 19

[2] G. Hermeler, J.-Ch. Buhl, W. Hoffmann, *Catalysis Today* 8 (1991) 415

[3] C. Liu, S. Li, K. Tu, R. Xu, *J. Chem. Soc., Chem. Commun.* (1993) 1645

Notes

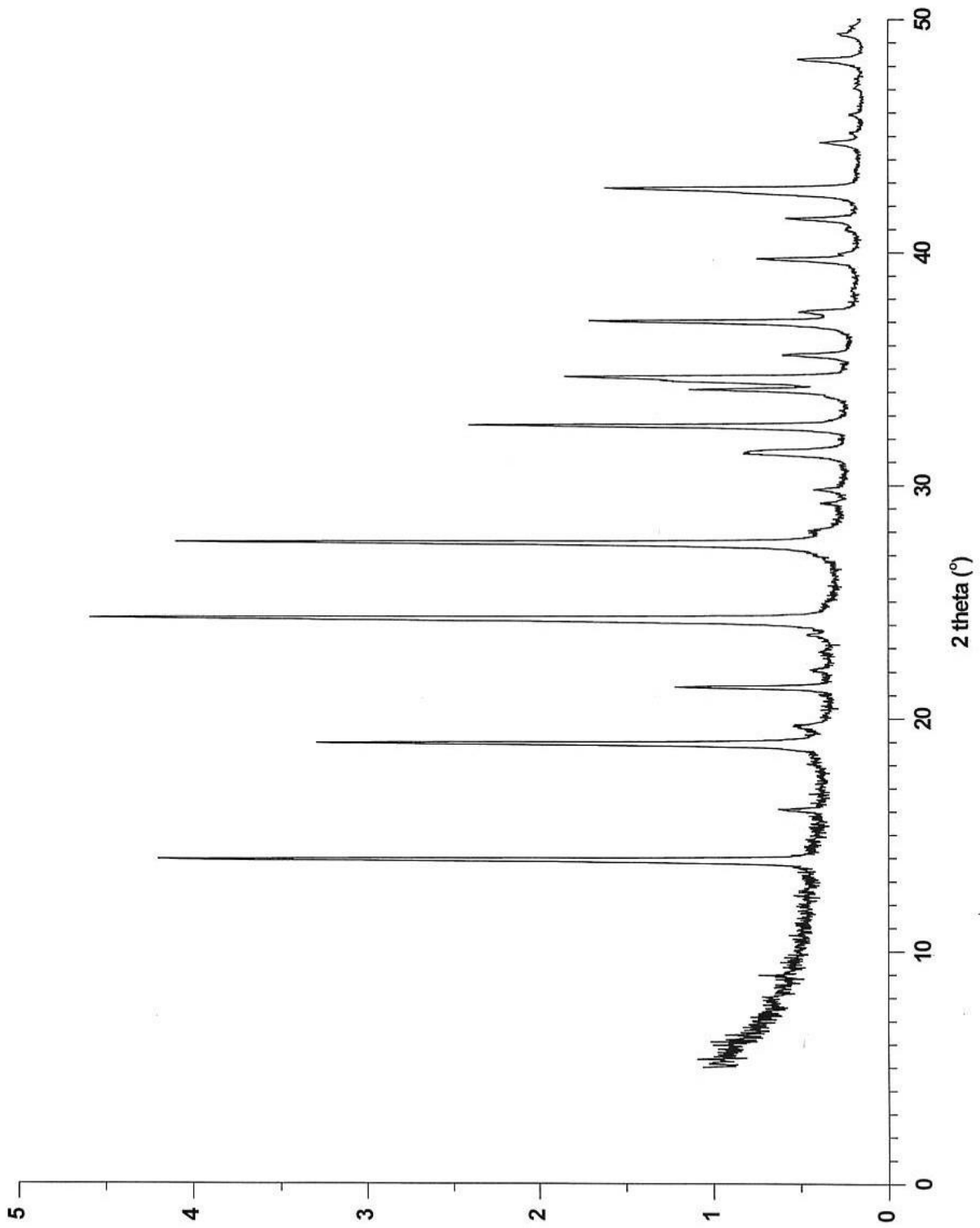
a. CAN-formation in the water-free system is reported using butane-1,3-diol. [3]

- b. Analysis of the guest anions according to the combination of simultaneous thermal analysis (TG, DTG, DTA), IR-spectroscopy and MAS NMR (^{13}C).
- c. Single crystals can be prepared from a gel consisting of [50 mg kaolin (heated at 1400°C for two hours) + 168 mg NaHCO_3 + 320 mg NaOH + 1 mL distilled water] treated at 500°C for 48 hours in a silver-lined steel autoclave.

CAN

Cancrinite

Si(50), Al(50)



CDO

CDS-1

Si(100)

Contributed by Yoshihiro Kubota

Verified by S. Inagaki, K. Komura, T. Sano, B. Bellet, J-L. Paillaud

Type Material: CDS-1, Si₃₆O₇₂
PLS-1, Si₁₈O₃₄(OH)₄K_{1.3}·1.7(CH₃)₄NOH (precursor material of CDS-1)

Method: T. Ikeda, Y. Akiyama, Y. Oumi, A. Kawai, and F. Mizukami [1]

Batch Composition: 1.0 SiO₂ : 0.015 KOH : 0.22 (CH₃)₄NOH : 16.2 H₂O : 3.41 1,4-dioxane

Source Materials

deionized water (DI)
potassium hydroxide (0.5 mol/L aqueous solution, KOH)
tetramethylammonium hydroxide (15 wt.% aqueous solution, (CH₃)₄NOH)
1,4-dioxane (Sigma Aldrich)
silica (Cab-O-Sil M5)

Batch Preparation (for 4 g dry product as PLS-1)

- (1) [25.0 g water + 10.0 g silica + 22.0 g (CH₃)₄NOH aq.^a + 0.5 g KOH aq.^b], stir in a vessel
- (2) [(1) + 50.0 g 1,4-dioxane], vigorously stir for 1 h at room temperature

Crystallization

Vessel: Teflon-lined stainless steel autoclave (300 mL)^c
Temperature: 150 °C
Time: 10 days
Agitation: no

Product Recovery

- (3) Filter and wash with acetone and water
- (4) Dry at 70 °C in a convection oven for 12 h
- (5) Yield: 3.5 g

Calcination^d

From 400 to 900 °C; under vacuum at 10⁻³ to 10⁻⁸ Torr^e

Product Characterization

XRD: CDO
Crystal size and habit: thin platelet-like crystals with a length < 2 μm and a thickness of > 100 nm (approximately).

Reference

- [1] T. Ikeda, Y. Akiyama, Y. Oumi, A. Kawai, F. Mizukami, *Angew. Chem. Int. Ed.* 43 (2004) 4892.
- [2] S. Inagaki, T. Yokoi, Y. Kubota, T. Tatsumi, *Chem. Commun.* (2007) 5188.

- [3] A. Kawai, T. Ikeda, Y. Kiyozumi, H. Chiku, F. Mizukami, Mater. Chem. Phys. 99 (2006) 470
- [4] K. Komura, T. Kawamura, Y. Sugi, Catal. Commun. 8 (2007) 644

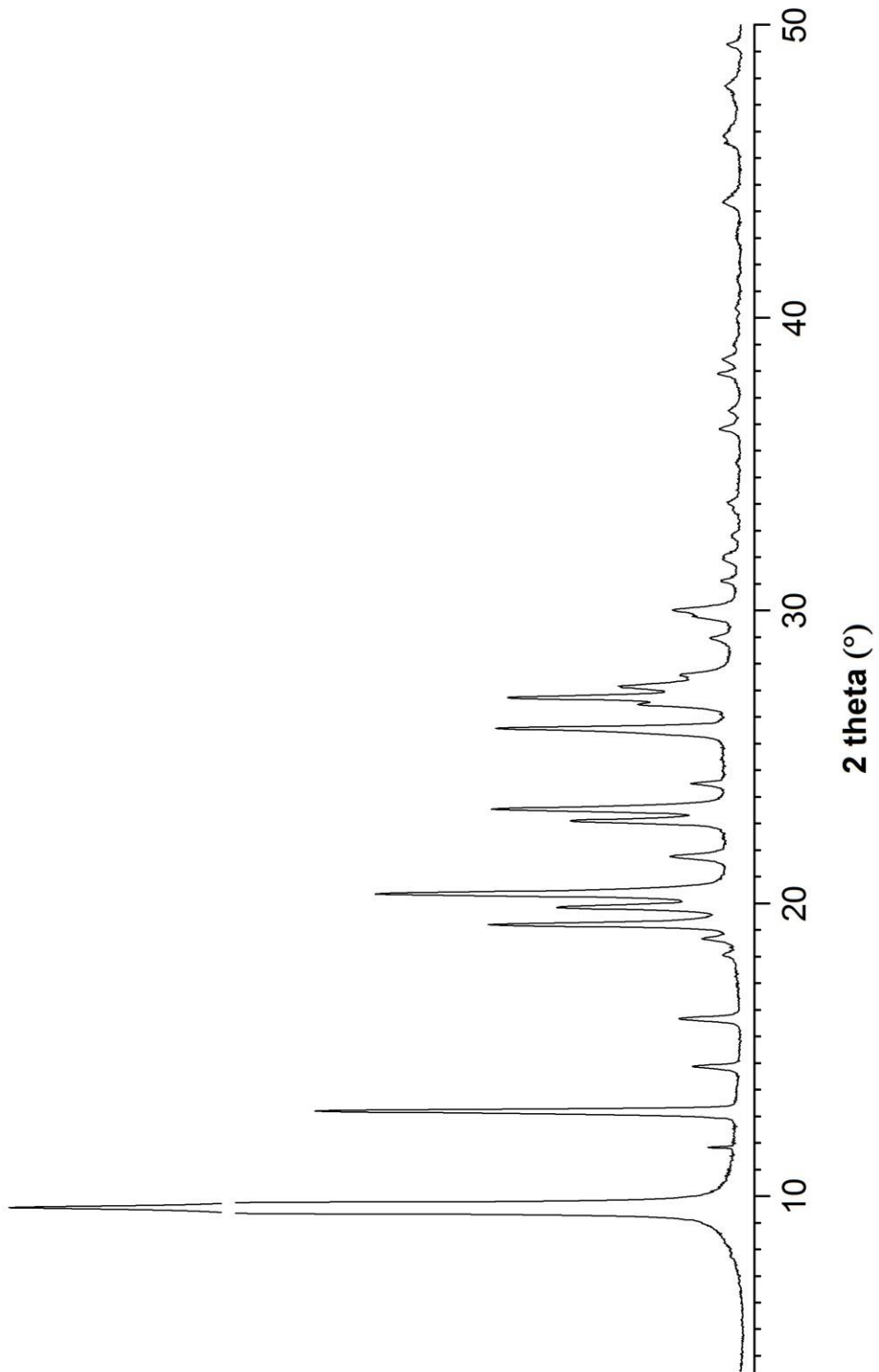
Notes

- a. 15 wt.% aqueous solution
- b. 0.5 mol/L aqueous solution
- c. 150 mL autoclave is also utilized
- d. The topotactic conversion from PLS-1 to CDS-1 requires the calcination treatment.
- e. Typically, 500 °C, 12 h, ambient pressure (evacuation not required), according to Ref. [2]

CDO

CDS-1

Si(100)



CHA

Chabazite

Si(68), Al(32)

Contributed by Thomas R Gaffney

Verified by J. Warzywoda, J. Cejka and Liu Xinjin

Type Material $K_{11}[Al_{11}Si_{25}O_{72}]:40 H_2O$

Method M. Bourgogne, J.-L Guth, R Wey [1]

Batch Composition 0.17 Na₂O : 2.0 K₂O : Al₂O₃ : 5.18 SiO₂ : 224 H₂O

Source Materials

demineralized water

potassium hydroxide (J. T. Baker reagent grade, 45% KOH solution)

(Na,H) Zeolite Y (UOP LZY-64)^a

Batch Preparation (for 25 g dry product)

(1) [198.2 mL water + 26.8 mL KOH (45% solution), mix

(2) [(1) + 25.0 g Zeolite Y], seal in a polypropylene bottle and shake for 30 s

Crystallization

Vessel: polypropylene bottle with a screw-top lid

Temperature: 95 °C (steam chamber)

Time: 96 hours

Agitation: none

Product Recovery

(1) Remove bottle from the steam chamber and filter to recover solids while still hot ^b

(2) Wash two times with 500 mL water per wash

(3) Dry at ambient temperature ^c

(4) Yield: 99% based on alumina, 83% based on silica

Product Characterization

XRD: CHA with no reflections from FAU. Competing phases; FAU when insufficient crystallization times are used ^d

Elemental Analysis: 0.02 Na₂O : 0.98 K₂O : Al₂O₃ : 4.32 SiO₂ (dry basis)^{e,f}

Crystal Size and Habit: Sub-micron crystallites, 0.1 μm on average, multifaceted (some can be seen to be hexagonal platelets)

Reference

[1] M. Bourgogne, J.-L Guth, R. Wey, US Patent 4 503 024 (1985)

Notes

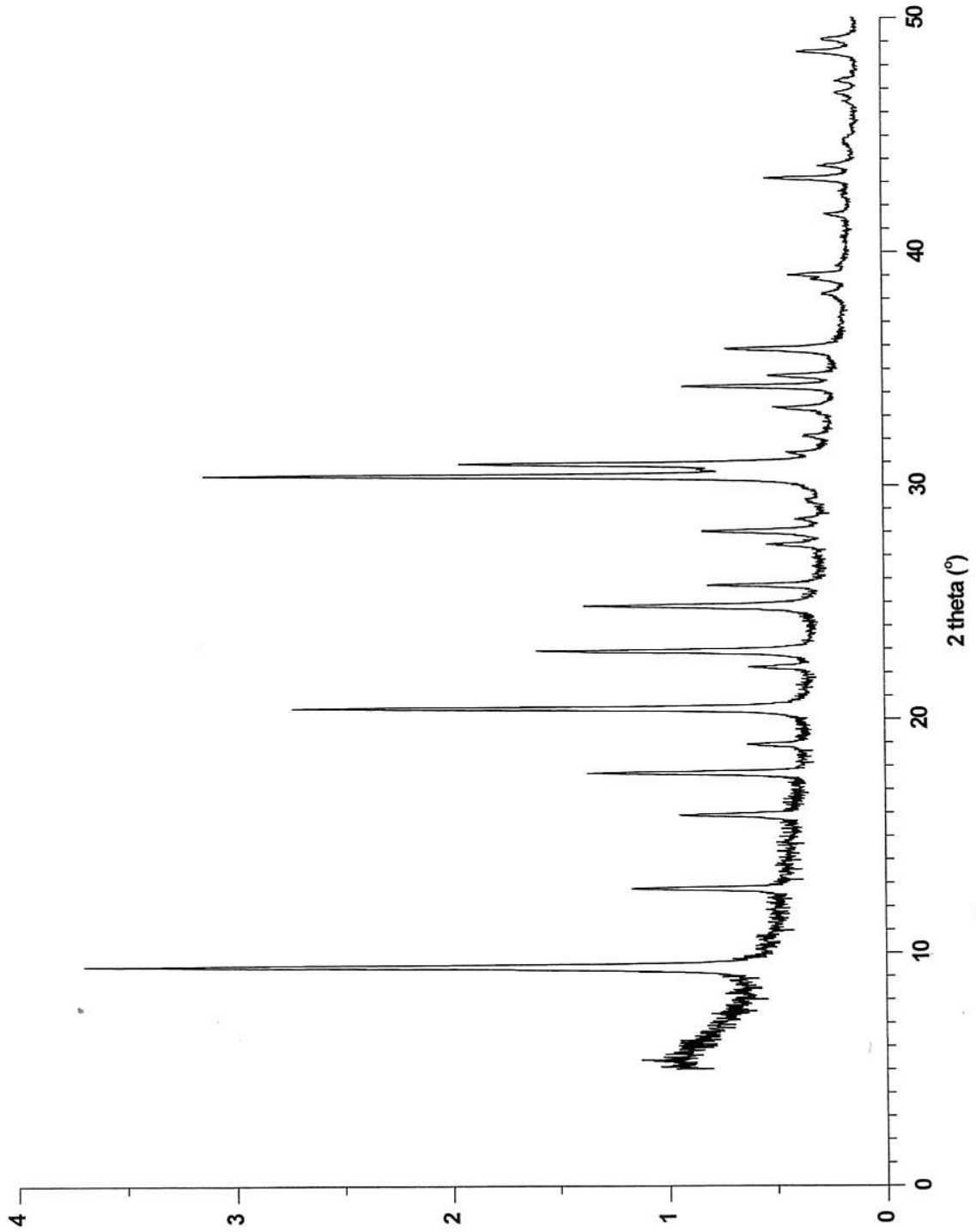
- a. The Na/Al ratio of the NaHY starting materials should be less than 0.17. LZY-64 was prepared by heating NH₄⁺ exchanged type Y to 550 °C (at 2 °C/minute) and calcining at 550 °C for 2 hours. Caution: ammonia is liberated during the calcination. Use adequate ventilation and safety precautions.

- b. pH = 13.5 after crystallization treatment.
- c. The product is stable to drying in an oven at 110°C.
- d. Converting samples of Zeolite Y which contain large crystals or are formed (pelleted, beaded) to chabazite requires longer reaction times.
- e. The framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 4.32 by ^{29}Si NMR.
- f. For preparing more siliceous product, Nalco 2326 silica (14.5% SiO_2) was used as the silica source. Synthetic chabazite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$ forms from a reaction mixture of composition: 0.17 Na_2O : 4.31 K_2O : Al_2O_3 : 8 SiO_2 : 500 H_2O . Addition of more silica to the reaction mixture (batch SiO_2 : $\text{Al}_2\text{O}_3 > 8$) leads to incomplete conversion of Zeolite Y, and the product is a mixture of CHA and FAU.

CHA

Chabazite

Si(68), Al(32)



Contributed by L T. Yuen and S. I. Zones

Verified by R. Lobo and L Schreyeck

Type Material (aRN, bNa) $[Al_{2.4}Si_{33.6}O_{72}] : wH_2O^a$ (w = 1 to 7)
(RN = N,N,N, trimethyl-1-adamantammonium)

Method S. I. Zones, R. A. Van Nordstrand [1]

Batch Composition 10 Na₂O : 2.5 Al₂O₃ : 100 SiO₂ : 4400 H₂O : 20 RN-OH

Source Materials

sodium hydroxide (1 N), (Baker, reagent grade)
N,N,N, trimethyl-1-adamantanionium hydroxide (RN-OH)(0.72M)^b
deionized water
aluminum hydroxide (Reheis F-2000 dried gel, 50% Al₂O₃)
fumed silica (Cab-Q-Sil, M5 grade, 97% SiO₂)

Batch Preparation (for 0.6 g product)

- (1) [2.00 g 1N NaOH + 2.78 g 0.72 M RN-OH + 3.22 water], add sequentially to the Teflon cup of a Parr 23 mL autoclave ^c
- (2) [(1) + 0.05 g aluminum hydroxide], mix until solution clears
- (3) [(2) + 0.60 g fumed silica], mix until uniform

Crystallization

Vessel: Teflon-lined 23 mL autoclave (Parr model 4745)
Temperature: 160°C ^d
Time: 4 days
Agitation: none

Product Recovery

- (1) Cool to room temperature ^e
- (2) Filter in a medium frit glass funnel
- (3) Wash with about one liter of water
- (4) Air dry at room temperature with vacuum pulling through frit
- (5) Yield: 0.57 g, 74% based on TO₂

Product Characterization

XRD: CHA (only crystalline phase); competing phases when observed: analcime or quartz; impurities can occur at this temperature or higher.
Elemental Analyses: RN is approximately 15 wt% and SiO₂/Al₂O₃ = 28 by ICP
Crystal Size and Habit: cubes of 2-5 μm with some occasional intergrowth.

References

- [1] S. I. Zones, R A. Van Nordstrand, Zeolites 8 (1988) 166
- [2] S. I. Zones, US Patent 4 544 538 (1985)
- [3] S. I. Zones, Trans. Faraday Soc. 87 (1991) 3709

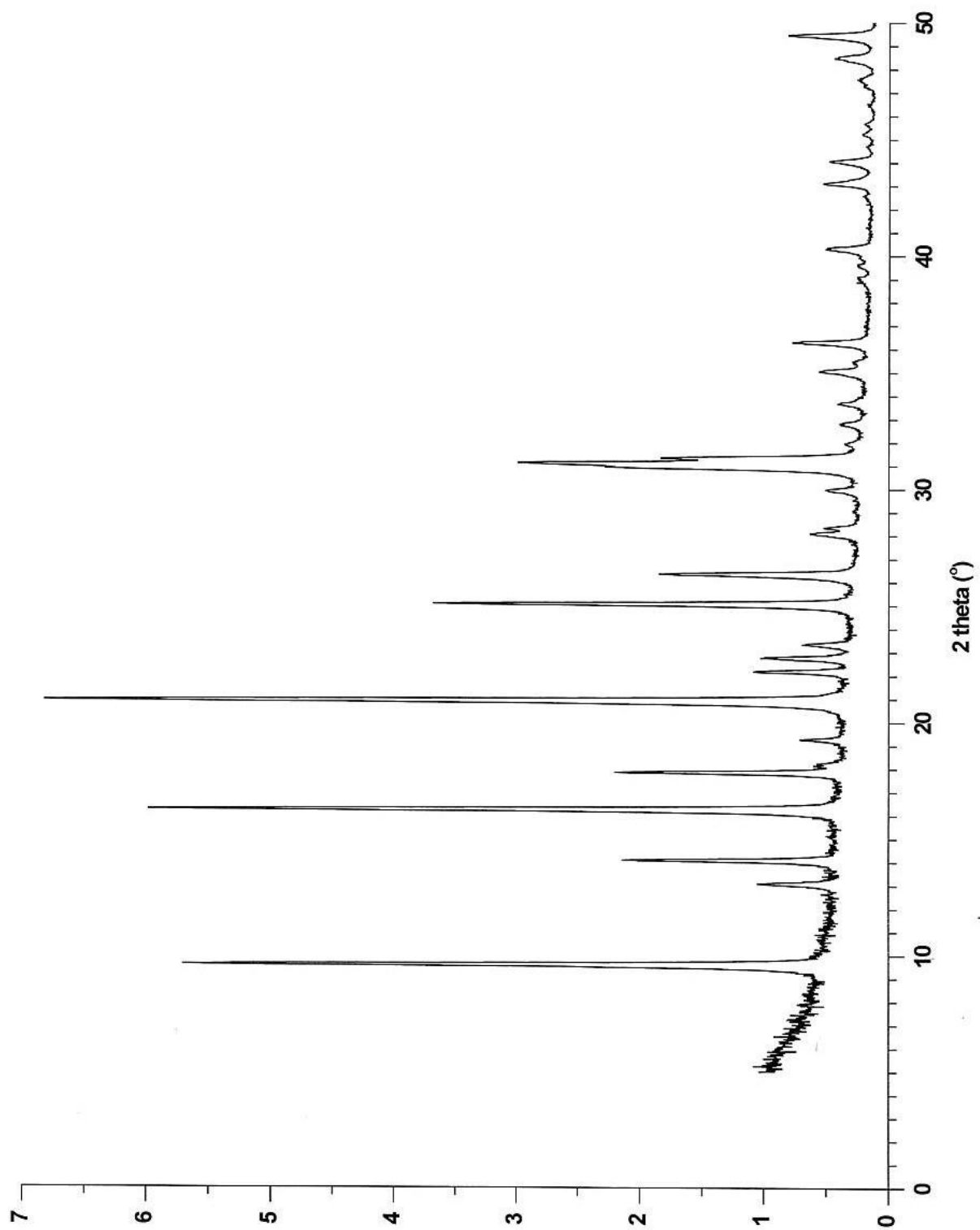
Notes

- a. Typical values: a 1.4 to 2.9, b = 0.7 to 4.3
- b. The description of template preparation is given in [2]. The fastest synthesis of this product is from FAU sources [3].
- c. The Teflon cup is washed between runs with HF (48%), water, KOH solution, and water again.
- d. The reactor is placed into a Blue M convection-heating oven preset at 160°C.
- e. PH of the treated batch should measure in the range of 12.20 to 12.64 using a calibrated probe.

CHA

SSZ-13

Si(93), Al(7)



CHA

SAPO-34

Al(47), P(32), Si(21)

Contributed by A. M. Prakash

Verified by J. López Nieto and N. Tusar

Type Material mR[Al₁₇P₁₂Si₇O₁₂] (R = morpholine)

Method A. M. Prakash, S. Unnikrishnan [1]

Batch Composition Al₂O₃ : 1.06 P₂O₅ : 1.08 SiO₂ : 2.09 R : 66 H₂O ^{a,b}

Source Materials

distilled water

phosphoric acid (Merck, 85%)

pseudoboehmite (Vista Catapal-B, 70% Al₂O₃)

fumed silica (Degussa Aerosil-200 99+% SiO₂)

morpholine (Aldrich, 99% C₄H₉O)

Batch Preparation (for 20 g product) ^c

- (1) [18.0 g water + 15.37 g phosphoric acid], mix
- (2) [(1) + 9.20 g pseudoboehmite], add slowly (2 hours) with stirring
- (3) [(2) + 10 g water], stir thoroughly for 7 hours
- (4) [4.09 g fumed silica + 11.62 g morpholine + 15 g water], mix thoroughly
- (5) [(3) + (4)], add (4) dropwise to (3) while stirring
- (6) [(5) + 24 g water], stir thoroughly for 7 hours; pH of gel = 6.4 to 7.5

Crystallization

Vessel: 150 mL Teflon-lined autoclave

Incubation: 24 hours at 38°C without agitation ^d

Temperature: 200°C

Time: 24 hours

Agitation: none

Product Recovery

- (1) Decant the mother liquor
- (2) Dilute with distilled water and filter
- (3) Wash 3 to 4 times with distilled water
- (4) Dry at 100°C for 6 hours
- (5) Yield: 98% based on alumina

Product Characterization

XRD: SAPO-34 (CHA) [1], $a_0 = 13.78 \text{ \AA}$, $c_0 = 14.85 \text{ \AA}$; competing phase: AlPO₄ (cristobalite) when silica and/or template concentration is low.

Elemental Analysis: 1.0 Al₂O₃: 0.68 P₂O₅: 0.87 SiO₂: 0.59 R: 1.07H₂O

Crystal size and habit: 5 to 20 μm crystals with cubic-like rhombohedral morphology. [1]

Reference

- [1] A. M. Prakash, S. Unnikrishnan, J. Chem. Soc. Faraday Trans. 90 (1994) 2291

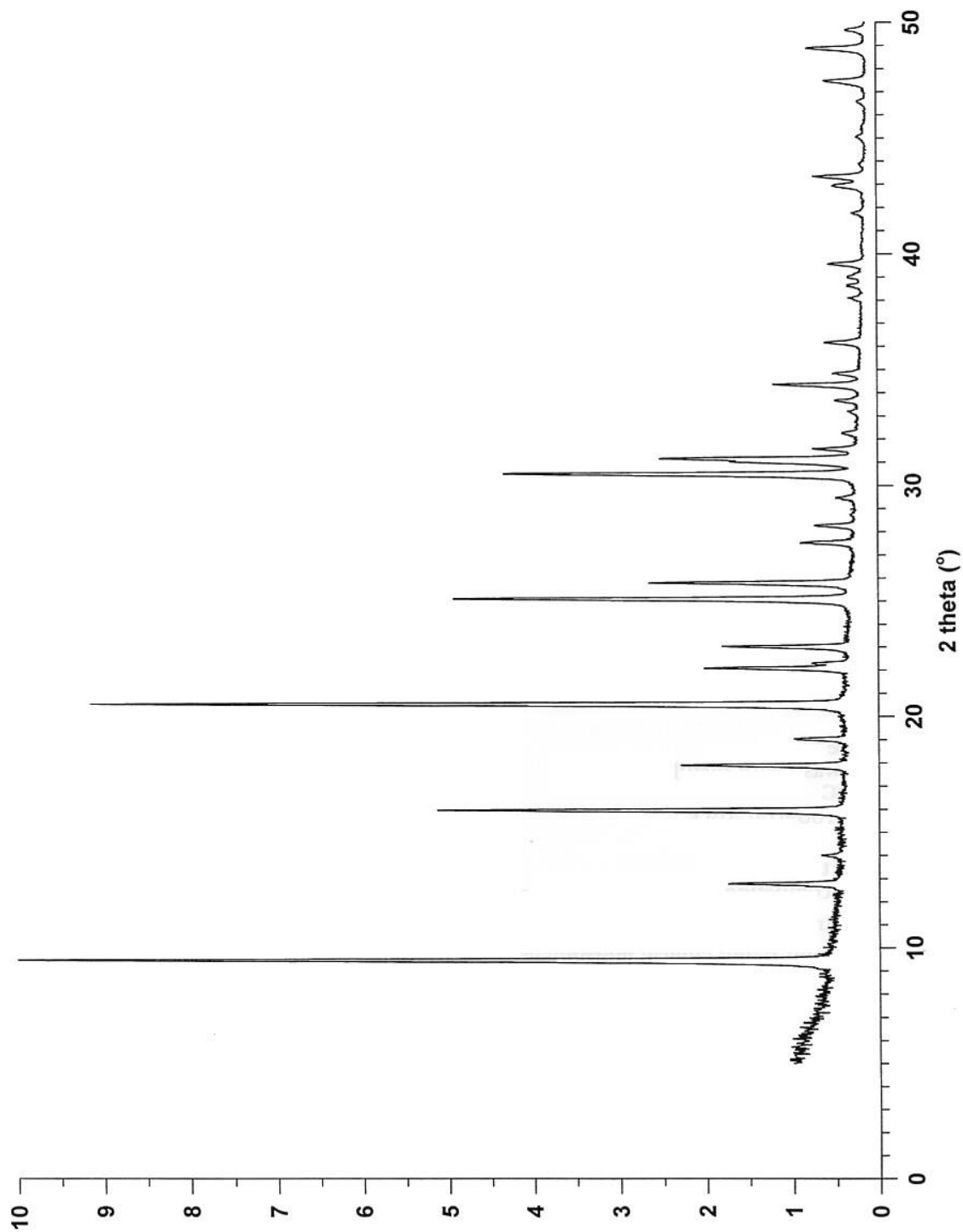
Notes

- a. H₂O includes water from phosphoric acid, pseudoboehmite and added water.
- b. Concentration of SiO₂ and organic template can vary over a range without affecting the phase purity. At low concentration of silica (SiO₂/Al₂O₃ ≤ 0.3) or template (R/Al₂O₃ ≤ 1.5), however, dense phase AlPO₄-cristobalite co-crystallizes with SAPO-34.
- c. Use Teflon or stainless steel equipment throughout.
- d. Although SAPO-34 crystallizes without aging, the crystallinity of the resulting product can be improved by aging.

CHA

SAPO-34

Al(47), P(32), Si(21)



CHA

SAPO-44

Al(48), P(34), Si(18)

Contributed by S. Ashtekar, S. V.V. Chilukuri and D. K. Chakrabarty

Verified by A. Prakash and He Chang-Qing

Type Material 5.0 (C₆H₁₁NH₂) [Si_{6.5}Al_{17.3}P_{12.2}O₇₂] wH₂O^a

Method S. Ashtekar, S. V.V. Chilukuri, D. K. Chakrabarty [1]

Batch Composition Al₂O₃:1.0 P₂O₅:1.0 SiO₂:1.9 R : 63 H₂O^b (R = cyclohexylamine)

Source Materials

distilled water
orthophosphoric acid (85% H₃PO₄)
pseudoboehmite (Catapal-B, Vista, 70% Al₂O₃)
cyclohexylamine (99+%)
fumed silica (99+% SiO₂)

Batch Preparation (for 16 g product)

- (1) [90 g water + 34.59 g orthophosphoric acid + 21.86 g pseudoboehmite, mix thoroughly
- (2) [60 g water + 28.27 g cyclohexylamine + 9 g fumed silica], mix thoroughly
- (3) [(1) + (2)], mix thoroughly with vigorous agitation

Crystallization

Vessel: stainless steel autoclave
Temperature: 190°C
Time: 48 hours
Agitation: none

Product Recovery

- (1) Filter and wash with distilled water
- (2) Dry at 110°C
- (3) Yield near 100% on Al₂O₃

Product Characterization

XRD: CHA; competing phase: SAPO-5 (when gel C₆H₁₁NH₂/Al₂O₃ ratio < 1.9)
Elemental Analysis: (Si_{0.18}Al_{0.48}P_{0.34})O₂^a
Crystal Size and Habit: cubical morphology with 10-50 μm diameter [1]

Reference

- [1] S. Ashtekar, S. V. V. Chilukuri, D. K. Chakrabarty, J. Phys. Chem. 98 (1994) 4878

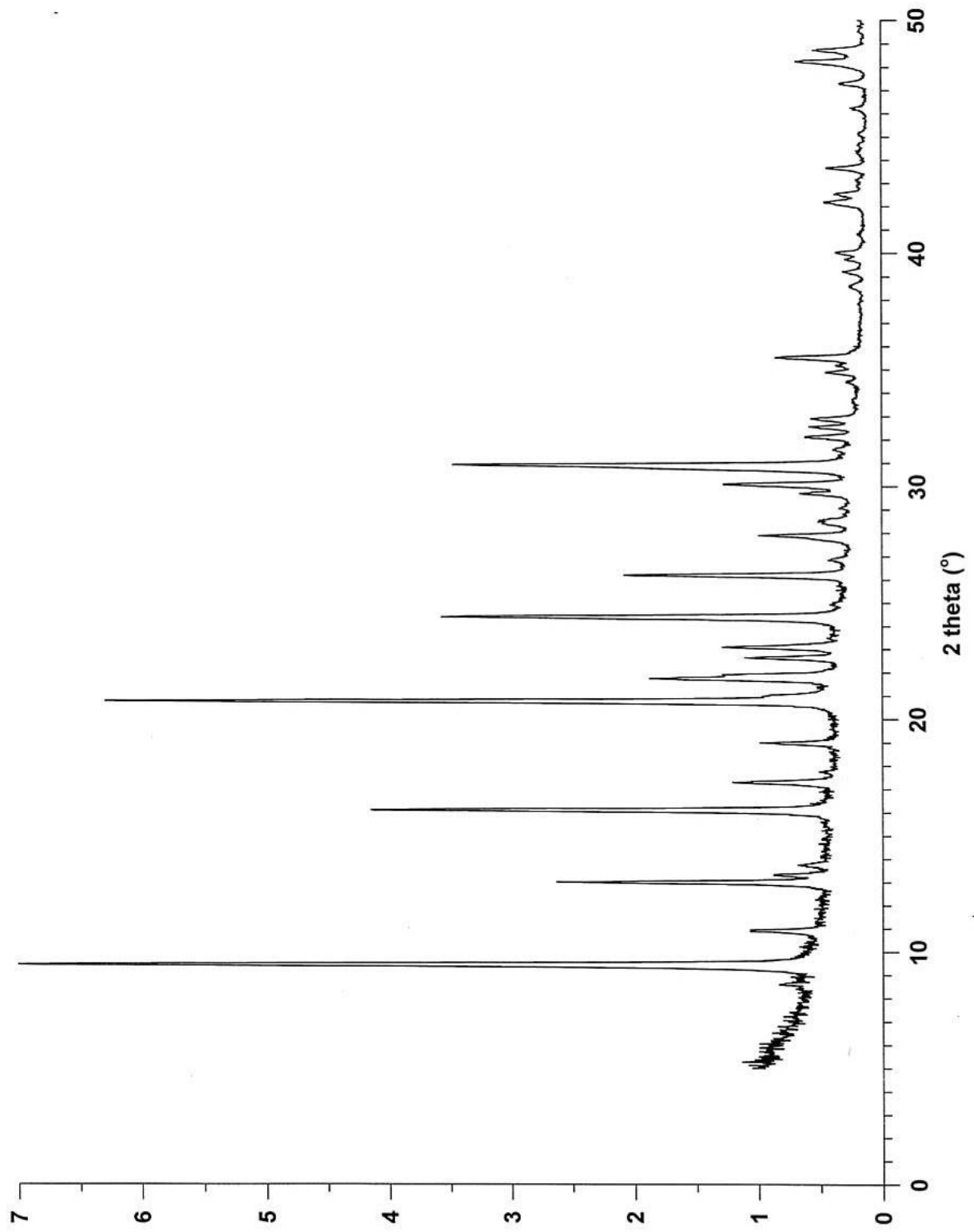
Notes

- a. Cations assumed to be protonated amine or surface hydroxyl.
- b. H₂O includes water from pseudoboehmite and orthophosphoric acid.

CHA

SAPO-44

Al(48), P(34), Si(18)



CLO

Cloverite (GaPO₄)

P(50), Ga(50)

Contributed by Céline Schott-Darie

Verified by S. Bradley, W. Schmidt and R Fricke

Type Materials 8{[Ga₉₆P₉₆O₃₇₂(OH)₂₄(QF)₂₄(H₂O)_n] (Q = quinuclidine [1])

Method A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L Delmotte, J.-L Guth, J. F. Joly [2]

Batch Composition Ga₂O₃ : P₂O₅ : HF : 80 H₂O : 6 Q^a

Source Materials

phosphoric acid (Fluka, 85% H₃PO₄)

distilled water

gallium sulfate [Ga₂(SO₄)₃·xH₂O] (Strem Chemicals, wt.% Ga ~18)^b

hydrofluoric acid (Fluka, 40% HF)

quinuclidine (Fluka, 97% C₇H₁₃N)

Batch Preparation (for 1 g product)

- (1) 10.95 g phosphoric acid + 2.2 g H₂O + 3.14 g gallium sulfate hydrate + 2.2 g H₂O
stir until dissolved
- (2) [(1) + 0.2 g HF + 2.7 g quinuclidine], mix until uniform. Initial pH = 4 to 4.5

Crystallization

Vessel: PTFE-lined autoclave

Temperature: 150°C

Time: 24 hours

Agitation: none

Product Recovery

- (1) Filter, wash with distilled water, dry at 60°C
- (2) Yield: approximately 60% on Ga₂O₃ and P₂O₅

Product Characterization

XRD: Characteristic strong reflections at d 25.4, 9.1 and 8.5 Å; competing phases are GaPO₄-a and GaPO₄-b [2] when the starting molar ratio F/Ga₂O₃ <0.5 [3]
Elemental Analysis (anhydrous form): Q_{0.14}Ga_{0.48}P_{0.52}O₂F_{0.13}. Crystal Size and Habit: small cubes, less than 1 μm^c

References

- [1] M. Estermann, L B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, Nature 352 (1991) 320
- [2] A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L Delmotte, J.-L Guth, J. F. Joly, Zeolites 12 (1992) 226

- [3] J. Patarin, C. Schott-Darie, A. Merrouche, H. Kessler, M. Soulard, L Delmotte, J.-L Guth and J. F. Joly in Proceedings from the 9th International Zeolite Conference, R. von Ballmoos, J. B. Higgins and M. J. Treacy (eds), Butterworth-Heinemann, Stoneham, 1992, p. 263

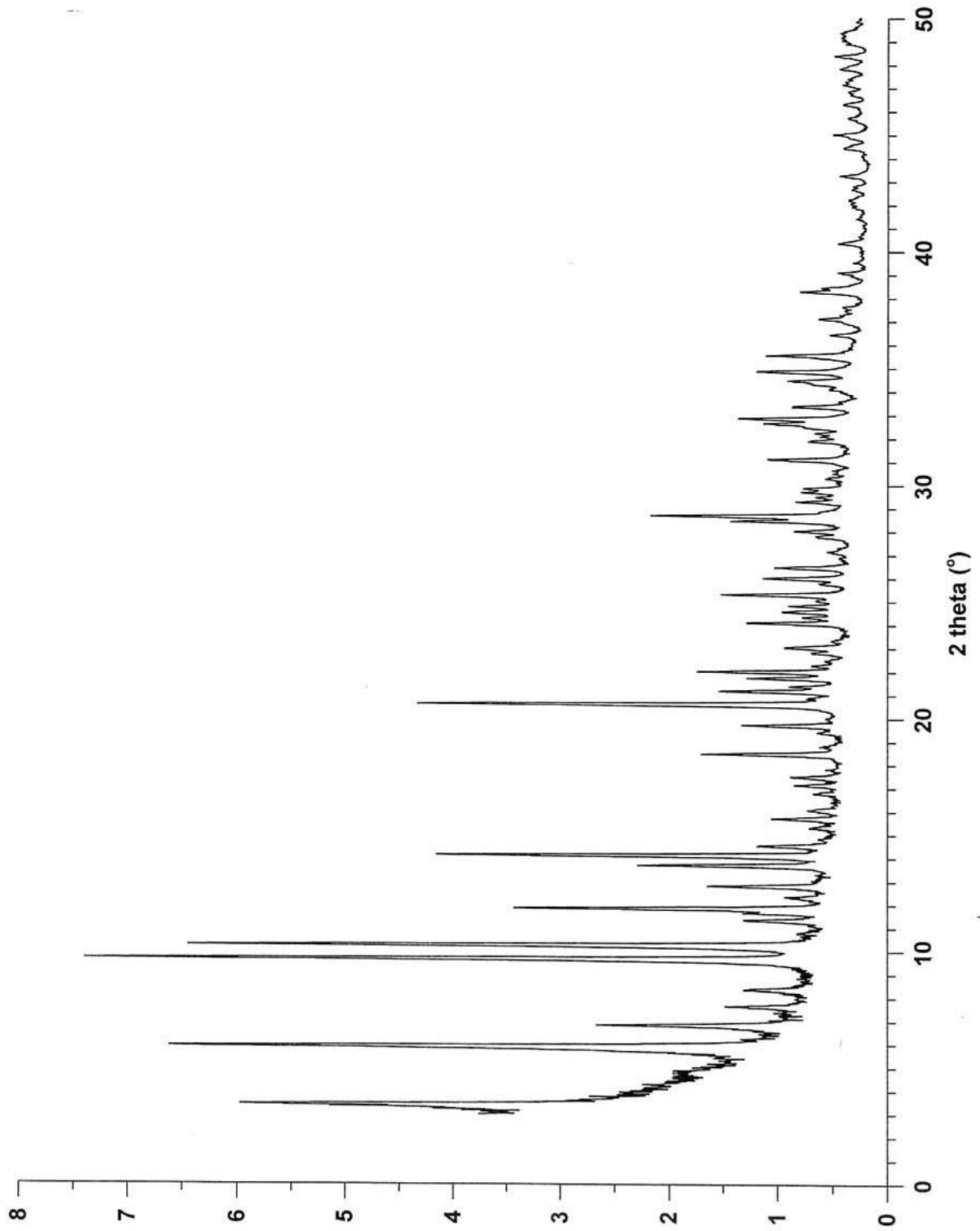
Notes

- a. The acceptable range for HF/Ga₂O₃ is 0.75 to 2.
- b. Aldrich Ga₂(SO₄)₃ acceptable substitute.
- c. Crystals are typically cubes with apparent truncatures when large (20 μm or more). Increase in crystal size has been achieved by decreasing the amount of fluoride in the starting mixture to F/Ga₂O₃ <0.5 [3].

CLO

Cloverite (GaPO₄)

P(50), Ga(50)



CON

CIT-1

Si(96), B(4)

Contributed by Mark E. Davis

Verified by S. B. Hong, E.-P. Ng, J. Shin

Type Material: [H₂][B₂Si₅₄O₁₁₂]

Method: Raul F. Lobo and Mark E. Davis [1]

Batch Composition: 50SiO₂ : B₂O₃ : 10ROH : 5NaOH : 3000H₂O

Source Materials

sodium boratedecahydrate (Na₂B₄O₇·10H₂O)

sodium hydroxide (NaOH)

template ROH (N,N,N-trimethyl(-)-cis-myrtanyl ammonium)

distilled water (DD)

fumed silica (Cab-0-Si1 grade M-5 or Aerosil 200, Degussa)

Synthesis of template (*N,N,N*-trimethyl(-)-cis-myrtanyl ammonium hydroxide)

10 g of (-)-*cis*-myrtanylamine were dissolved in 40 mL of methanol. To this solution were added 10.47 g K₂CO₃ and 21.95 g methyl iodide. The mixture was stirred for several minutes and then refluxed at 40 °C for 24 h. The reaction mixture was filtered, and the solid filtrate was washed with an additional 20 mL of methanol. The combined methanol solutions were heated at 50 °C in a rotavapor. A white solid is formed in the flask, which is then extracted with 2 portions each of 40 mL of chloroform. Recrystallization was performed in a ca. 1:10 (volume ratio) chloroform–*n*-hexane mixture.

The exchange of the iodide salt into a hydroxide was performed as follows: 4.5 g iodide salt was dissolved in 13.8 g distilled water and passed through 11.6 g of Amberlite IRN-78 OH anion exchange resin. The collected solution was concentrated in a rotavapor at 70 °C.

Batch Preparation (for 23.85 g initial gel)

- (1) [6.60 g of 13.0 wt.% ROH + 15.89 g distilled water], stir
- (2) [0.0767 g sodium borate decahydrate (Na₂B₄O₇·10.0H₂O) + 0.08 g NaOH + (1)], stir until dissolved
- (3) [1.20 g fumed silica (Aerosil 200, Degussa) + (2)], stir until a homogeneous gel is obtained

Crystallization

Vessel: pure-silica glass tubes^a or Teflon-lined 23 mL autoclave

Temperature: 150 C^b

Time: 42 days

Agitation: no

Product Recovery

- (1) Dilute reaction mixture with water

(2) Centrifuge and wash with water

Product Characterization

XRD: CON; competing phase: SSZ-33

Crystal size and habit: CIT-I crystals (typically 3 μm \times 3 μm \times 6 μm)

Reference

[1] Lobo, R.F. and Davis, M.E. J. Am. Chem. Soc. 117 (1995) 3766

[2] Christopher W. Jones, Son-Jong Hwang, Tatsuya Okubo and Mark E. Davis. Chem. Mat. 13 (2001), 1041

[3] Mark E. Davis and F. Lobo. U.S. Pat. 5,512,267 (1996)

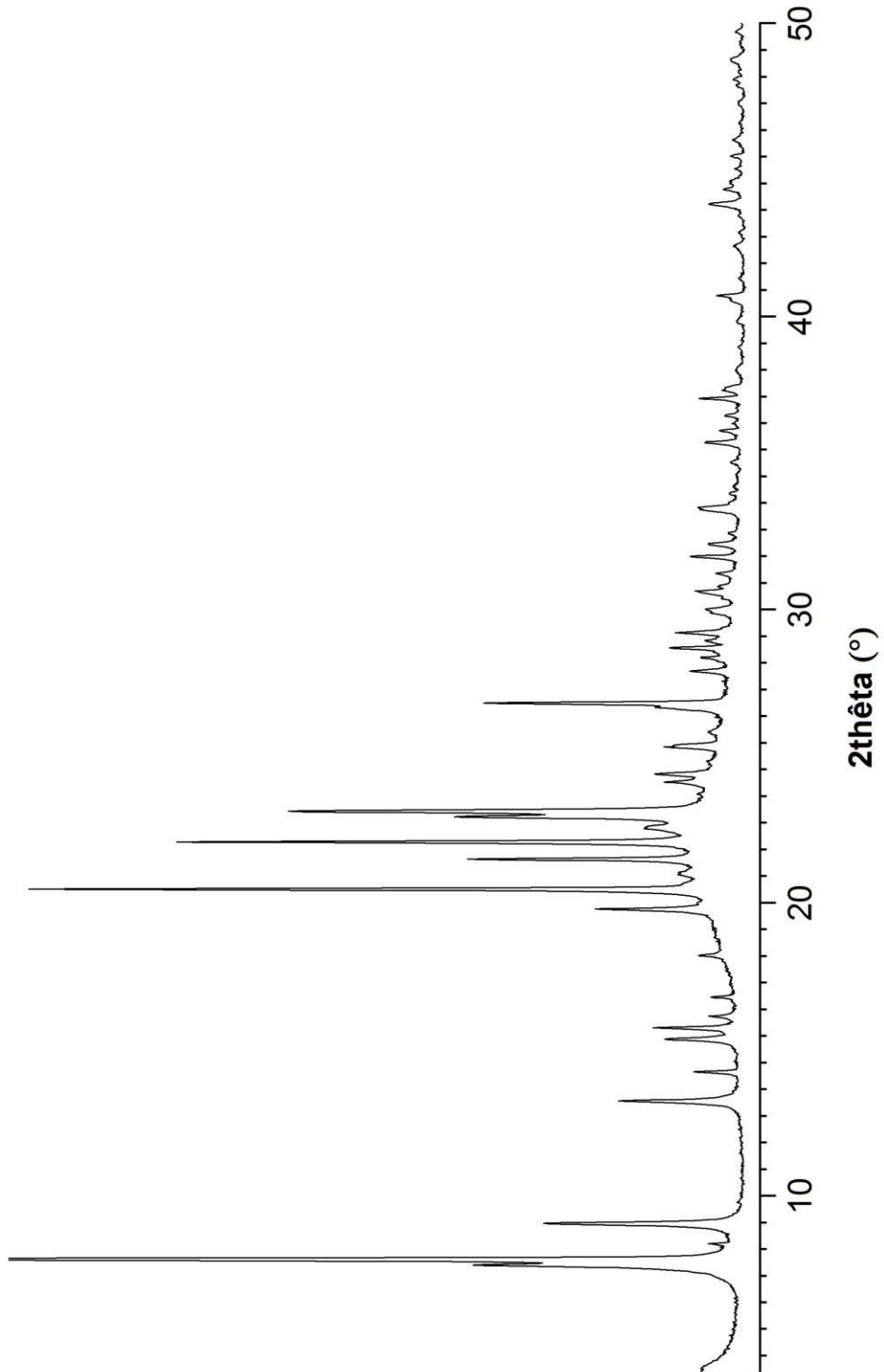
Notes

- a. 25 mm i.d., 100 mm long approximately 85% filled with the gel
- b. heated statically in convection oven

CON

CIT-1

Si(96), B(4)



Contributed by Lynne Bridget McCusker

Verified by S. B. Hong, E.-P. Ng, J. Shin

Type Material: $[\text{Si}_{64}\text{O}_{128}] \cdot 2(\text{Cp}^*)_2\text{CoF}_{0.75}\text{OH}_{0.25}$
(Cp* = pentamethylcyclopentadienyl)

Method: T. Wessels, C. Baerlocher, L.B. McCusker, and E.J. Creighton [1]

Batch Composition: 100 SiO₂ : 40 [(Cp*)₂Co]F : 3125 H₂O

Source Materials

distilled water
silica cabosil M5 (Aldrich)
[(Cp*)₂Co]OH aqueous solution (8.95 wt%)
HF aqueous solution (38 wt % J.T. Baker)

Batch Preparation (for 2.05 g product)

- (1) [27.8 g of Cabosil M5 + 68.4 g of water], stir until homogeneous to prepare a silica slurry
- (2) [6.60 g of sample (1) + 49.15 g of 8.95 wt % aqueous [(Cp*)₂Co]OH solution], stir with a magnetic stirrer for 1.5 h
- (3) [0.67 g of aqueous 38 wt % HF (J. T. Baker) in about 70 g of water + (2)^a], vigorous stirring for 20 min
- (4) concentrate (3) by removing excess water under reduced pressure

Crystallization

Vessel: Teflon-lined autoclave
Temperature: 170° C
Time: 25 days
Agitation:

Product Recovery

- (1) Filter and wash extensively with water
- (2) Yield: 2.05 g

Product Characterization

XRD: pure phase
Elemental analysis: 32Si:1.03Co: 19.13C:0.75F
Crystal size and habit: needlelike crystallites

Reference

- [1] T. Wessels, C. Baerlocher, L.B. McCusker, and E.J. Creighton, J. Am. Chem. Soc., 121, (1999) 6242
- [2] Stacey I. Zones and Cong-Yan Chen. U.S. Pat. 6,103,215 (2000)

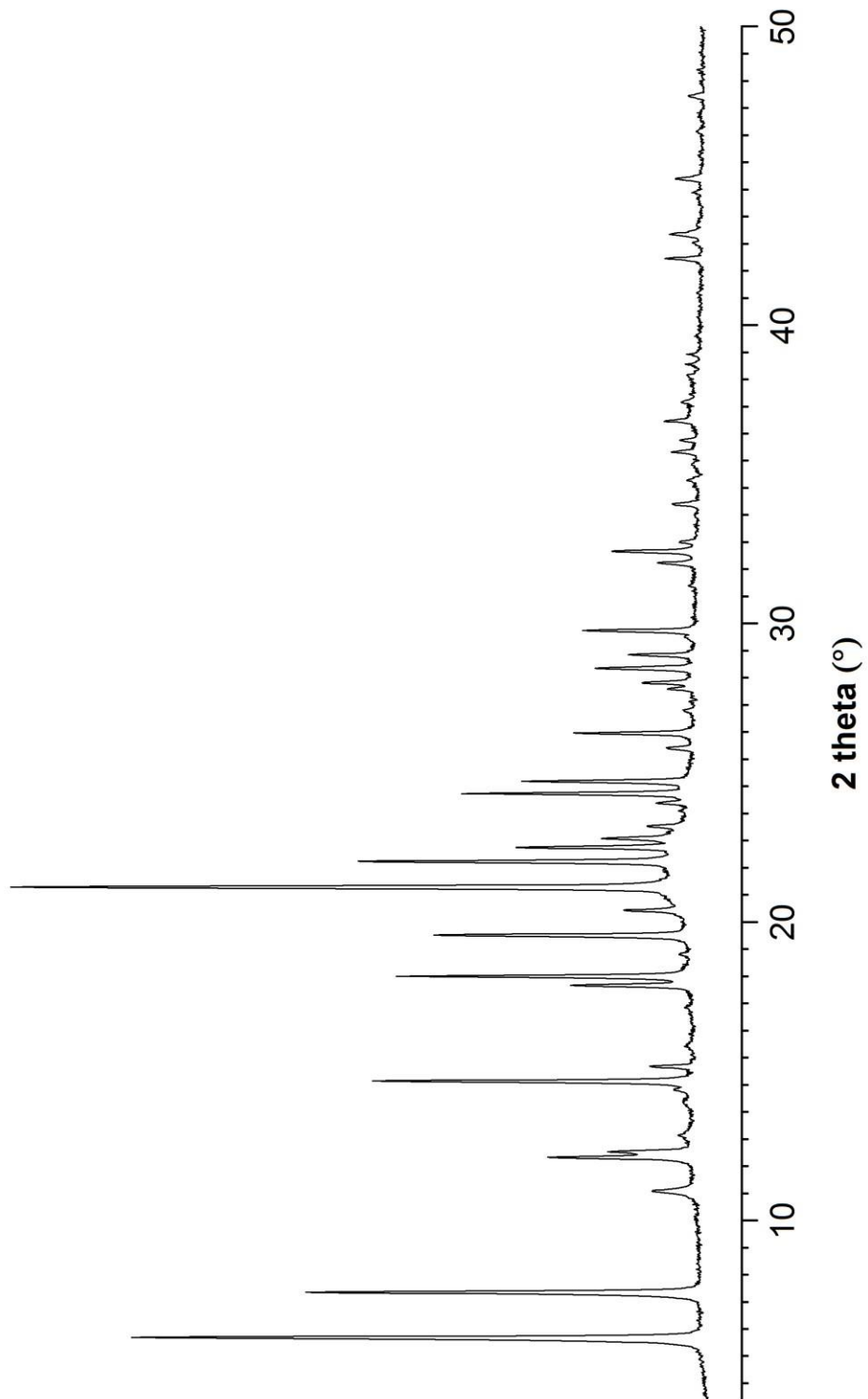
Notes

- a. HF solution was slowly added to (2)

DON

UTD-1F

Si(98), Co(2)



EAB

TMA-E

Si(74), Al(26)

Contributed by Rosario Aiello and Flaviano Testa

Verified by B. Schoeman and by B. Subotic

Type Material $[\text{Na}_{6.84}(\text{TMA})_{3.05}] [(\text{AlO}_2)_{9.25}(\text{SiO}_2)_{26.75}] \cdot 17.12 \text{ H}_2\text{O}^{\text{a}}$ (TMA = tetramethylammonium)

Method R. Aiello, R. M. Barrer [1]

Batch Composition 5 (TMA)₂O : 3 Na₂O : Al₂O₃:15 SiO₂ : 500 H₂O

Source Materials

distilled water

tetramethylammonium hydroxide (Fluka, purum, 25% aqueous solution)

sodium hydroxide (Carlo Erba, pellets, reagent grade, 30% aqueous solution)

alumina (Pfaltz and Bauer, Al(OH)₃, 65% Al₂O₃)

silica (Sigma, fumed, 99+% SiO₂)

Batch Preparation (for 1.4 g dry product)

- (1) [13.78 g water + 9.10 g tetramethylammonium hydroxide solution + 2.00 g sodium hydroxide solution], mix until dissolved
- (2) [(1) + 0.39 g alumina], mix until homogeneous
- (3) [(2) + 2.25 g silica], mix thoroughly

Crystallization

Vessel Teflon container

Time: 14 days

Temperature: 80 ± 2 °C

Agitation: container is rotated

Product Recovery

- (1) Filter and wash thoroughly
- (2) Dry at ambient temperature
- (3) Yield: near 100% on Al₂O₃

Product Characterization

XRD: EAB (only phase observed); competing phase: FAU (trace sometimes present)^b

Elemental Analyses: (Na₂O)_{0.74} : ((TMA)₂O)_{0.33} : Al₂O₃ : 5.74 SiO₂^c

Crystal Size and habit: 1-2 μm faceted spherulites^{d,e}

Reference

- [1] R. Aiello, R. M. Barrer, J. Chem. Soc. A (1970) 1470

Notes

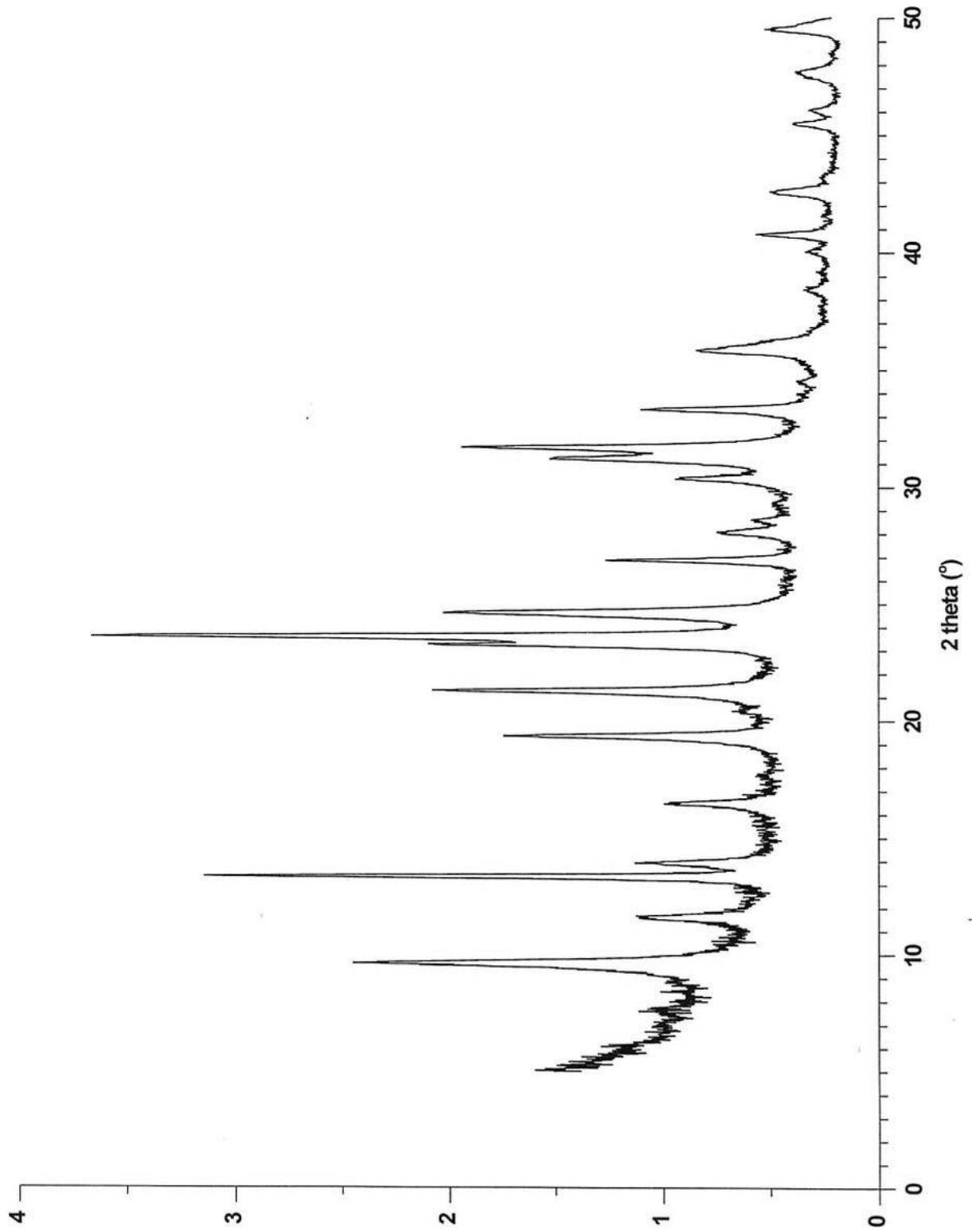
- a. Excess cations attributed to SiO⁻ fragments in the framework.

- b. FAU traces were observed from systems with lower TMA/Na ratio and with lower H₂O content.
- c. As reported in Ref. [1] for samples obtained both from batches with Na⁺/ (TMA)⁺ = 0.5/0.5 and 0.2/0.8.
- d. TMA⁺ could not be removed by NaNO₃ exchange.
- e. By thermal analysis, water is first lost endothermally, followed by exothermal oxidative decomposition of TMA⁺.

EAB

TMA-E

Si(74), Al(26)



Contributed by Juliusz Warzywoda

Verified by T. Gier and by M. Sato

Type Material K₁₀ (Al₁₀Si₁₀O₄₀): wH₂O (w ~8)

Method R M. Barrer, B. M. Munday [1]

Batch Composition 19.9 K₂O : Al₂O₃ : 2 SiO₂ : 378 H₂O

Source Materials

deionized water

potassium hydroxide (pellets, 85% KOH min.)

kaolin (~Al₂Si₂O₅(OH)₄)

Batch Preparation (for 0.8 g product)

- (1) [18.2 g water + 7.95 g potassium hydroxide]; dissolve KOH pellets in HDPE ^a bottle
- (2) [(1) + 0.78 g kaolin]; seal the bottle and shake for 15 seconds ^b

Crystallization

Vessel: HDPE bottle

Temperature: 80°C

Time: 12 days

Agitation: occasional shaking

Product Recovery

- (1) Filter to recover solids
- (2) Wash with deionized water until pH of wash water is neutral
- (3) Dry at 80°C
- (4) Yield: 0.83-0.86 g (dry) (90% on Al or Si)

Product Characterization

XRD: Barrer K-F (no competing phases) [2]

Elemental Analyses: K₂O : Al₂O₃ : 2 SiO₂ : 3 H₂O [3]

Crystal Size and Habit: inter-penetrating prismatic crystals, 2 μm or less

References

- [1] R. M. Barrer, B. M. Munday, J. Chem. Soc. (A) (1971) 2914
- [2] J. D. Sherman in ACS Symp. Series 40, J. R. Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 30
- [3] R. M. Barrer, J. W. Baynham. J. Chem. Soc. (1956) 2882

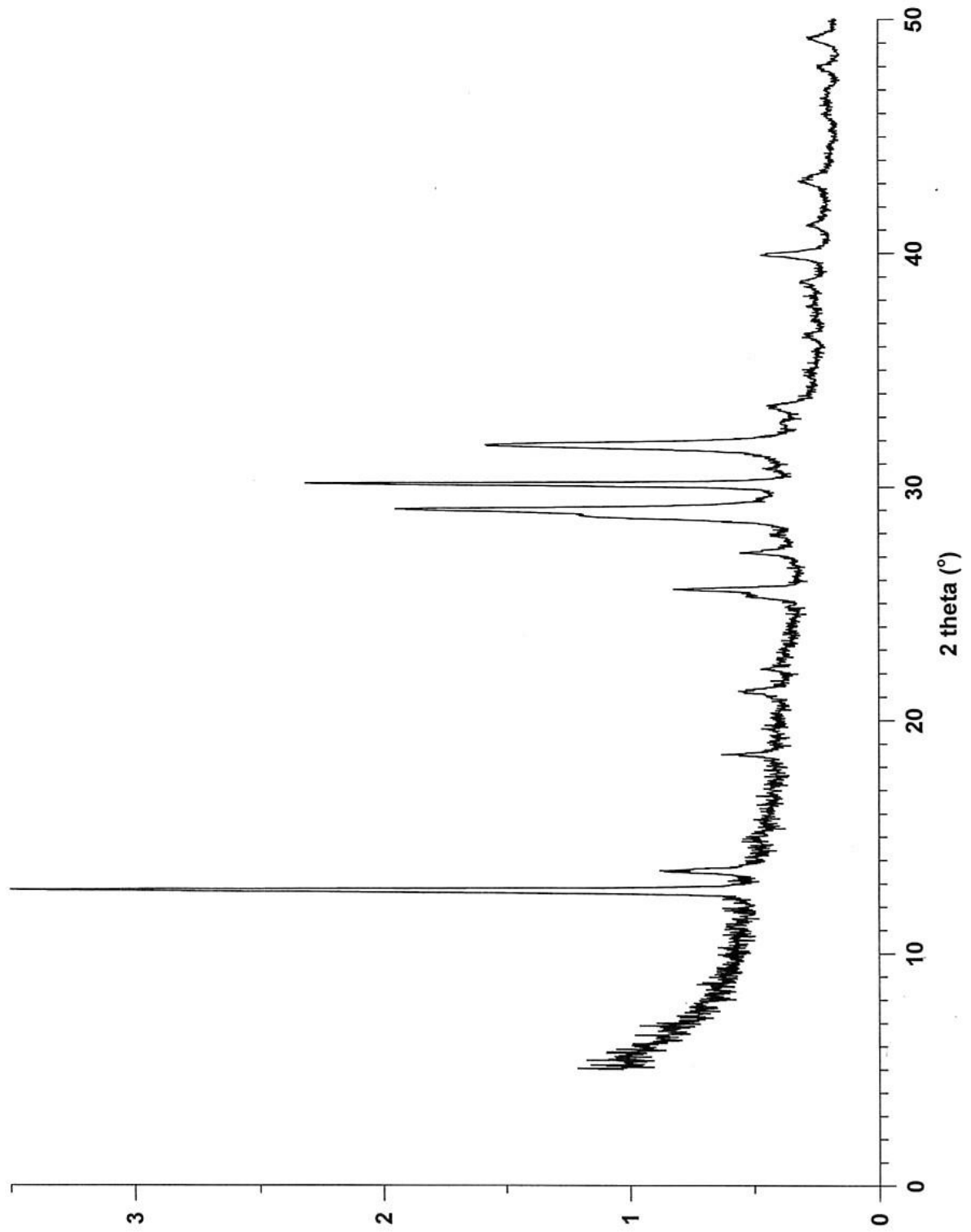
Notes

- a. High density polyethylene.
- b. Upon addition of kaolin to the KOH solution, a slowly settling suspension of solids, rather than a homogeneous gel, is formed.

EDI

Barrer K-F

Si(50), Al(50)



Contributed by Juliusz Warzywoda

Verified by: T. Gier and by M. Sato

Type Material K₁₀ (Al₁₀Si₁₀O₄₀) · wH₂O (w ~ 8)

Method J. Warzywoda, R W. Thompson [1]

Batch Composition 5.26 K₂O : Al₂O₃ : 3 SiO₂ : 94.5 H₂O

Source Materials

deionized water

potassium hydroxide (pellets, 85% KOH min.)

aluminum (wire, 99.999% Al)

silica (Cab-O-Sil M5, amorphous fumed SiO₂)

Batch Preparation (for 4 g product)

- (1) [20.0 g water + 9.26 g potassium hydroxide]; dissolve KOH pellets in HDPE ^a bottle. Divide into two equal portions
- (2) [First half (1) + 0.719 g aluminum];^b dissolve the Al wire in half of the KOH solution by heating under reflux in a Teflon flask. Cool, filter and store in a HDPE bottle
- (3) [Second half (1) + 2.42 g silica]; dissolve the silica in the remaining KOH solution and heat at 80-95°C in a HDPE bottle. Cool, filter and store in a HDPE bottle^c
- (4) [(2) + (3)]; heat (2) and (3) in HDPE bottles to 80-95°C and mix together. Mix the resulting gel for 1-2 minutes at 1000 rpm with a mechanical stirrer to homogenize it ^e

Crystallization

Vessel: HDPE bottle

Temperature: 95°C

Time: 96 hours

Agitation: static conditions with occasional mixing

Product Recovery

- (1) Filter to recover solids
- (2) Wash with deionized water until the pH of wash water is neutral
- (3) Dry at 80°C
- (4) Yield: 4.4 to 4.7 g (near 100% based on Al₂O₃)

Product Characterization

XRD: Linde Type F (ref. [2], Table III, page 35)

Elemental Analyses: K₂O : Al₂O₃ : 2SiO₂ : 3H₂O [3]

Crystal size and habit: small submicron prismatic crystals forming 0.5 to 3 μm aggregates

References

- [1] J. Warzywoda, R W. Thompson, Zeolites 11(1991) 577
- [2] J. D. Sherman, in ACS Symp. Series 40, J. R Katzer (ed.), Am. Chem. Soc., Washington, D.C., 1977, p 30
- [3] R M. Barer, J. W. Baynham, J. Chem. Soc. (1956) 2882

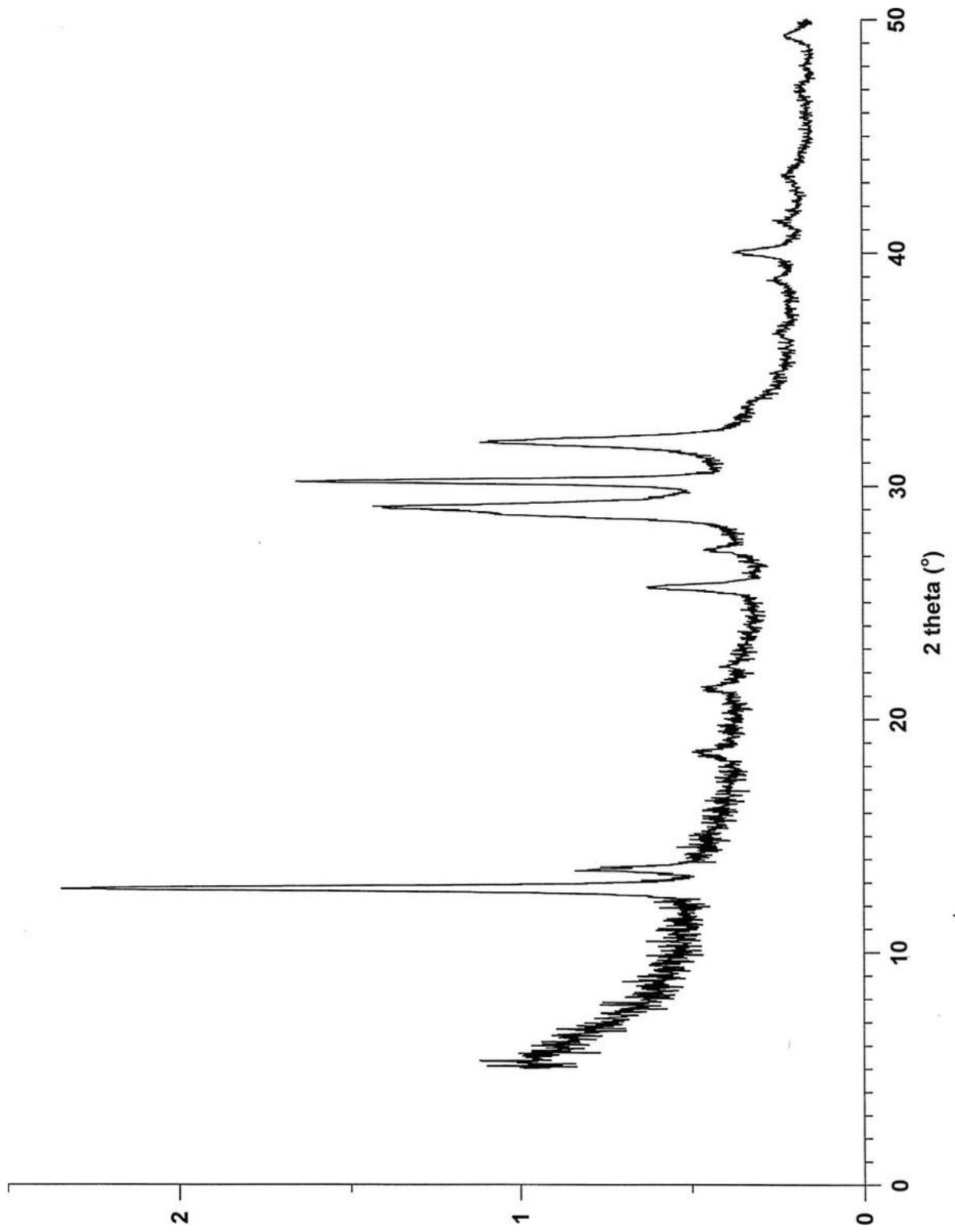
Notes

- a. High density polyethylene.
- b. The dissolution of aluminum powder in these caustic solutions generates heat and hydrogen and can be somewhat violent.
- c. To avoid precipitation of solids from solutions (2) and (3), carry out crystallization immediately after solution preparations is complete.
- d. A viscous alumino silicate gel is formed instantaneously.
- e. If no mechanical stirring is used, the gel appears to be very viscous with no visible fluid phase, and homogenization may be difficult. Brief heating of the gel at 95°C will give a fluid phase and hand shaking can be used to homogenize it.

EDI

Linde Type F

Si(50), Al(50)



EDI

Nanosized Linde F

Si(60), Al(40)

Contributed by Hussein Awala

Verified by S. Komaty, L. Tosheva, E.-P. Ng

Type Material [Al₄Si₆ O₂₀]

Method J. Kecht, S. Mintova, T. Bein [1]

Batch Composition 2.37 (TMA)₂O : 0.05 Na₂O : 1.00 Al₂O₃ : 4.16 SiO₂ : 244 H₂O : 0.50 CuO : 15 NH₃

Source Materials

colloidal silica, Ludox HS-30 (SiO₂) (30 %, Aldrich)
aluminium isopropoxide (> 98 %, Sigma-Aldrich)
ammonium hydroxide solution (28 wt. % NH₃ in water, Sigma-Aldrich)
copper nitrate trihydrate (Sigma-Aldrich)
tetramethylammonium hydroxide pentahydrate (Sigma)
double distilled water (dd H₂O)

Batch Preparation

- (1) [139 mg Cu(NO₃)₂ + 2.8 g of dd H₂O + 1.0 g of ammonium hydroxide + 0.98 g of TMAOH], mixed well at ambient temperature, then after complete dissolution [468 mg aluminium isopropoxide and 0.96 g silica (HS-30) were added]^a
- (2) Stirring for 30 min (formation of blue-colored transparent suspension)

Crystallization

Vessel: stainless steel autoclave (150 mL)
Aging: 3 days at room temperature
Hydrothermal treatment: 100 °C for 3 days
Agitation: none

Product Recovery

Centrifugation and redispersion in water; washed till pH of 10

Product Characterization

XRD: EDI; competing phases: no
Crystal size: cubic particles with size 80-150 nm

References

[1] J. Kecht, S. Mintova, T. Bein, Micropor. Mesopor. Mater. 116 (2008) 258

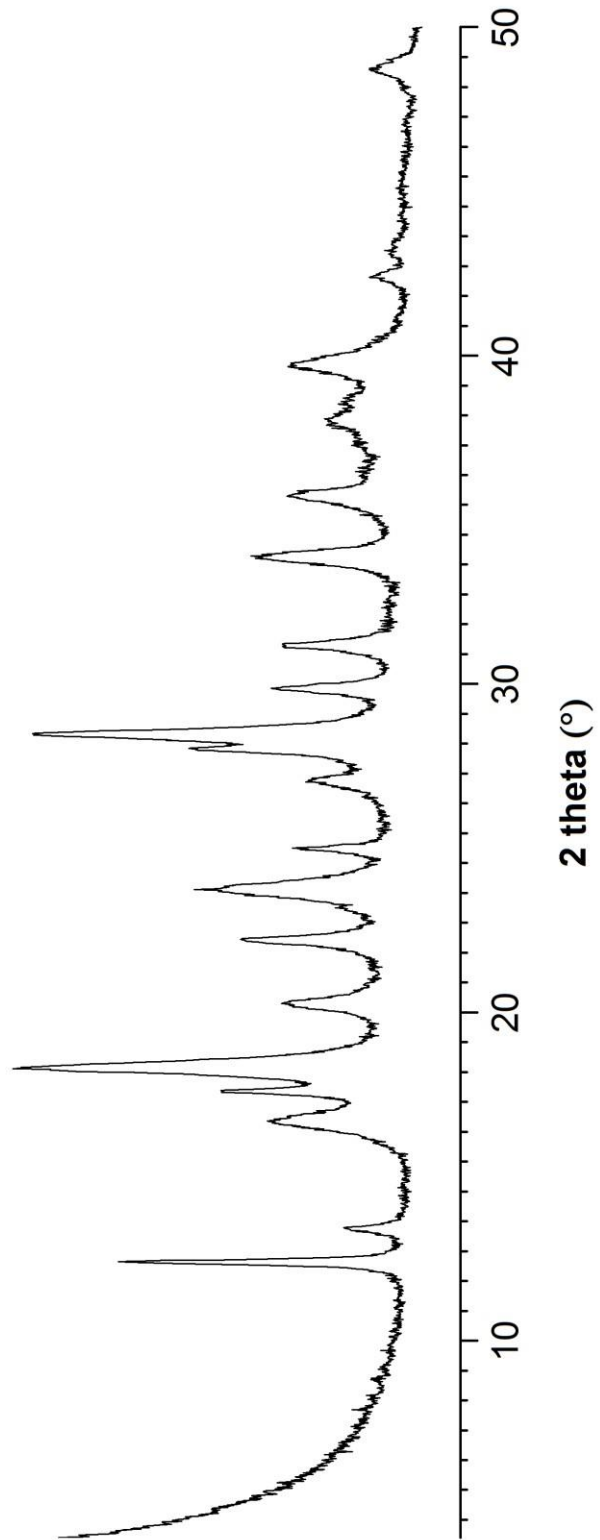
Notes

- a. The starting mixture is prepared in a polypropylene bottle

EDI

Linde Type F

Si(50), Al(50)



EMT

EMC-2

Si(79), Al(21)

Contributed by Jens Weitkamp

Verified by Kuei-Jung Chao and T. Chatelain

Type Material Na₂₀[Al₂₀Si₇₆O₁₉₂]. (18-crown-6)₄ [1]

Method J. Weitkamp, R Schumacher [1-3]

Batch Composition 2.2 Na₂O : Al₂O₃ : 10 SiO₂ : 140 H₂O : 0.87 (18-crown-6)

Source Materials

demineralized water

sodium hydroxide (Fluka reagent grade)

sodium aluminate (Riedel-de Haen; 54% Al₂O₃, 41% Na₂O)

crown ether (Fluka 18-crown-6)

silica sol (Bayer AG, VP 4039, 30% SiO₂)

Batch Preparation (for 19 g product)^a

- (1) [39 g water + 6.05 g NaOH solution (50%) + 7.26 g sodium aluminate + 8.81 g (18-crown-6)], dissolve under continuous stirring
- (2) [(1) + 77 g silica sol], stir vigorously

Crystallization

Vessel: stainless steel autoclave (150 mL)

Incubation: one day at room temperature

Temperature: 110 °C

Time: 12 days

Agitation: none

Product Recovery

- (1) Filter and wash extensively with demineralized water
- (2) Dry at 120 °C for 16 hours
- (3) Yield: approximately 19 g (still containing the template and some adsorbed water), 56% based on Al^b

Product Characterization

XRD: EMT; competing phases: GIS and FAU

Elemental Analyses SiO₂/Al₂O₃ = 7.6 (by AES/ICP and ²⁹MAS NMR) [2]

Crystal Size and Habit: hexagonal, 4-5 μm mean diameter, 0.5 to 1.0 μm thick

References

- [1] F. Delprato, L Delmotte, J.-L Guth, L Huve, Zeolites 10 (1990) 546
- [2] J. Weitkamp, R. Schumacher, in Proceed. Ninth Int. Zeo. Conf., R. von Ballmoos, J. B. Higgins, M. M. J. Treacy, (eds.), Butterworth-Heinemann, Boston, 1993, p. 353
- [3] J. Weitkamp, R Schumacher, U. Weib, Chem.-Ing. Tech. 64 (1993) 1109

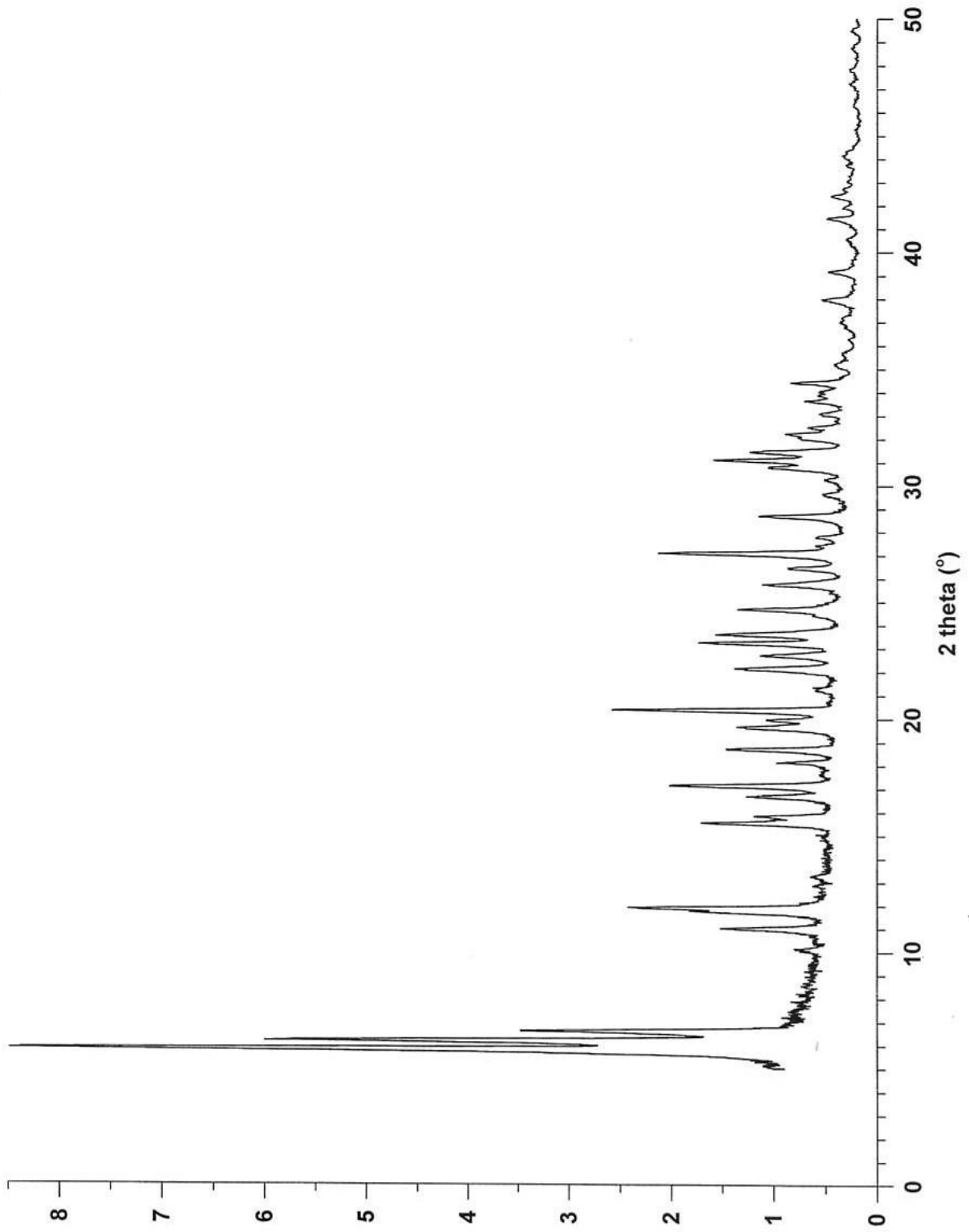
Notes

- a. This synthesis has been successfully scaled-up by a factor of four (yield 69 g).
- b. Calcination at 540°C in air for 16 hours removes template.

EMT

EMC-2

Si(79), Al(21)



Contributed by Eng-Poh Ng

Verified by I. Kondofersky, A. Khartchenko, D. Wales

Type Material: $[\text{Na}^{+}_{14} \text{K}^{+}_{2} (\text{H}_2\text{O})_{27}] [\text{Al}_9\text{Si}_{27} \text{O}_{72}]$

Method: E.-P. Ng, D. Chateigner, T. Bein, V. Valtchev, S. Mintova [1]

Batch Composition 5.15 SiO₂ : 1 Al₂O₃ : 17.6 Na₂O : 222 H₂O

Source Materials

distilled water

sodium hydroxide (99%, Merck)

sodium aluminate (56.7% Al₂O₃, 39.5% Na₂O, Strem-chemicals)

sodium silicate (29% SiO₂, 8% Na₂O, Prolabo)

Batch Preparation

- (1) [100.00 g water + 1.61 g sodium hydroxide + 9.047 g sodium aluminate], stir in a plastic flask until dissolved
- (2) [(1) + 44.00 g sodium hydroxide], stir until dissolved, cool with ice bath^a
- (3) [57.692 g sodium silicate + 20.00 g sodium hydroxide + 80.00 g H₂O], stir until dissolved, cool with ice bath^a
- (4) Add (2) slowly into (3) under vigorous stirring, keep stirring for 5 min^b

Crystallization

Vessel: 250 mL polypropylene bottle

Temperature: 30 °C

Time: 36 hours

Agitation: none

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Centrifuge and wash with water until pH 7.5
- (3) Dry at 60°C in conventional oven or freeze-dry
- (4) Yield: approximately 14 g

Product Characterization

XRD: EMT; competing phase^c: SOD, FAU (when prolonging aging time)

Elemental analysis: 52 SiO₂ : 22 Al₂O₃^c

Crystal size and habit: hexagonal thin plate-like crystals with a size of 10-15 nm

References

- [1] E.-P. Ng, D. Chateigner, T. Bein, V. Valtchev, S. Mintova, *Science* 335 (2012) 70
- [2] E.-P. Ng, J.-M. Goupil, A. Vicente, C. Fernandez, R. Retoux, V. Valtchev, S. Mintova, *Chem. Mater.* 24 (2012) 4758

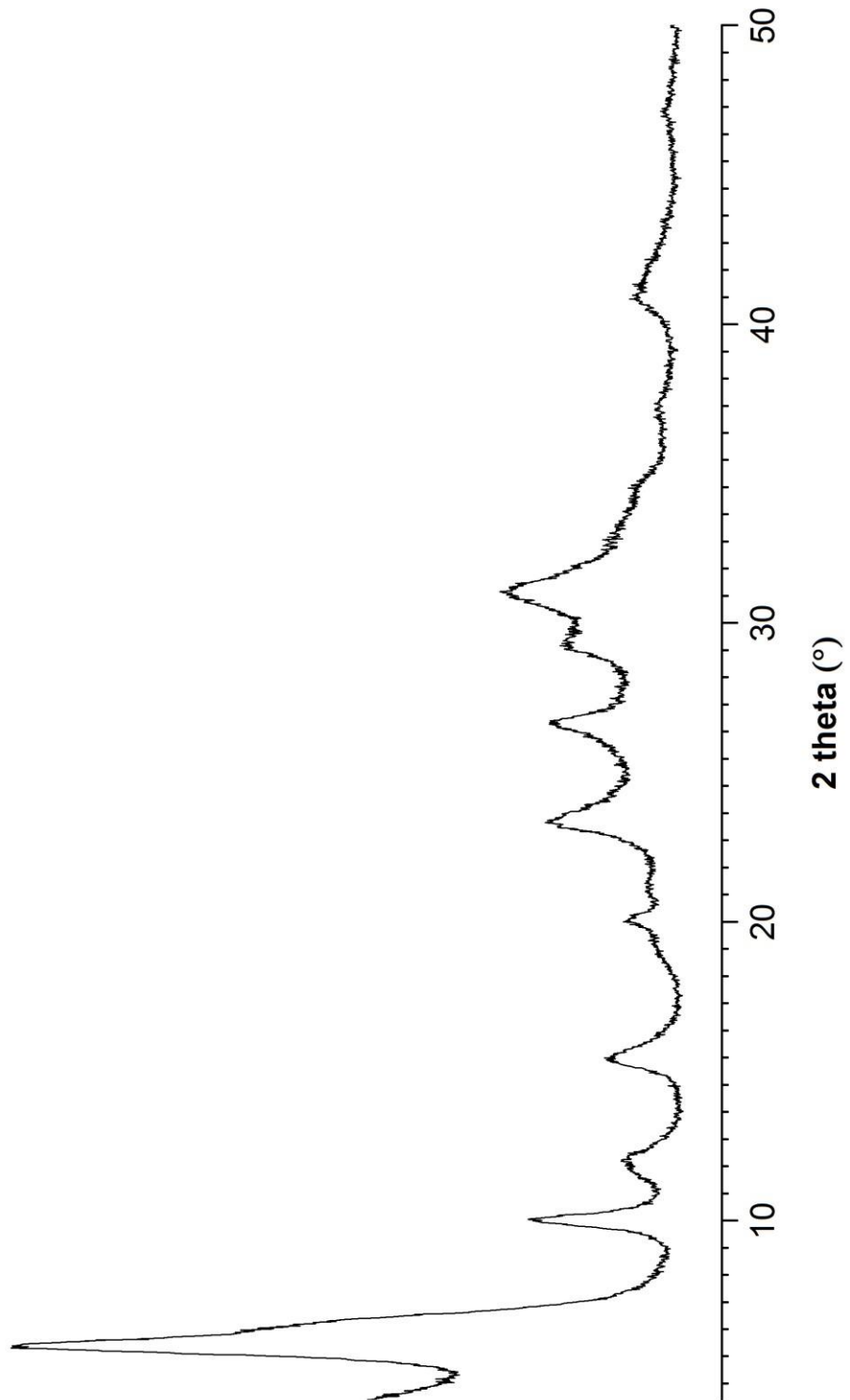
Notes

- a. Clear solutions are obtained
- b. White cloudy solution slowly forms
- c. According to Ref [2]

EMT

Na-EMC-2

Si(53), Al(47)



ERI

Erionite

Al(25), Si(75)

Contributed by Anastasia Kharchenko

Verified by K. L. Wong, V. Georgieva

Type Material: $[\text{Na}^{+}_{14} \text{K}^{+}_{2} (\text{H}_2\text{O})_{27}] [\text{Al}_9\text{Si}_{27} \text{O}_{72}]$

Method: S. Ueda, M. Nishimura, M. Koizumi [1]

Batch Composition: 15 Na₂O : 5 K₂O : 60 SiO₂ : Al₂O₃ : 0.1 TMA₂O : 350 H₂O

Source Materials

- double distilled water (dd H₂O)
- tetramethylammonium hydroxide (10% aq. solution)
- sodium hydroxide (99%)
- potassium hydroxide (85%)
- aluminum foil (99.99%)
- colloidal silica sol (0.5278 g/ml SiO₂)

Batch Preparation

- (1) [1.95 g NaOH + 0.96 g KOH + 3.7 g H₂O], stir in a flask
- (2) [(1) + 0.13 g TMAOH + 0.08 g Al], stir until Al is dissolved
- (3) [(2) + 10 ml SiO₂]

Crystallization

- Vessel: Teflon-lined stainless steel autoclave (100 ml)
- Temperature: 100°C
- Time: 6 days

Product Recovery

- (1) Suction filtration
- (2) Washing with hot water
- (3) Drying at 110°C for 24h

Product Characterization

- XRD: ERI, Competing phase: OFF
- Crystal size and habit: particles of 1 μm, shape of hexagonal prism

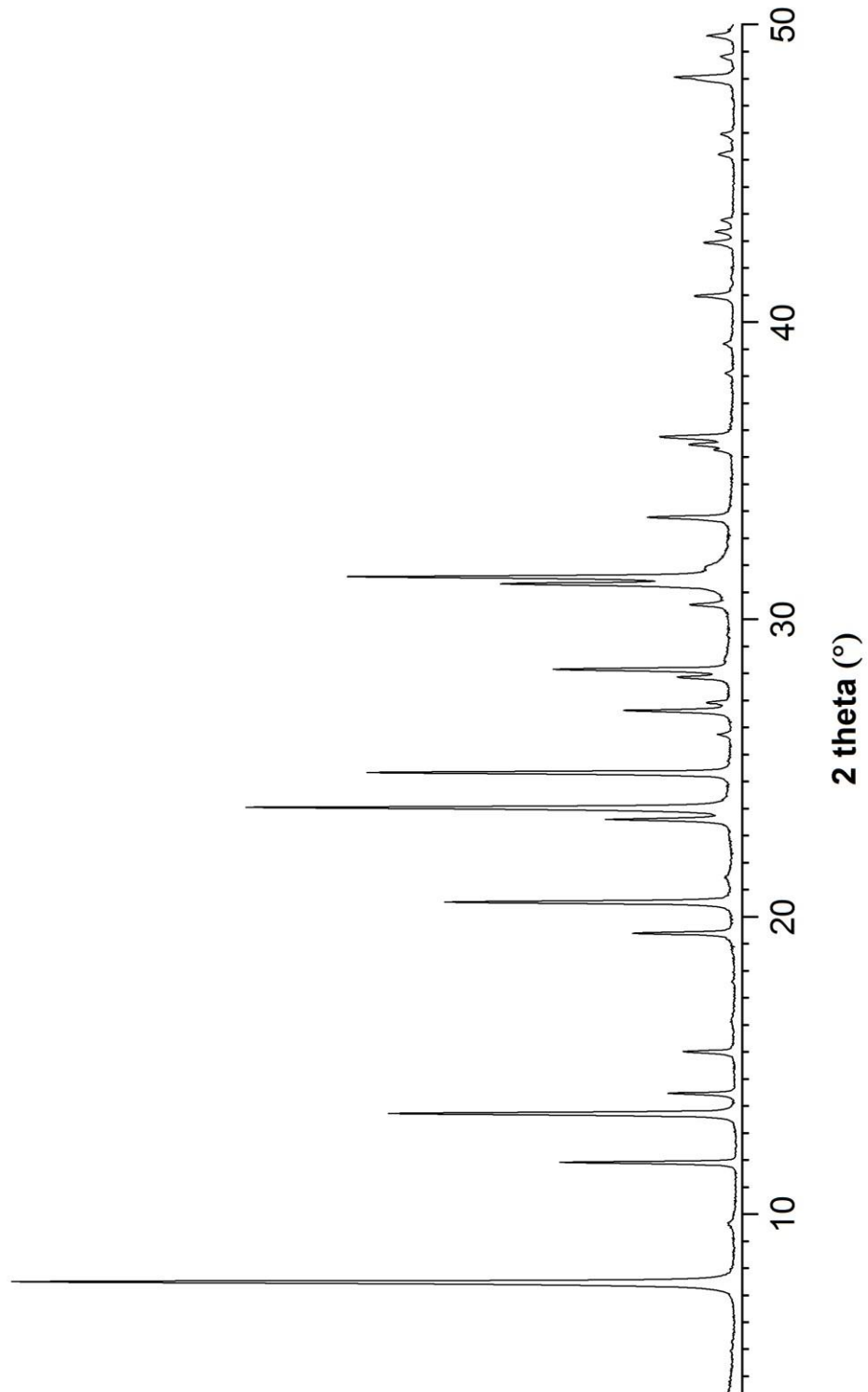
Reference

- [1] S. Ueda, M. Nishimura, M. Koizumi, Elsevier Science Publishers B.V. Zeolites (1985) 105

ERI

Erionite

Al(25), Si(75)



EUO

[Ga] EU-1

Si(96.5), Ga(3.5)

Contributed by A. N. Kotasthane

Verified by S. Lambert, H. Kessler, and T. Loiseau

Type Material Na₅[Ga₄Si₁₀₈O₂₂₄] · wH₂O (w ~ 26)

Method G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy [1]

Batch Composition 7.0 Na₂O : Ga₂O₃ : 36.6 SiO₂ : 4.0 R : 5.55 H₂SO₄ : 926 H₂O^a
(R = hexamethonium dibromide (C₁₂H₃₀N₂Br₂))

Source Materials

demineralized water
sodium hydroxide, reagent grade (97%)
silica sol (27.4% SiO₂, 0.5% Na₂O)
sulfuric acid (AR BDH, 98%)
gallium(III)sulfate (Aldrich 99.99%)
hexamethonium bromide monohydrate (HM-Br₂, Aldrich)

Batch Preparation (for 24 g product)

- (1) [30.0 g water + 5.41 g sodium hydroxide], mix until dissolved, pH = 13.8 ± 0.2
- (2) [81.0 g silica sol + 20 g water], mix until uniform, pH = 9.8 ± 0.2
- (3) [(1) + (2)], mix until uniform, pH = 13.6 ± 0.2
- (4) [30 g water + 2.6 g sulfuric acid + 4.3 g gallium sulfate], mix until dissolved; heating on hot plate for 15 minutes essential, pH = 0.08 ± 0.02
- (5) [(3) + (4)], add (4) drop-wise to (3) with good mixing
- (6) [30 g water + 15.2 g HM-Br₂], mix until dissolved. pH = 7.2 ± 0.2
- (7) [(5) + (6)], add (6) to (5) with good mixing. Adjust final batch to pH = 12.6 with 1 M NaOH^b

Crystallization

Vessel: stainless-steel autoclave (Parr, 300 mL capacity)
Temperature: 170 °C
Time: 6 days
Agitation: propeller mixer (250 RPM)

Product Recovery

- (1) Cool and filter to recover solids. Slurry pH after crystallization = 10.5 ± 0.2
- (2) Wash extensively with demineralized water until filtrate pH < 9
- (3) Dry at 110 °C for 12 to 15 hours
- (4) Yield: approximately 24 g (56% on Ga₂O₃, 79% on SiO₂)

Product Characterization

XRD: Pure EU-1 phase (EUO framework topology) having characteristic strong reflections at d = 4.30, 3.99 and 3.28 Å without any impurity phases. On longer crystallization (above 6 days), alpha quartz appears

Elemental Analysis: 92.4% SiO₂, 5.24% Ga₂O₃ 2.36% Na₂O (SiO₂/Ga₂O₃= 55.0, Na₂O/Ga₂O₃ = 1.3 6) ^{c,d}

Crystal Size and Habit: Homogeneously distributed small spheres (2-3 μm)

Reference

- [1] G. N. Rao, V. P. Shiralkar, A. N. Kotasthane, P. Ratnasamy, in Synthesis of Microporous Materials, Vol. I, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York (1992) p 153

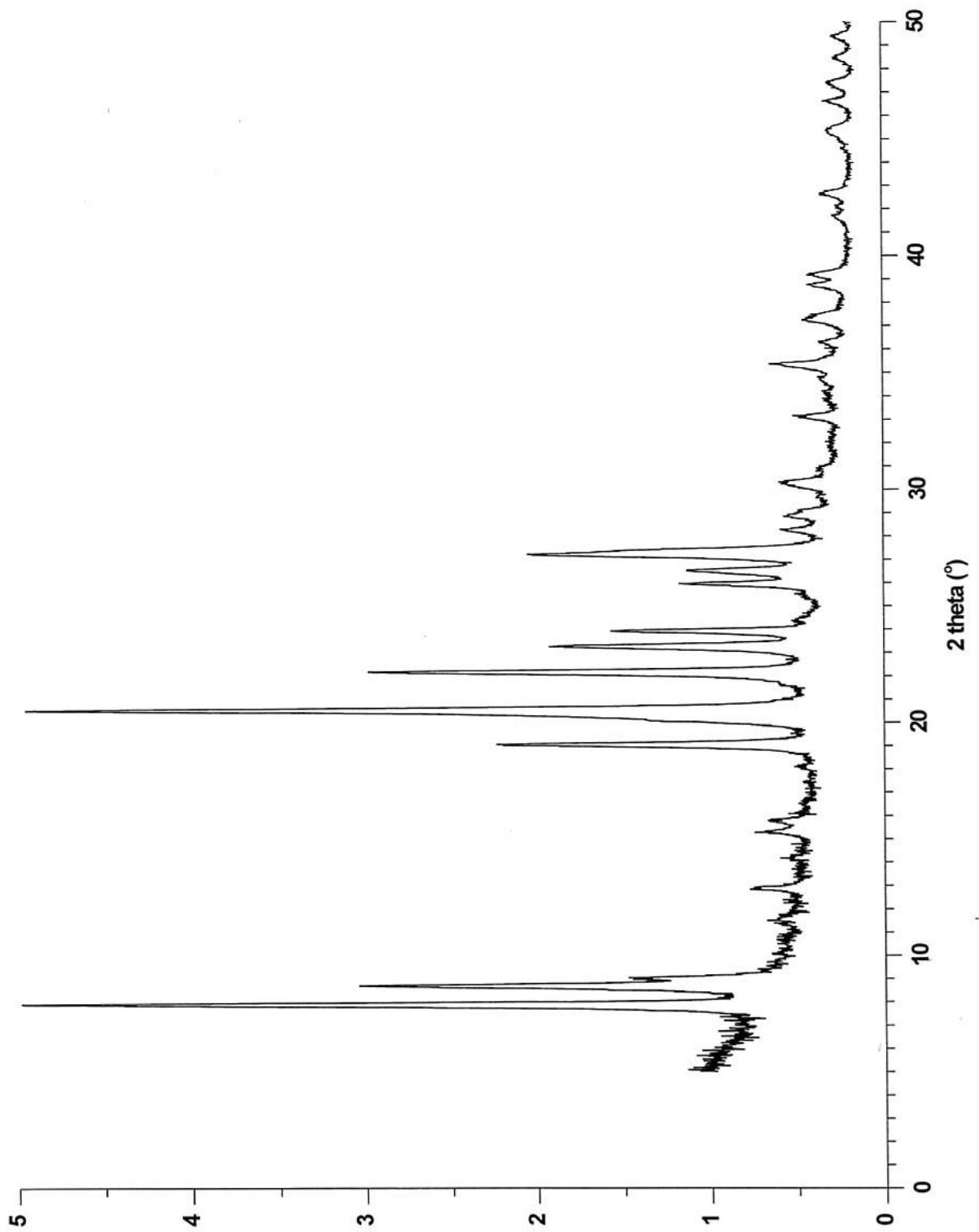
Notes

- a. Increasing SiO₂/Ga₂O₃ in gel from 35 to 70 and to 110 gives SiO₂/Ga₂O₃ in product of 79 and 100 respectively. For products with SiO₂/Ga₂O₃ greater than 100, the preferred template is equimolar benzyldimethylamine + benzyl chloride. [1]
- b. The Na₂O content of the silica source is significant. If gel pH is less than 12.0, it should be adjusted with NaOH solution.
- c. By thermal analysis: template burnout 300-700°C (approximately 10% weight loss).
- d. By ⁷¹Ga MAS NMR: chemical shift is 170 ppm (Ga³⁺ in tetrahedral environment).

EUO

[Ga] EU-1

Si(96.5), Ga(3.5)



FAU

Linde Type X

Si(55), Al(45)

Contributed by Hans Lechert and Philip Staelin

Verified by D. Ginter, E. Basaldella and E. Fallabella Sousa-Aguiar

Type Material $\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384} : w\text{H}_2\text{O}$ ($w \sim 260$)

Method H. Lechert, H. Kacirek [1, 2]

Batch Composition $\text{NaAlO}_2 : 4 \text{SiO}_2 : 16 \text{NaOH} : 325 \text{H}_2\text{O}^{\text{a,b}}$

Source Materials

distilled water

sodium hydroxide (99+% NaOH)

alumina trihydrate (Merck, 65% Al_2O_3)^c

sodium silicate solution (27.35% SiO_2 , 8.30% Na_2O , 1.37 g/mL)

Batch Preparation (for 42 g product)

- (1) [100 g water + 100 g sodium hydroxide], stir until dissolved
- (2) [(1) + 97.5 g alumina trihydrate], stir at 100°C until dissolved, cool to 25°C
- (3) [(2) + 202.5 g water], mix
- (4) [100 g of solution (3) + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
- (5) [219.7 g sodium silicate solution + 612 g water + 59.12 g sodium hydroxide], mix until dissolved
- (6) [(4) + (5)], combine quickly and stir for 30 minutes^d

Crystallization

Vessel: polyethylene bottles

Temperature: 90°C

Time: 8 hours

Agitation: none

Product Recovery

- (1) Filter and wash to pH < 10
- (2) Dry at 100°C, equilibrate over saturated aqueous NaCl
- (3) Yield: near 100% on Al_2O_3

Product Characterization

XRD 100% FAU, $a_0 = 24.92 \text{ \AA}$, competing phases: LTA, GIS, ANA, SOD

Elemental Analysis: $\text{NaAlO}_2 \cdot 1.24 \text{SiO}_2^{\text{f}}$

Crystal Size and Habit: spherical aggregates, 0.8 μm dia.

References

- [1] H. Lechert, H. Kacirek, Zeolites 11(1991) 720
- [2] H. Lechert, H. Kacirek, Zeolites 13 (1992) 192
- [3] G. H. K uhl, Zeolites 7 (1987) 451

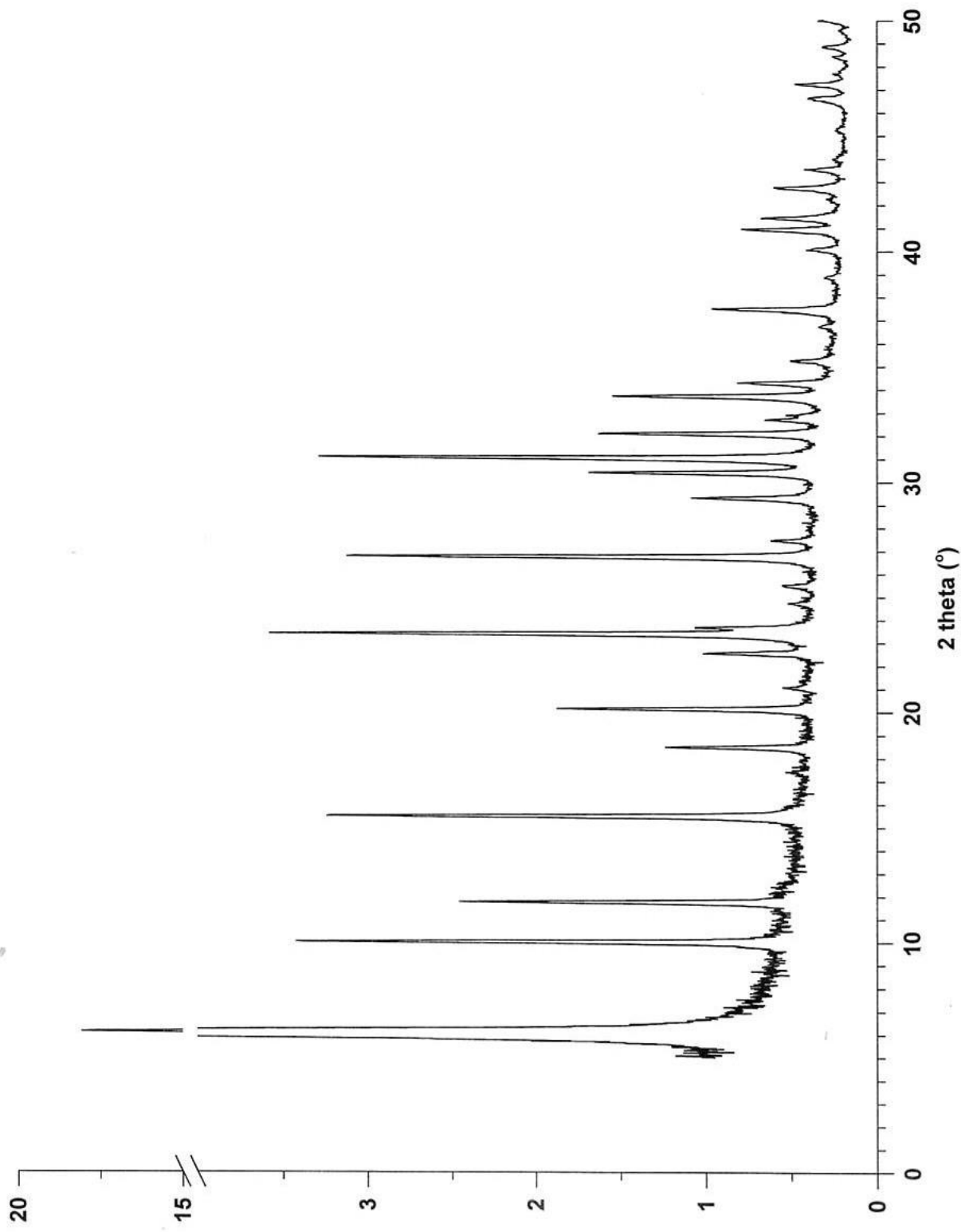
Notes

- a. NaX zeolites are easily obtained with gel $\text{SiO}_2/\text{NaAlO}_2 = 1.4\text{-}5.0$, $\text{NaOH}/\text{NaAlO}_2 = 3.8\text{-}20$ and $\text{H}_2\text{O}/\text{NaAlO}_2 = 150\text{-}400$.
- b. Crystallization at lower water contents suffers from the high initial viscosities of the batches, thus preventing sufficient homogenization. NaX can be obtained without precautions down to $\text{H}_2\text{O}/\text{NaAlO}_2 = 80$. The crystallizing zeolite and its composition depend strongly on the alkalinity being held in the solution phase during the nucleation and growth of the zeolite. For a given batch composition, if the water content is decreased appreciably, the alkalinity will increase. If there are reasons to decrease the water content, the NaOH content should be decreased. Good results were obtained by reducing the alkali content proportional to the water content.
- c. For the batch preparation, the authors would always prefer sodium aluminate instead of alumina trihydrate. Problems often occurred with the solubility of the $\text{Al}(\text{OH})_3$ at the given NaOH concentration, depending on the alumina source. Sodium aluminate is usually available only in technical-grade quality. If only small quantities of NaX or pure substances are desired, it was preferable to use AlCl_3 as the alumina source and to increase the NaOH content of the batch by 3 NaOH on the given batch composition to: $\text{AlCl}_3 : 4 \text{SiO}_2 : 20 \text{NaOH} : 325 \text{H}_2\text{O}$. The resulting NaCl does not disturb the crystallization.
- d. Longer times of homogenization give narrower particle size distributions.
- e. Preferable crystallization temperatures: 67° to 97°C . For safety the crystallization time should be increased to 12 to 14 hours. Experiments have shown that in the given batches up to 30 hours at 90°C no other zeolite impurities were observed.
- f. The Si/Al ratio of the product depends strictly on the NaOH concentration in the batch. Below 2.0 NaOH/liter, the nucleation rate of NaX goes almost to zero and nucleation of GIS occurs, which grows faster than NaX. Pure FAU with $\text{Si}/\text{Al} > 1.5$ in the product cannot be obtained without seeding. Above about 3.0 NaOH/liter, analcime or sodalite is obtained. Below $\text{Si}/\text{Al} = 12.4$, NaA appears. [3]

FAU

Linde Type X

Si(55), Al(45)



FAU

Silica Type X (LSX)

Si(50.5), Al(49.5)

Contributed by Gunter Kühl

Verified by M. Ludvig and D. Millar

Type Material $\text{Na}_{73}\text{K}_{22}\text{Al}_{95}\text{Si}_{97}\text{O}_{384} : \text{wH}_2\text{O}$

Method G. H. Kühl [1]

Batch Composition 5.5 Na_2O : 1.65 K_2O : Al_2O_3 : 2.2 SiO_2 : 122 $\text{H}_2\text{O}^{\text{a-c}}$

Source Materials

distilled water

sodium aluminate (Nalco 680, 45.6% Al_2O_3 , 29.65% Na_2O)

potassium hydroxide, reagent grade (usually ~86% KOH)

sodium hydroxide, reagent grade (usually ~97% NaOH)

sodium silicate solution (PQ Corp. N-brand clarified, 28.7% SiO_2 , 8.9% Na_2O)

Batch Preparation (for 29 g dry product)^d

(1) [30 g water + 22.37 g sodium aluminate], stir until dissolved

(2) [70 g water + 21.53 g potassium hydroxide + 31.09 g sodium hydroxide], stir until dissolved

(3) [(1) + (2)], mix thoroughly^e

(4) [(3) + 71.8 g water + 46.0 g sodium silicate solution], mix thoroughly^f

Crystallization

Vessel: sealed polypropylene or Teflon jar

Incubation: 3 hours at 70°C without stirring

Temperature: 93-100°C

Time: 2 hours

Agitation: either with or without stirring

Product Recovery

(1) Dilute the reaction mixture with distilled water

(2) Filter and wash with 0.01 N NaOH^g

(3) Dry at ambient temperature (drying at 110-125°C acceptable)

(4) Yield: 99+% based on alumina

Product Characterization

XRD: FAU ($a_0 = 25.03 \text{ \AA}$);^h competing phases: LTA (when gel $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$),

SOD (concentration is too high), P (extended aging or crystallization times)

Elemental Analysis: 0.77 Na_2O . 0.23 K_2O . Al_2O_3 . 2.04 SiO_2

Crystal Size and Habit: multi-faceted spherulites of 2-6 μm dia. with 111 faces exposed [1]

Reference

[1] G. H. Kühl, Zeolites 7 (1987) 451

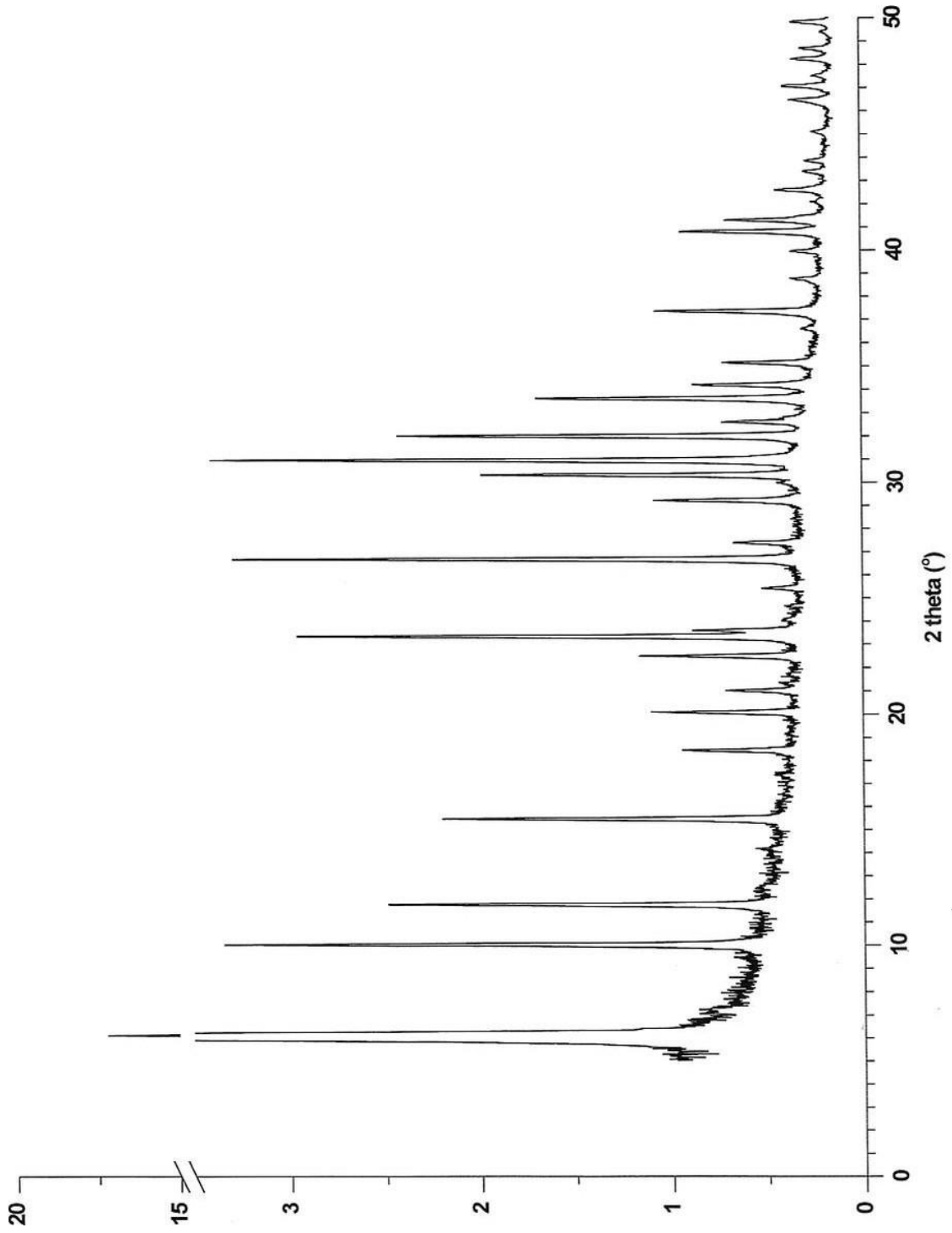
Notes

- a. H₂O includes water from sodium aluminate, waterglass, free and bound water in NaOH + KOH, and added water.
- b. (K₂O + Na₂O)/SiO₂ can be reduced to 2.25 without loss of product quality. However, at least for the initial crystallizations, a value of 3.25 is recommended.
- c. The ratio: Na₂O/(Na₂O + K₂O) is critical; it should be in the range 0.77 to 0.78.
- d. Use plastic or stainless steel equipment throughout.
- e. Solution (1) should be perfectly clear, but it is probably acceptable if a clear solution (3) is obtained after adding NaOH and KOH.
- f. The mixture must not gel before it is well mixed. It usually takes several minutes before a gel if formed.
- g. Wash or exchange in 0.01 N NaOH to prevent hydrolysis; low-silica X hydrolyzes as easily as NaA.
- h. The lower SiO₂/Al₂O₃ ratio enhances the line intensities, the presence of K⁺ attenuates them.

FAU

Low-Silica Type X (LSX)

Si(50.5), Al(49.5)



FAU

Linde Type Y

Si(71), Al(29)

Contributed by David Ginter

Verified by G. Price and C. Kuntz

Type Material $\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}] : 250 \text{ H}_2\text{O}$

Method D. M. Ginter, A. T. Bell and C. J. Radke [1]

Batch Composition^a

Seed Gel (5% of Al): 10.67 $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

Feed Stock Gel (95% of Al): 4.30 $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

Overall Gel: 4.62 $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 180 \text{ H}_2\text{O}$

Source Materials

deionized water

sodium aluminate solid (Strem Chemical^b 1.27 Na/Al, 6.1% H_2O)

sodium hydroxide pellets (J. T. Baker, 99% NaOH)

sodium silicate solution (PQ Corp, N Brand, 28.7 wt% SiO_2 , 8.9 wt% Na_2O)^c

Batch Preparation (for 32 g anhydrous product)

Seed Gel

- (1) [19.95 g water + 4.07 g sodium hydroxide + 2.09 g sodium aluminate], stir in 50 mL plastic bottle until dissolved
- (2) (1) + 22.72 g sodium silicate solution], stir moderately for at least 10 minutes; after stirring, cap the bottle and let the solution age at room temperature for 1 day^d

Feedstock Gel

- (3) [130.97 g water + 0.14 g sodium hydroxide + 13.09 g sodium aluminate], stir in a 500 mL plastic beaker until dissolved
- (4) [(3) 142.43 g sodium silicate solution], stir vigorously with a high-shear turbine mixer^f until the gel appears somewhat smooth; cover the beaker until the addition of the seed gel

Overall Gel

- (5) [(4) + 16.50 g of (2)], slowly add seed gel (2) to feedstock gel (4) under high shear;^f move the beaker during mixing to ensure the entire gel volume encounters the high shear from the turbine (up to 20 minutes)^g

Crystallization

Vessel: 300 mL polypropylene bottle (sealed)

Incubation: One day at room temperature g Temperature: 100°C ^g

Time: After about 5 h, the gel will separate into a solid (containing the NaY Zeolite) that will settle to the bottom, and a hazy supernatant liquid. Continue heating until the supernatant is clear indicating complete crystallization (no more than 2 additional hours)^g

Product Recovery

- (1) Centrifuge; decant supernatant
- (2) Filter the wet solid product; wash with distilled water until pH of filtrate is below 9
- (3) Dry at 110°C
- (4) Yield: approximately 32 g of anhydrous NaY (about 98% on Al₂O₃)

Product Characterization

XRD FAU; characteristic strong reflections at $d = 14.28, 8.75$ and 7.46 \AA , $a_0 = 24.72 \text{ \AA}$

Competing phases (if present): GIS, GME, CHA

Elemental Analysis; NaAlO₂. 2.43 SiO₂

Crystal Size and Habit: octahedral crystals, <1 μm

References

- [1] D. M. Ginter, A. T. Bell, C. J. Radke, in Synthesis of Microporous Materials, Vol. 1, Molecular Sieves, M. L. Occelli, H. E. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p 6
- [2] T. Linder, C. Kurtz, personal communications

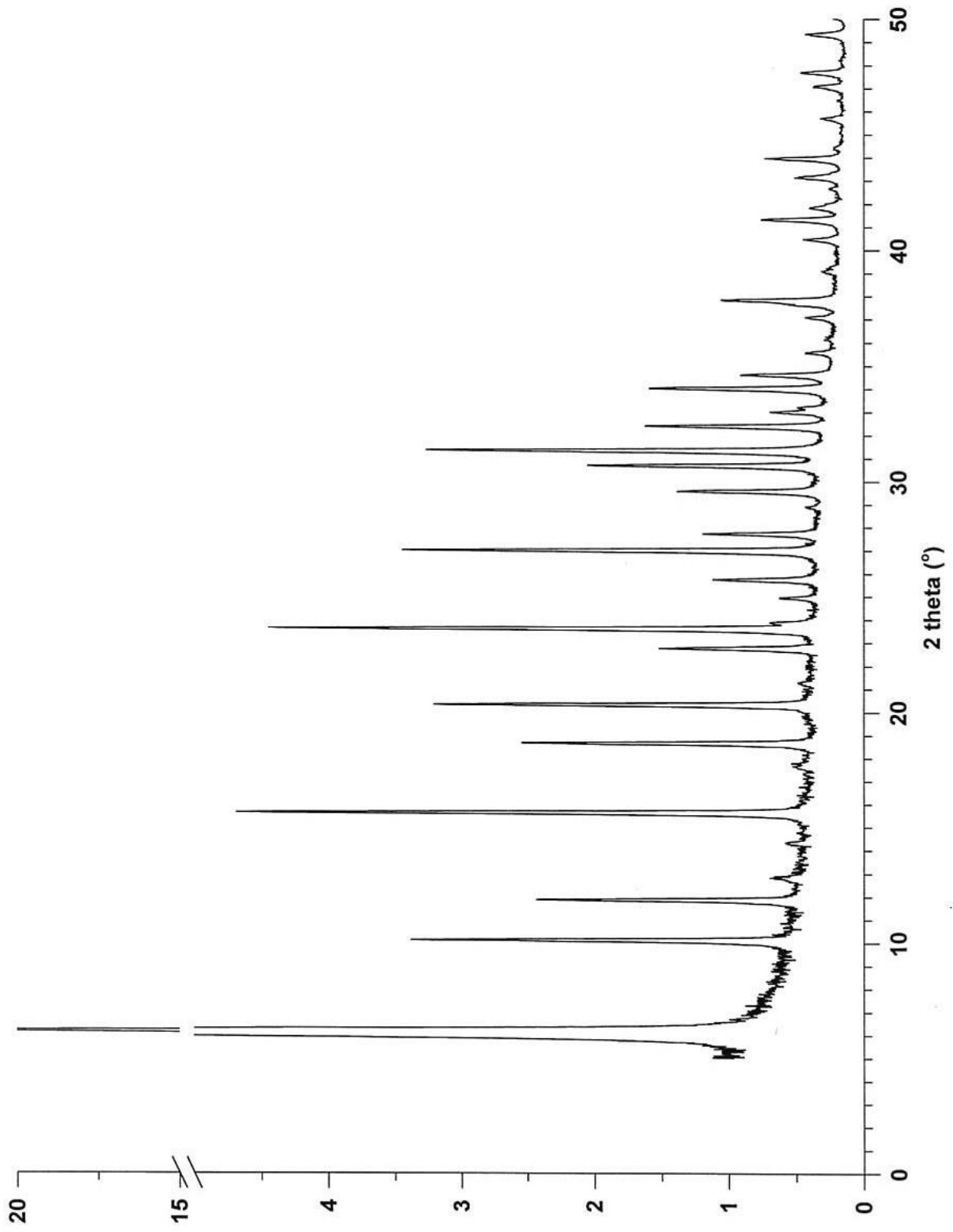
Notes

- a. This procedure is reliable only for the production of submicron NaY crystals and is limited in the range of sizes and compositions that can be produced using slight procedural modifications.
- b. Also available as solutions with this Na/Al ratio from Alcoa and U. S. Aluminate.
- c. It should be clear of precipitated material.
- d. Solution is clear when prepared; during aging, a loose gel forms which contains the NaY seeds.
- e. May be prepared concurrently with the seed gel or just prior to mixing the overall gel.
- f. 1600 rpm with 2.5 inch diameter, 4 paddle radial mixer (minimum) recommended.
- g. If a GIS (NaP) impurity is produced, it can be eliminated by reducing the Na aluminate in (1) to 1.40 g and aging the seed gel for 1 to 5 days prior to blending it into the feedstock. Further aging of the composite is optional with this seed, and pure product has been obtained after crystallization at 90°C for 22 hours. [2]

FAU

Linde Type Y

Si(71), Al(29)



Contributed by Hussein Awala

Verified by I. Kondofersky, A. Kharchenko, S. Komaty, B. Dong

Type Material: Na₈₈ [Al₈₈ Si₁₀₄O₃₈₄] w:H₂O (w ~220)

Method: H. Awala, J-P. Gilson, R. Retoux, P. Boullay, J-M. Goupil, V. Valtchev, S. Mintova [1]

Batch Composition: 9 Na₂O : 1.1 Al₂O₃ : 10 SiO₂ : 122 H₂O

Source Materials

aluminum powder (325 mesh, 99.5 %, Alfa Aesar)
sodium hydroxide (Sigma-Aldrich, 97 %)
silica sol (Ludox-HS 30, 30 wt. % SiO₂, pH=9.8, Aldrich)
distilled water

Batch Preparation

- (1) [2.5 g of NaOH, 3 g dd H₂O, 0.297 g aluminum powder]
- (2) [10 g colloidal silica, 1.1 g NaOH and 1 g dd H₂O]
- (3) [(1) drop wise added to (2); mixing of 1 and 2 in ice bath], stirring and aging for 24 h^a
- (4) Freeze dried, in order to adjust the water content

Crystallization

Vessel: polypropylene bottle
Temperature: 50 °C
Time: 24 h

Product Recovery

- (1) Centrifugation (25 000 rpm, 4h) and whasing with dd water till pH=7
- (2) Freeze-dried the final products
- (3) Yield: about 80 %

Product Characterization

DLS: mono-dispersed particles, average particle size of 10 nm
XRD: FAU
TEM: octahedral morphology
Elemental analysis: ICP (Inductively Coupled Plasma) and (TEM-EDX): Si/Al ~ 1.1

References

- [1] H. Awala, J-P. Gilson, R. Retoux, P. Boullay, J-M. Goupil, V. Valtchev, S. Mintova, Nat Mater. 14 (2015) 447

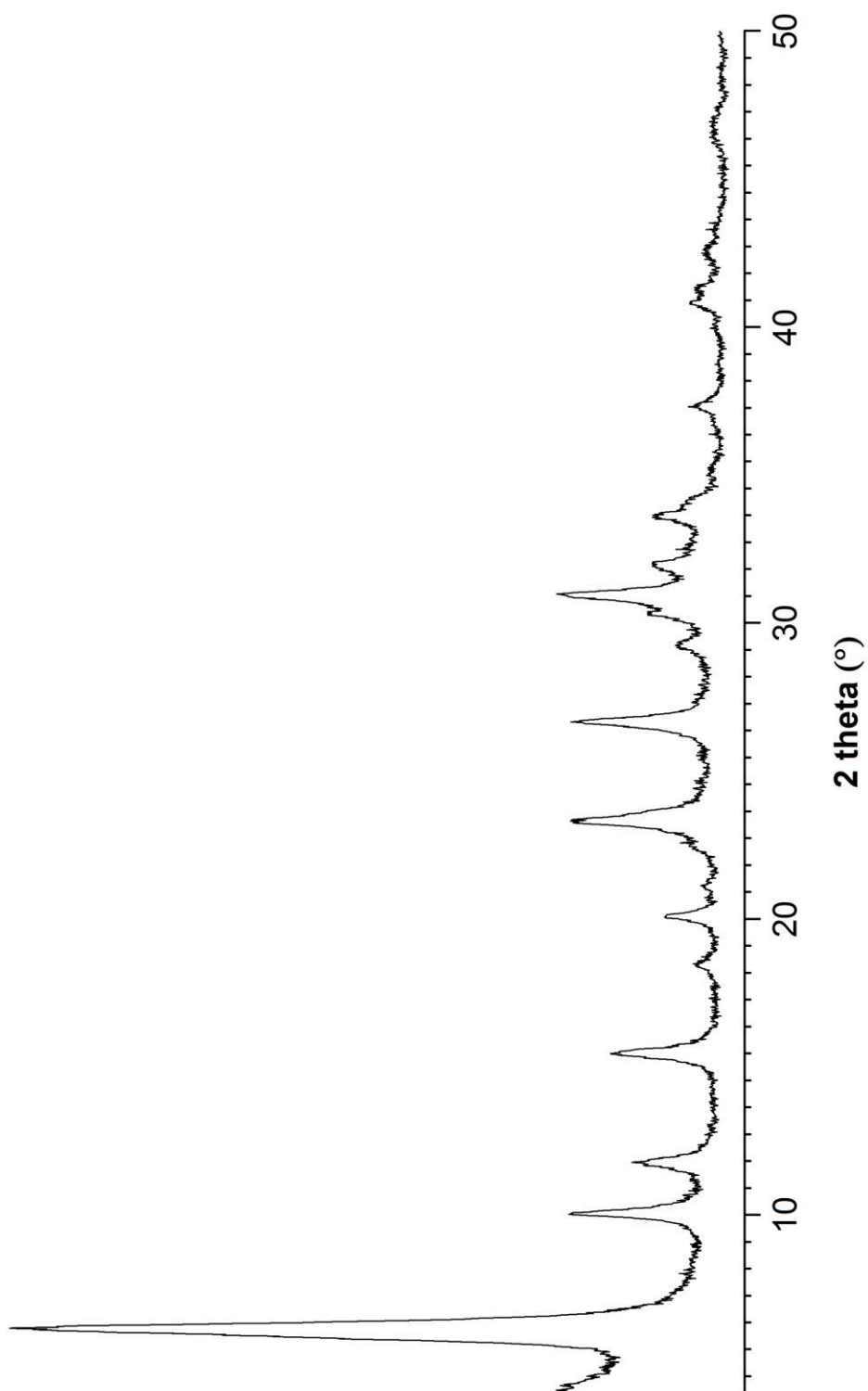
Notes

- a. Clear solution is obtained

FAU

Nanosized Linde Type Na-X

Si(54), Al(46)



Contributed by Moussa Zaarour and Svetlana Mintova

Verified by D. Stosic, D. Wales, X. Zou

Type Material: [TMA_x] [Si_{1.7x}Al_xO_{5.4x}]

Method: S. Mintova, N. H. Olson, T. Bein [1]

Batch Composition: 5.5 (TMA)₂O : 2.3 Al₂O₃ : 10 SiO₂ : 570 H₂O

Source Materials

silica solution (Grade HS-30, 30%, Aldrich)

aluminum isopropoxide [Al(OiPr)₃] (Aldrich)

tetramethylammonium hydroxides pentahydrate (TMAOH.5H₂O, 97%, Aldrich)

distilled water

Batch Preparation

(1) [2.5 g Al(OiPr)₃ + 20.72 g H₂O], stir

(2) [5.26 g TMAOH.5H₂O + (1)], stir^a

(3) [5.1 g silica solution + (2) under stirring], stir 30 min

Crystallization

Vessel: Teflon-lined stainless steel autoclaves

Age 24 h at 40 °C

Temperature: 100 °C

Time: 48 h

Product Recovery

(1) Centrifugation (20.000 rpm, 2 h), redispersion in water in ultrasonic bath; washing till pH=8

(2) Stable colloidal suspension of nanosized crystals

Product Characterization

DLS: 25-45 nm in diameter

XRD: FAU

HRTEM: fully crystalline, uniform, single crystals octahedral morphology

References

[1] S. Mintova, N. H. Olson, T. Bein, *Angew. Chem. Int. Ed.* 38 (1999) 3201

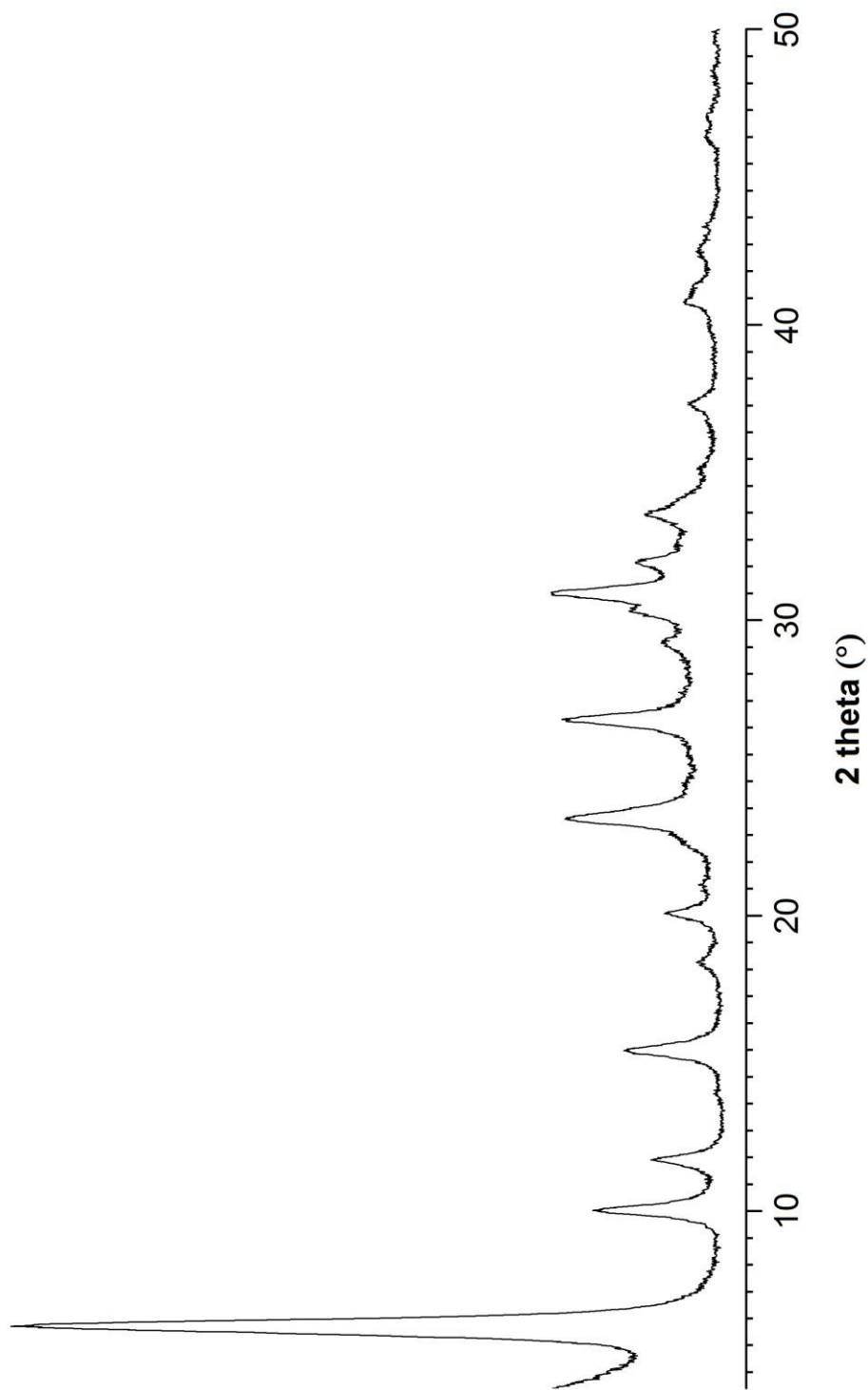
Notes

a. Clear solution is obtained

FAU

Nanosized Linde Type TMA-Y

Si(63), Al(37)



FAU

High-Si Faujasite EMC-1^a

Si(79), Al(21)

Contributed by Joël Patarin

Verified by C-n. Wu, by I. Dwyer, and by J. Zhao

Type Material Na₄₀[Al₄₀Si₁₅₂O₃₈₄]. (15-Crown-5)₈ (H₂O)₆₀

Method T. Chatelain, J. Patarin, M. Soulard, J.-L Guth, P. Schulz [1]

Batch Composition 2.1 Na₂O : 10 SiO₂ : Al₂O₃ : 0.5(15-crown-5) : 100 H₂O

Source Materials

distilled water
crown ether (Aldrich 15-crown-5, 98%)
sodium hydroxide (Fluka, 98%)
sodium aluminate (Carlo Erba, 56% Al₂O₃, 37% Na₂O)
silica sol (Ceca, 40% SiO₂)

Batch Preparation^b (for 15 g product)^c

- (1) [17.75 g water + 2.25 g crown ether], dissolve under continuous stirring
- (2) [(1) + 1.65 g sodium hydroxide], dissolve under continuous stirring
- (3) [(2) + 3.64 g sodium aluminate], dissolve under continuous stirring
- (4) [(3) 30.00 g silica sol] stir with a magnetic bar at approximately 200 rpm Continue stirring for 24 hours at room temperature.^d Gel pH = 13.5-14

Crystallization

Vessel: Teflon-lined stainless steel autoclave (150 mL)
Temperature: 110°C
Time: 8 days
Agitation: none
Final pH = approximately 12.5

Product Recovery

- (1) Filter and wash with distilled water until pH of the filtrate is close to 6
- (2) Dry at 60-70°C overnight
- (3) Yield: 99% based on alumina (as-synthesized product containing the organic template and some water)^e

Product Characterization

XRD FAU, a₀=24.57Å
Elemental Analysis: SiO₂/Al₂O₃ 7.6 (by atomic absorption spectroscopy and ²⁹Si MAS NMR)
Crystal Size and Habit: truncated octahedra, 1 μm dia.

References

- [1] T. Chatelain, J. Patarin, M. Soulard, J.-L Guth, P. Schulz, Zeolites 15 (1995) 90

- [2] D. Anglerot, F. Fitoussi, P. Schulz, T. Chatelain, F. Dognier, J. Patarin, J.-L Guth, in *Synthesis of Porous Materials, Zeolites, Clays and Nanostructures*, M. L. Occelli, H. Kessler (eds.), Marcel Dekker, New York, 1996, p. 325

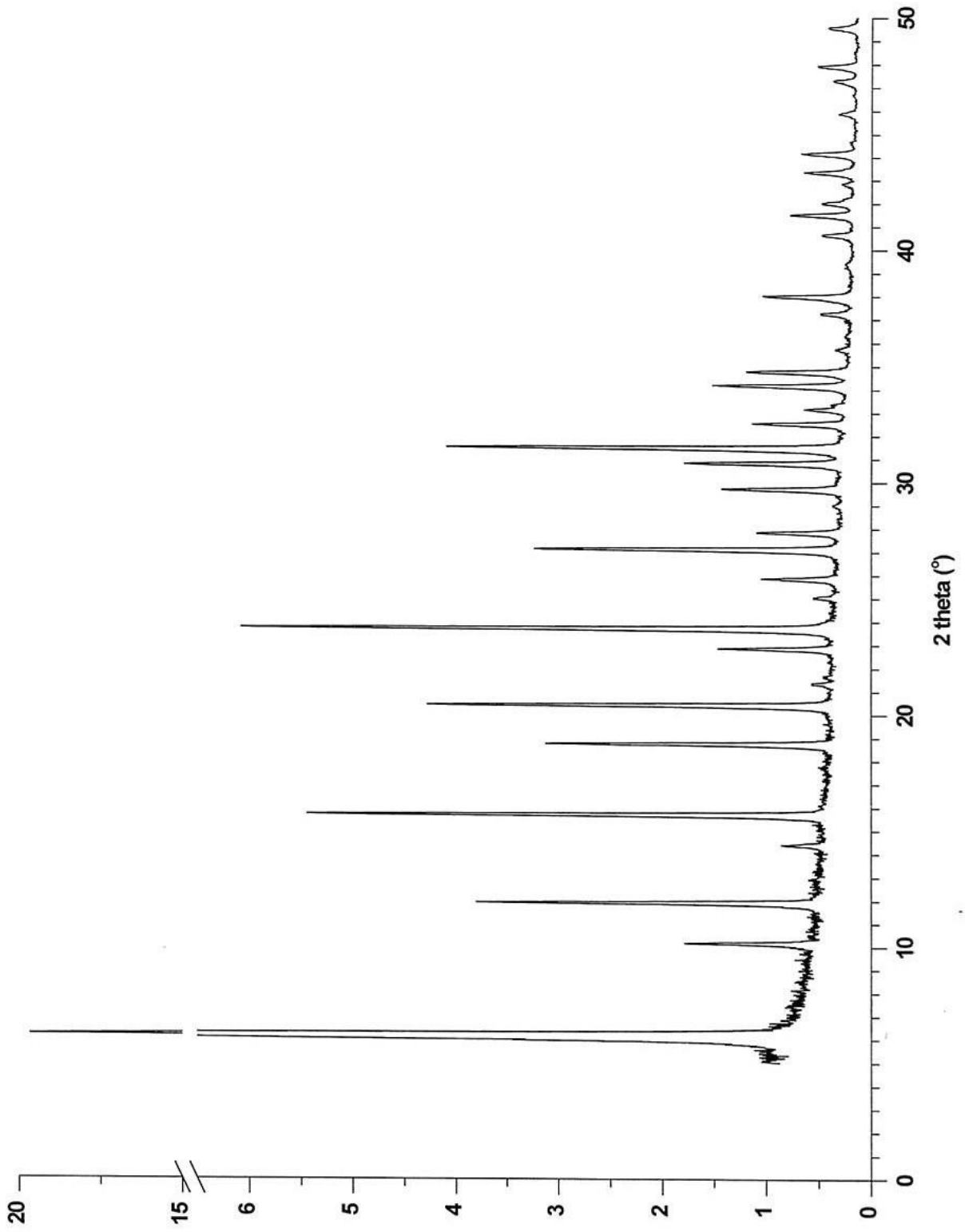
Notes

- a. EMC-1 = Elf Mulhouse Chemistry number one.
- b. The starting mixture is prepared in a polypropylene bottle.
- c. This synthesis has been successfully carried out at the kilogram scale [2].
- d. The mixture is aged in a closed polypropylene bottle.
- e. Calcination at 450°C in air removes the template.

FAU

High-Si Faujasite EMC-1^a

Si(79), Al(21)



FAU

[Ga] Type Y

Si(61), Ga(39)

Contributed by Mario Occelli

Verified by F. Machado, S. Iwamoto and M. Levinbuk

Type Material Na₇₆Ga₇₆Si₁₁₆O₃₈₄ : w H₂O

Method M. L Occelli [1]

Batch Composition 4.0 Na₂O : Ga₂O₃9.8 SiO₂ : 150 H₂O

Source Materials

deionized water

sodium hydroxide, reagent grade (usually ~.97% NaOH)

gallium oxide (99.99%)

silica sol (Dupont HS-40, 39% SiO₂, 0.5% Na₂O)

Batch Preparation

- (1) [32.0 g water + 32.0 g sodium hydroxide + 18.7 g gallium oxide], dissolve gallium oxide in 50% NaOH at 80°C with stirring until a clear solution is obtained. Cool to ambient temperature
- (2) [(1) + 70.6 g water], mix ^a
- (3) [150.2 g silica sol + 70 g water], mix
- (4) [(3) + (2)], add the sodium gallate solution dropwise to the vigorously-stirred, diluted silica sol. Continue stirring for 16 hours at ambient temperature

Crystallization

Vessel: one-liter round-bottomed flask with reflux condenser

Incubation: 16 h at 25°C with stirring

Temperature: 95°C ^b

Time: 90 hours ^c

Product Recovery

- (1) Filter and wash with deionized water until pH < 10
- (2) Dry at 110°C
- (3) Yield: near 100% on Ga₂O₃

Product Characterization

XRD: FAU; no other crystalline phases or amorphous material observed

Elemental Analyses: 38.7 wt% Ga₂O₃, 38.0 wt% SiO₂, 12.5 wt% Na₂O (0.98

Na₂O Ga₂O₃ : 3.06 SiO₂) ^d

References

[1] M. L Occelli, US Patent 4 803 060 (1989)

[2] M. L Occelli, A. E. Schweizer, H. Eckert, A. Auroux, P. S. Iyer, Appl. Catalysis (to be submitted)

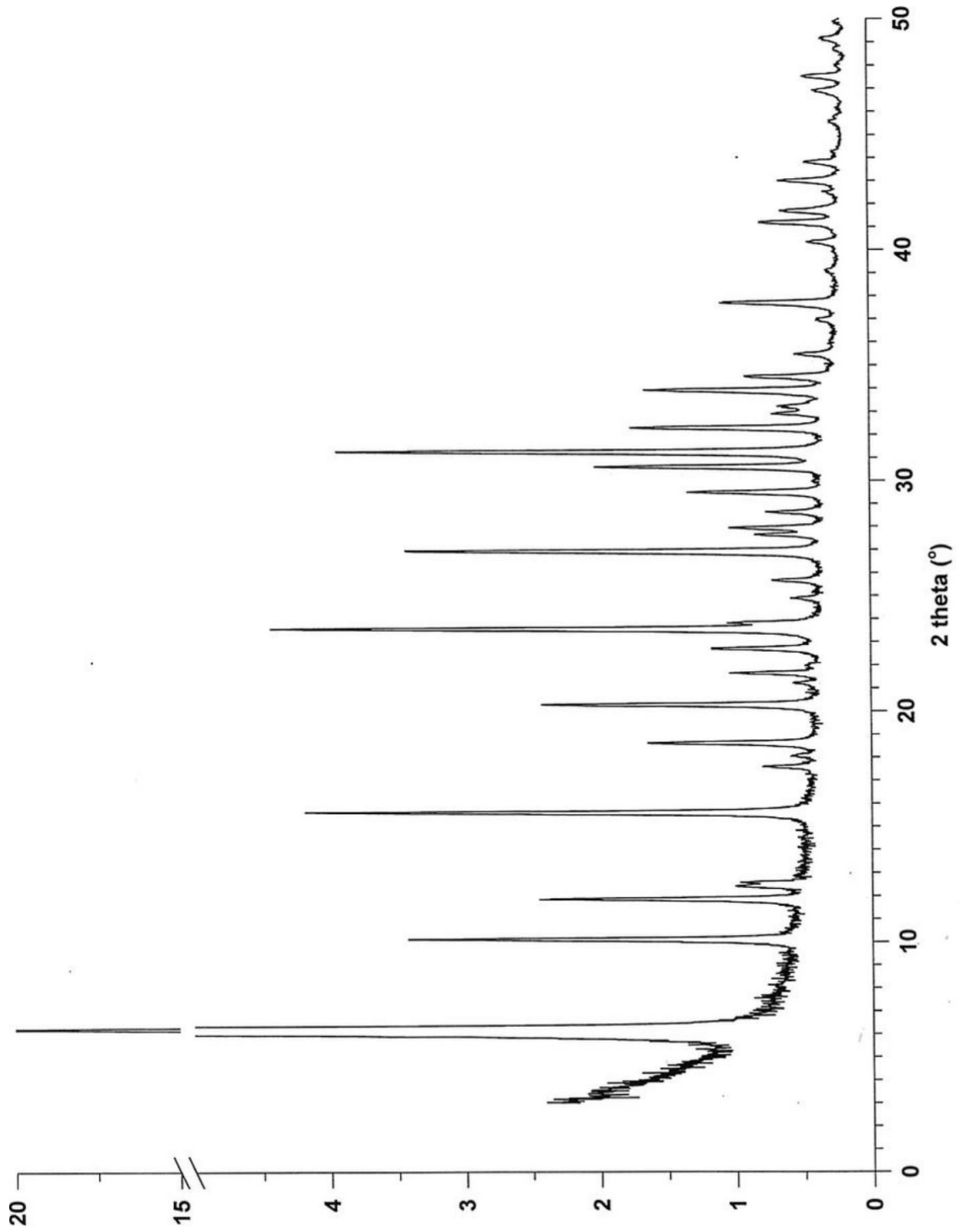
Notes

- a. Diluted sodium gallate solution must be clear.
- b. The temperature of the stirred, cold-aged hydrogel is raised to 95°C. When the hydrogel reaches 95°C the stirring is immediately stopped.
- c. Method to reduce crystallization time given in ref. [1, 2]
- d. After calcination at 600°C for 2 h; BET surface area 541 m²/g.

FAU

[Ga] Type Y

Si(61), Ga(39)



FAU

SAPO-37

Al(47), P(36), Si(17)

Contributed by M. J. Franco and J. Pérez-Pariente

Verified by J. Patarin and M. Ribeiro

Type Material (7TMA, 13TPA)[Al₉₀Si₃₃P₆₉O₃₈₄]
(TMA = tetramethyl ammonium, TPA = tetra-n-propyl ammonium)

Method M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz [1]

Batch Composition 0.025(TMA)₂O : 1.0(TPA)₂O : 1.0Al₂O₃ : 1.0P₂O₅ : 1.0SiO₂ : 50H₂O

Source Materials

deionized water

phosphoric acid (Riedel-de Haen, 85% H₃PO₄)

alumina (pseudoboehmite, Vista, 70% Al₂O₃)^a

tetrapropylammonium hydroxide (TPAOH), Alfa, 40% aqueous solution)^b

tetramethylammonium hydroxide (TMAOH. 5H₂O, Aldrich, 99%)

fumed silica (Aerosil 200, Degussa)

Batch Preparation (for 6.2 g product)^c

- (1) [20.69 g water + 23.04 g phosphoric acid + 14.56 g alumina]. Mix water and phosphoric acid at 293K and add the alumina very slowly with vigorous stirring (1500 rpm). Continue stirring for 8 hours at 293K in a temperature-controlled bath
- (2) [101.68 g tetrapropylammonium hydroxide (40% solution) + 0.90 g tetramethylammonium hydroxide + 6.00 g silica]. Dissolve the TMAOH in the TPAOH solution in a separate glass beaker. To this solution add the silica under vigorous stirring. Continue stirring for one hour
- (3) [(1) + (2)] Add silicate solution (2) slowly to aluminate slurry (1) under vigorous stirring. Continue stirring for 24 hours at 293 K. The final gel pH should be approximately 7.5

Crystallization

Vessel(s): 60 mL Teflon-lined stainless steel autoclave(s)

Temperature: 200°C^d

Time: 13 hours

Agitation: none

Product Recovery

- (1) Quench autoclave in cold water
- (2) Recover solids by centrifugation (6000 rpm)
- (2) Wash with cold distilled water
- (4) Dry at 80°C for 16 hours
- (5) Yield: 3.7 g solid/100 g of gel (19% on Al₂O₃)

Product Characterization

XRD: FAU-type, pure. Competing phases: AFI and SOD when other compositions and/or crystallization treatments are used

Elemental Analysis: $(\text{Si}_{0.17}\text{Al}_{0.47}\text{P}_{0.36})_{192}\text{O}_{384} \cdot 3.5(\text{TMA})_2\text{O} \cdot 6.5(\text{TPA})_2\text{O}^e$

Crystal Size and Habit: Crystals are quite homogeneous in size (approximately 4.0 μm dia.) and show interpenetrating octahedra morphology^f

Reference

- [1] M. J. Franco, J. Pérez-Pariente, A. Mifsud, T. Blasco, J. Sanz, *Zeolites* 12 (1992) 386

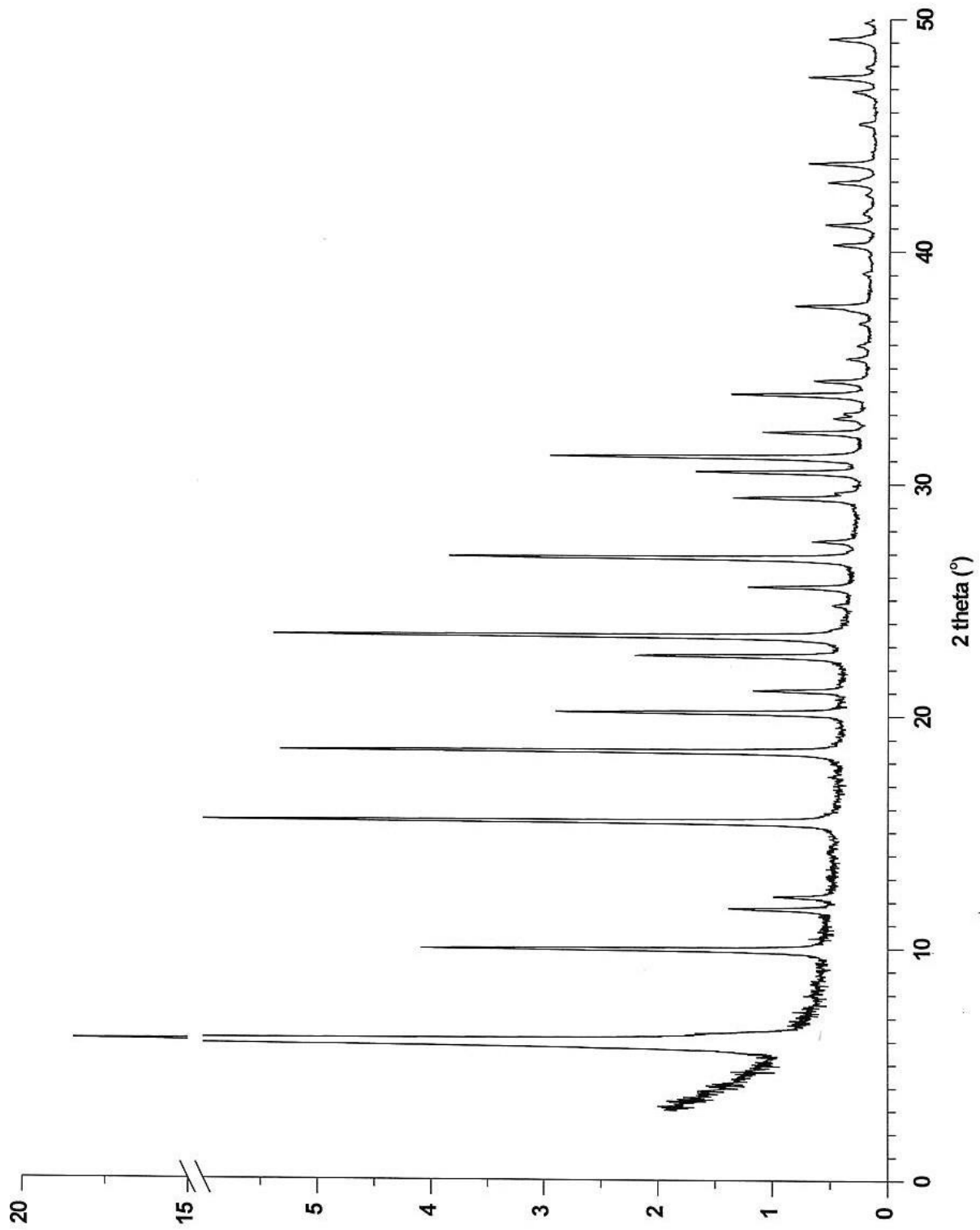
Notes

- a. B.E.T. surface area 271 m²/g; the alumina may be critical. Aluminum isopropoxide gave negative results.
- b. Commercial 20% TPAOH can be vacuum stripped to 40%; however, it is critical to make sure that there has not been decomposition of the TPAOH. For this reason, it is necessary to make a OH⁻ titration before and after the evaporation process to check that the total amount of OH has not changed. (Na + K) < 340 ppm
- c. During preparation of the gel, it is very important to use a closed vessel and a temperature controlled bath (293K) to ensure a constant water concentration in the gel. This vessel can be a polypropylene bottle with a hole in the cap to fit the rotating shaft of the stirring device. A stirring device with two movable Teflon blades is recommended.
- d. Heat-up rate: 2.5°/min.; autogenous pressure.
- e. Flow thermogravimetric analysis showed three different weight losses: 373 to 473K (water desorption), 473 to 688K (decomposition of TPA⁺ in the alpha cages), 588 to 973K (decomposition of TMA⁺ in the sodalite cages).
- f. Increasing (TPA)₂O/Al₂O₃ in gel from 1.0 to 1.5 (keeping TPA⁺/TMA⁺ = 40) decreased average crystal diameter from 4 to 2 μm and increased product yield by 100%. [1]

FAU

SAPO-37

Al(47), P(36), Si(17)



FER

ZSM-35

Si(87), Al(13)

Contributed by Jinxiang Dong

Verified by S. Weigel, L Schreyeck, and T. Beelen

Type Material Na₅[Al₅Si₃₁O₇₂] : wH₂O (w ~18)

Method P. A. Jacobs, J. A. Martens [1]

Batch Composition 1.85 Na₂O : Al₂O₃ : 15.2 SiO₂ : 592 H₂O : 19.7 C₂DN^a (C₂DN ethylenediamine)

Source Materials

distilled water
sodium hydroxide (Merck, reagent grade)
sodium aluminate (Hopkin & Williams, technical grade)^b
silica sol (Dupont Ludox AS-30, 30% SiO₂)
ethylenediamine (Merck, reagent grade)

Batch Preparation (for 10 g dry product)

- (1) [129 g water + 0.7 g sodium hydroxide + 3.3 g sodium aluminate], stir until dissolved
- (2) [46.47 g silica sol + 18.3 g C₂DN], mix
- (3) [(1) + (2)], mix thoroughly

Crystallization

Vessel: stainless steel autoclaves (250 mL)
Temperature: 177°C
Time: 10 days
Agitation: 15 rpm, tumbling [2]

Product Recovery

- 1) Filter solid products and wash with distilled water
- 2) Dry at 120°C
- 3) Yield: 60% on SiO₂

Product Characterization

XRD: FER (only crystalline phase); Competing phases: quartz, MOR, MFI
Elemental Analysis: SiO₂/Al₂O₃ = 13
Crystal Size and Habit: irregular, approximately 1 μm long

References

- [1] P. A. Jacobs, J. A. Martens, Stud. Surf. Sci. Catal. 33 (1987) 217
- [2] L. Schreyeck, personal communication
- [3] C. L Kibby, A. J. Perrota, F. L Massoth, J. Catal. 35 (1974) 256
- [4] W. Xu, I. Li, W. Li, H. Zhang, B. Hang, Zeolites 9 (1989) 468

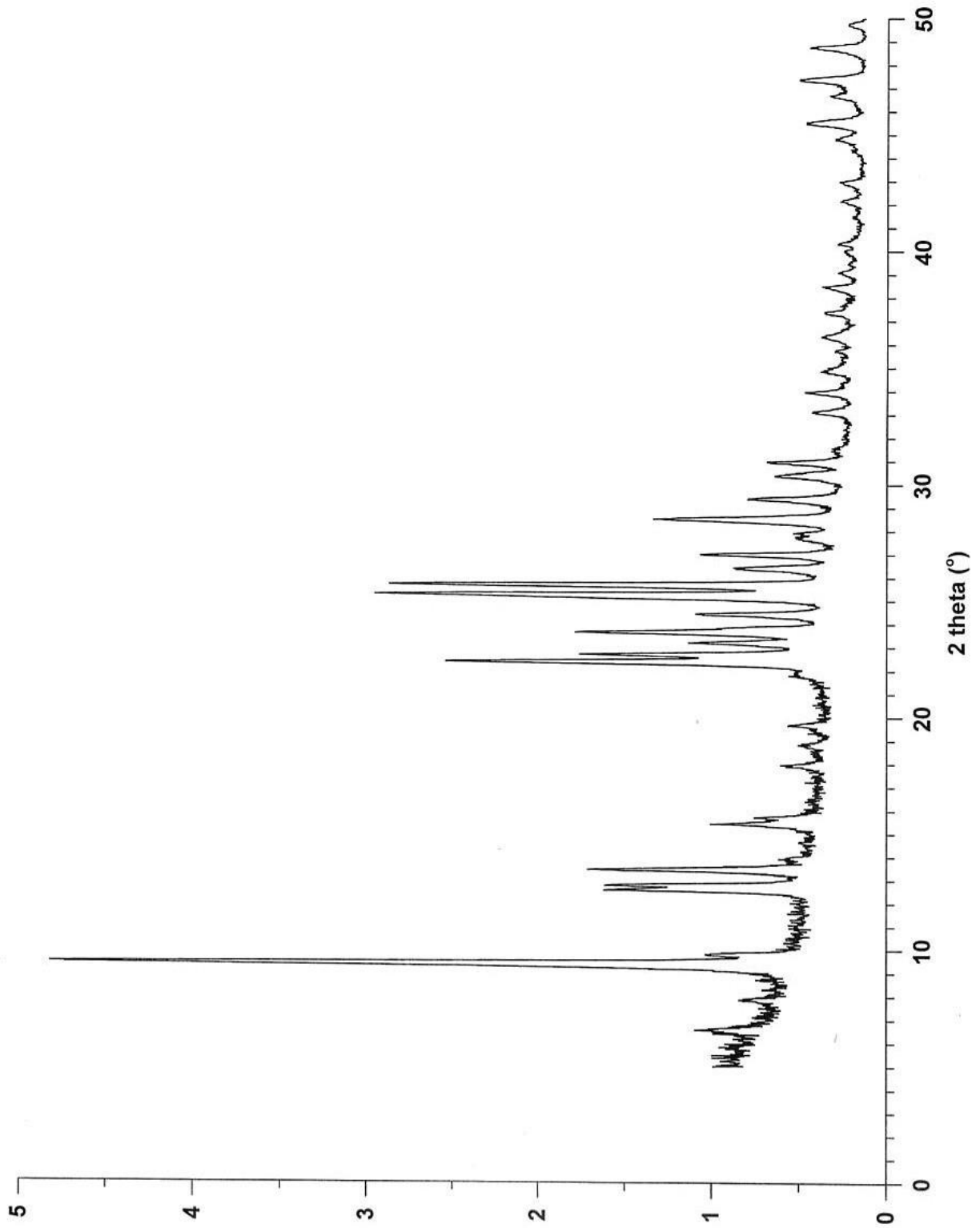
Notes

- a. Hydrothermal syntheses using different organic additives are reported in the literature, particularly pyrrolidine [1] and tetramethyl-ammonium cation [3]. Nonaqueous methods based on ethylenediamine plus triethyl-amine give good crystallinity and improved yield. [4]
- b. Assumed 1.28 Na/Al, 16% H₂O

FER

ZSM-35

Si(87), Al(13)



Contributed by Lovat V. C. Rees

Verified by Yingcai Long, P. Sidheswaran and G. Price

Type Material $(\text{NaAlO}_2)_7(\text{SiO}_2)_9$

Method L. V. C. Rees and S. Chandrasekhar [1]

Batch Composition Al_2O_3 : 2.2 SiO_2 : 5.28 NaF : 105.6 H_2O

Source Materials

distilled water
sodium fluoride (BDH Analar)
kaolinite (Al_2O_3 : 2.2 SiO_2 : 2 H_2O)^a

Batch Preparation (for 10 g dry product)

- (1) [87.7 g water + 10.4 g sodium fluoride], stir and make a slurry
- (2) [(1) + 12.7 g kaolin], mix thoroughly

Crystallization

Vessel: sealed polypropylene
Time: 60 days
Temperature: 85°C
Agitation: none
pH: initial 7.5, final 9-10

Product Recovery

- (1) Filter and wash thoroughly with distilled water
- (2) Exchange twice with NaCl solution
- (3) Wash with distilled water (adjusted to pH = 10 with NaOH)
- (4) Dry at 85°C for 24 hours
- (5) Rehydrate over water vapor from saturated NaCl solution

Product Characterization

XRD: Strong zeolite P competing phases: CHA, no SOD
Elemental Analysis: $\text{NaAlO}_2 \cdot 1.18 \text{SiO}_2$ (by atomic absorption spectroscopy)^{b,c}
Crystal Size and Habit: spherulitic particles of approximately 10 μm dia.

Reference

- [1] L. V. C. Rees, S. Chandrasekhar, Zeolites 13 (1993) 535

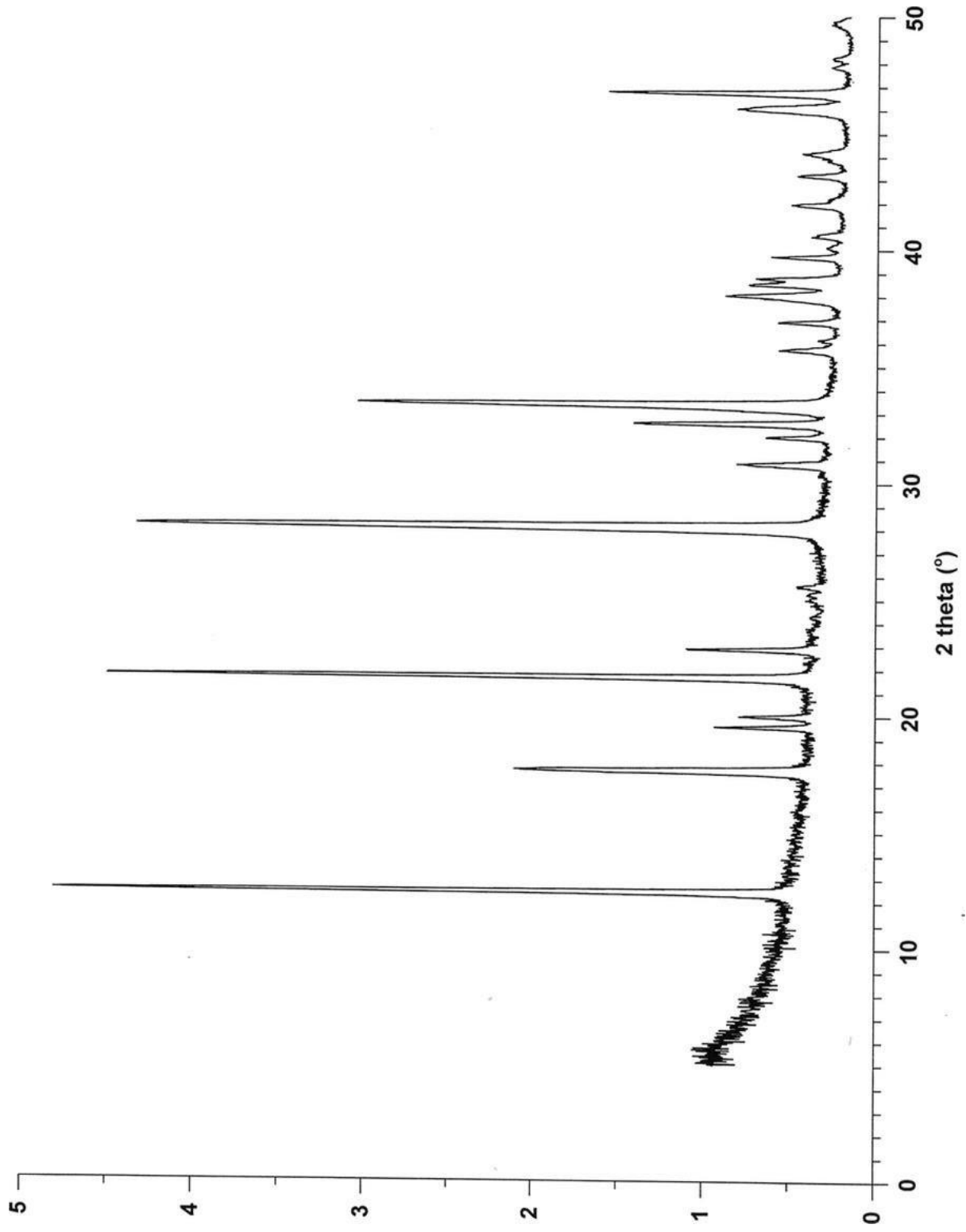
Notes

- a. Kaolinite from Trivandrum, Kerela, India
- b. Dissolution of the zeolite sample for atomic adsorption: 0.1 g sample was treated with 30 mL of a mixture of HCl (37%), HF (48%) and distilled water (ratio 1:1:1); the same was kept for two to three days for complete dissolution.
- c. ²⁹Si MAS NMR gave five lines with chemical shifts of -86.79, -91.55, -97.19, -102.86 and -107.10 ppm. ²⁷Al MAS NMR gave two lines, intense Al (tet) at 58.58 and weak (oct) at -0.42 ppm.

GIS

Zeolite P

Si(54), Al(46)



IMF

IM-5

Si(93), Al(7)

Contributed by Suk Bong Hong

Verified by J. Rimer, T. Okubo, W. Chaikittisilp

Type Material: $\text{Na}_{5.9}(\text{SDA})_{13.1}[\text{Al}_{21.1}\text{Si}_{266.9}\text{O}_{576}] : w \text{ H}_2\text{O}$
(SDA = 1,5-bis[*N*-methylpyrrolidinium]pentane (1,5-MPP))

Method: S.-H. Lee, D.-K. Lee, C.-H. Shin, Y.-K. Park, P. A. Wright, W. M. Lee, S. B. Hong [3]

Batch Composition: 4.5 (1,5-MPP) : 11.0 Na_2O : 1.0 Al_2O_3 : 30 SiO_2 : 1200 H_2O

Source Materials

deionized water

1,5-MPP dibromide^a

sodium hydroxide (Aldrich, 50% NaOH solution)

aluminium nitrate nonahydrate (Junsei, 98%, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)

silicon dioxide (Degussa Aerosil 200 or Cabot Cab-O-Sil M5)

Batch Preparation (for 3 g dry product)

- (1) [58.31 g water + 1.09 g aluminium nitrate nonahydrate + 5.03 g sodium hydroxide (50% solution)], stir until dissolved
- (2) [(1) + 5.14 g silica], mix thoroughly and stir for 30 minutes
- (3) [(2) + 5.25 g 1,5-MPP dibromide], stir for 24 hours^b

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 160 °C

Time: 14 days

Agitation: 100 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 90 °C
- (4) Yield: 3.1 g

Product Characterization

XRD: IMF; competing phase: ANA (when $\text{NaOH}/\text{SiO}_2 > 1.00$)

Elemental analysis: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25.3$ [3]

Crystal size and habit: needle-like crystallites of approximately 0.6–1.0 μm in length and less than 0.1 μm in diameter

References

- [1] E. Benazzi, J.L. Guth, L. Rouleau, PCT WO 98/17581, 1998
- [2] E. Benazzi, J.L. Guth, L. Rouleau, US Patent 6,136,290, 2000

- [3] S.-H. Lee, D.-K. Lee, C.-H. Shin, Y.-K. Park, P. A. Wright, W. M. Lee, S. B. Hong, *J. Catal.* 215 (2003) 151

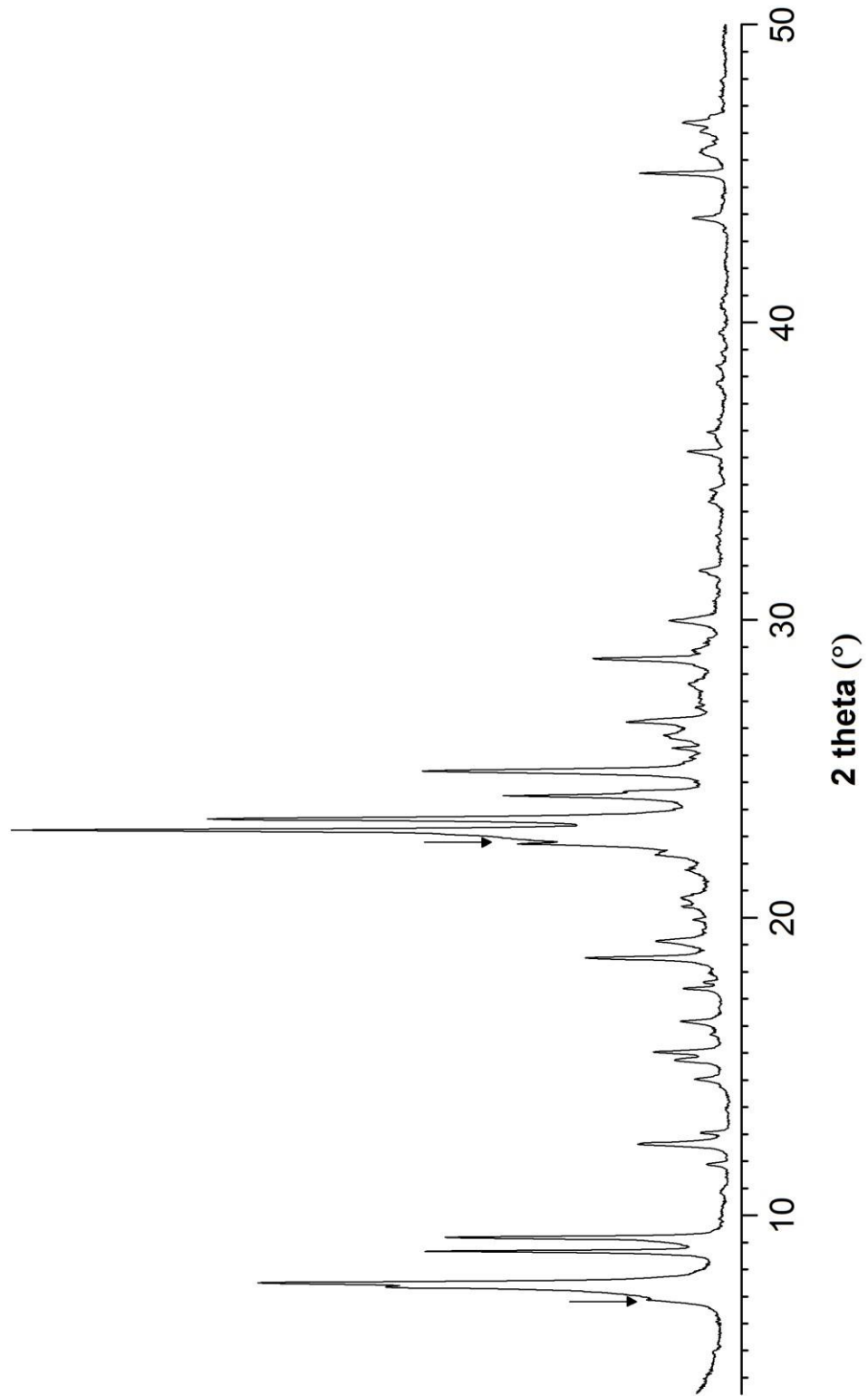
Notes

- a. template preparation procedure is given in [3].
- b. pH of the final gel is 12.8.

IMF

IM-5

Si(93)Al(7)



Contributed by Manuel Moliner

Verified by L. Tosheva, V. Georgieva, L. Lakiss

Type Material: [Si_{19.98}Ge_{26.02}O₉₂]

Method: A. Corma, M. J. Diaz-Cabanias, J. L. Jorda, C. Martinez, M. Moliner [1]

Batch Composition: 0.67 SiO₂ : 0.33 GeO₂ : 0.05 Al₂O₃ : 0.15 Hex(OH)₂ : 0.1 HexBr₂ : 0.3 HF : 1.5 H₂O

Source Materials

Ludox AS-40 (SiO₂) (40 %, Aldrich)
Germanium dioxide (GeO₂) (>99.9%, Aldrich)
Alumina (Al₂O₃) (78%, Sasol)
Hexamethonium hydroxide (Hex(OH)₂) (0.1M, Aldrich)
Hexamethonium bromide (HexBr₂) (>99.9%, Sigma)
Ammonium fluoride (NH₄F) (98 %, Sigma-Aldrich)
Double distilled water (H₂O)

Batch Preparation^a

- (1) [0.22 g HexBr₂ + 9.22 g Hex(OH)₂ + 0.04g Al₂O₃], dissolve under continuous stirring
- (2) [(1) + 0.2 g GeO₂], dissolve under continuous stirring
- (3) [(2) + 0.62 g Ludox AS-40], dissolve under continuous stirring
- (4) [(3) + 0.07 g NH₄F], dissolve under continuous stirring
- (5) Freeze-drying for 48h
- (6) Absorption of water (77% humidity)^b

Crystallization

Vessel: Teflon-lined stainless steel autoclave (5 mL)
Temperature: 180 °C
Time: 24 h

Product Recovery

- (1) Filtration, rinsed with distilled water
- (2) Dried at 70 °C overnight
- (3) Calcination of the material at 550 °C for 3 hours in an air stream

Product Characterization

XRD: ITQ-33
SEM: prismatic crystals, 5 μm

Reference

- [1] A. Corma, M. J. Diaz-Cabanias, J. L. Jorda, C. Martinez, M. Moliner, Nature 443 (2006) 842

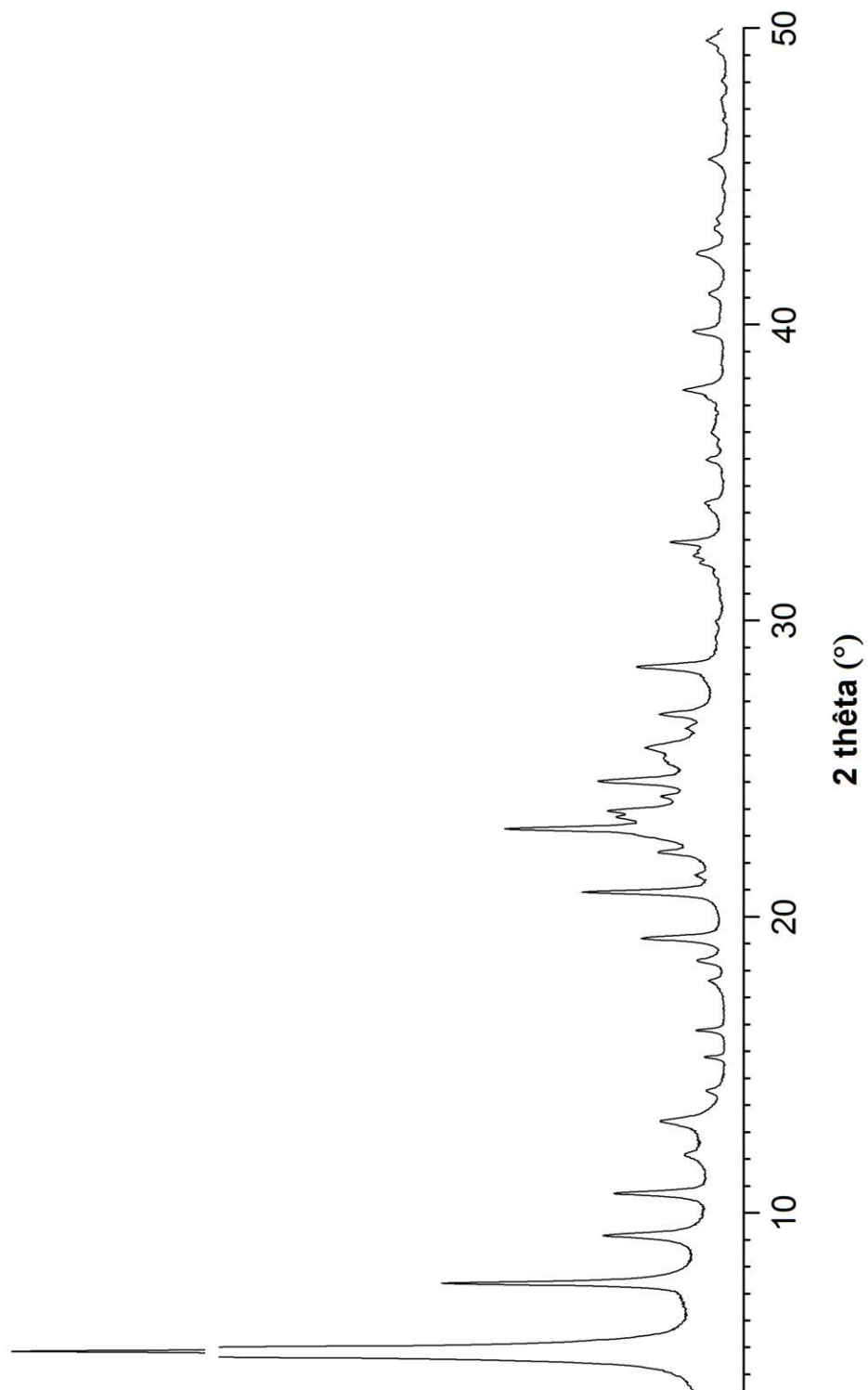
Notes

- b. The starting mixture is prepared in a polypropylene bottle
- c. Absorption of water in desiccator until the initial composition is reached

ITT

ITQ-33

Si(19.98), Ge(26.02)



KFI

ZK-5

Si(77). Al(23)

Contributed by J. P. Verduijn

Verified by J. Patarin, I. Kornatowski and S. Ahmed

Type Material $K_{22}[Al_{22}Si_{74}O_2]$: w H₂O

Method J. P. Verduijn [1]

Batch Composition 2.30 K₂O : 0.1 Sr(NO₃)₂ : Al₂O₃ : 10 SiO₂ : 160 H₂O

Source Materials

deionized water

potassium hydroxide (Baker 0222, pellets, 86.8% KOH)

alumina (Baker 0005, 98.6% Al(OH)₃)

silicic acid (AKZO SM 604, 90% SiO₂)^a

strontium nitrate (Fluka 85900)^b

Batch Preparation (for 57 g product)

- (1) [50.00 g water + 29.76 g potassium hydroxide + 15.80 g alumina], heat to boiling until clear; cool to room temperature and correct weight loss due to boiling
- (2) [96.97 g water + 66.77 g silicic acid], mix until smooth (approximately 6 minutes)
- (3) [75.08 g water + 2.124 g strontium nitrate], mix until dissolved
- (4) [(2) + (3) + 25.12 g water (rinse)], mix for 6 minutes
- (5) [(4) + (1) + 25.08 g water (rinse)], mix for 6 minutes^c

Crystallization

Vessel: 300 mL stainless steel autoclave^d

Time: 115 hours^e

Temperature: 150°C^f

Agitation: none

Product Recovery

- (1) Cool to room temperature^g
- (2) Filter and wash (5 times) with 650 mL water; the pH of the last wash water = 10.5
- (3) Dry in a 150°C oven for 16 hours
- (4) Yield: 57.2 g (97% on Al₂O₃)

Product Characterization

XRD: KFI (only crystalline product) Elemental Analysis: SiO₂/Al₂O₃ = 6.6

Crystal Size and Habit: ~ 0.5 μm

Reference

- [1] J. P. Verduijn, US Patent 4 944 249 (19 February 1991)

Notes

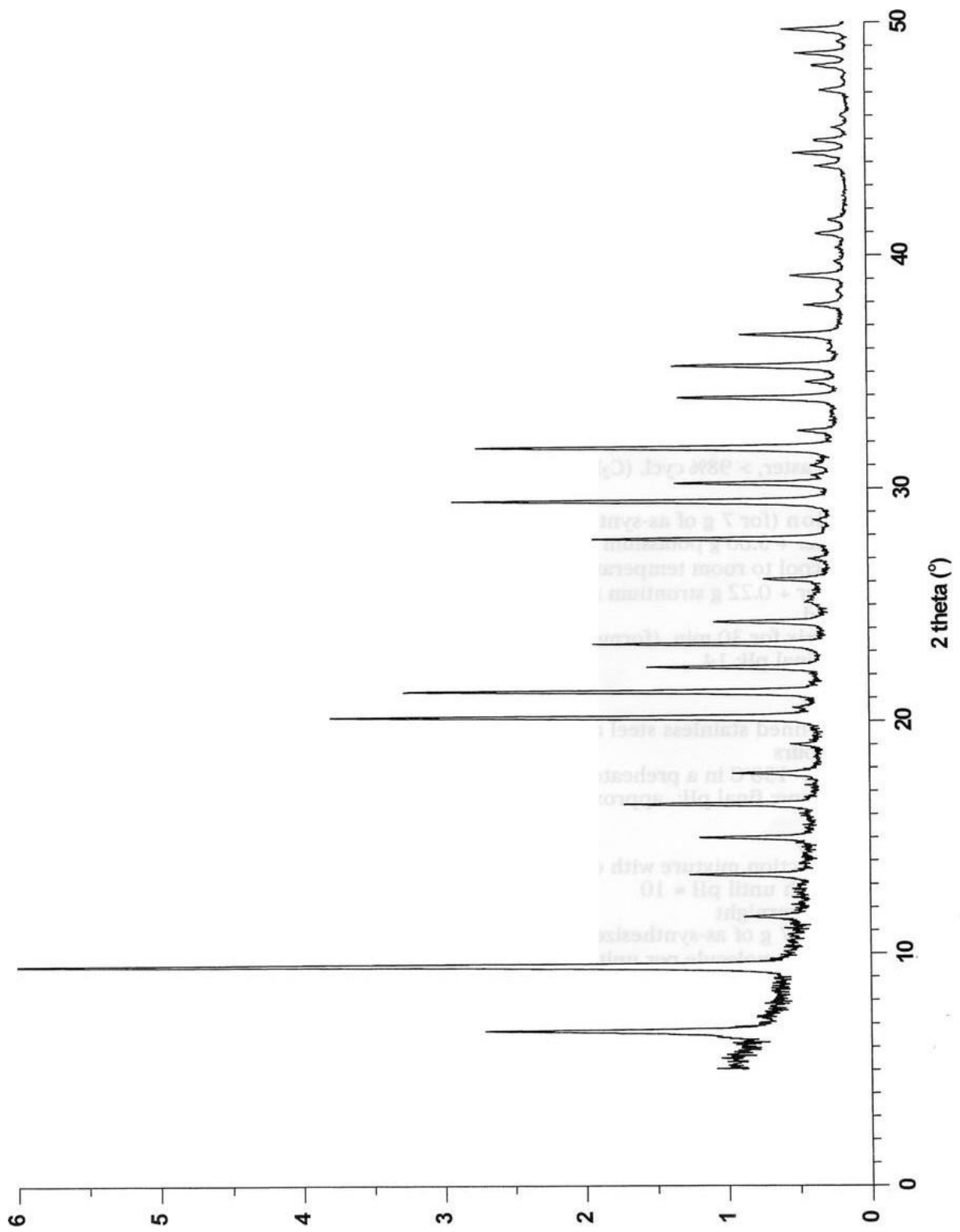
- a. Colloidal siicas such as Ludox HS-40 are also suitable silica sources.

- b. The Sr^{2+} sources used were $\text{Sr}(\text{OH})_2$ and $\text{Sr}(\text{NO}_3)_2$; there is no preference.
- c. The final gel is (visually) very homogeneous and pourable.
- d. No Teflon liner was used.
- e. Crystallization times (at 150°C) are not critical (90-140 hours).
- f. The autoclave was placed in a room temperature oven. The oven was heated within 2 hours to 150°C and kept at this temperature for 115 hours.
- g. The synthesis magma (after treatment has an amorphous appearance; no free mother liquor can be seen. This is typical for this type of synthesis.

KFI

ZK-5

Si(77). Al(23)



KFI

High-Silica KFI

Si(79), Al(21)

Contributed by Alain Matijasic and Joël Patarin

Verified by S. Schwarz, K. Strohmaier and S. Miller

Type Material $K_{18}Sr[Al_{20}Si_{76}O_{192}] \cdot 72 H_2O \cdot (18-C-6)$ (18-C-6 = Cycl. $(C_2H_4O)_6$)

Method T. Chatelain, J. Patarin, R Farré, O. Pétigny, P. Schulz [1]

Batch Composition 2.3 K_2O : 0.1 SrO : Al_2O_3 : 10 SiO_2 : 220 H_2O : 1.0(18-C-6)

Source Materials

distilled water

potassium hydroxide (Prolabo, 86% KOH)

aluminum hydroxide (Fluka, 99+% $Al(OH)_3$)

strontium nitrate (Prolabo >97% $Sr(NO_3)_2$)

silica sol (Dupont Ludox AS-40, 40% SiO_2)

18-C-6 (Lancaster, > 98% cycl. $(C_2H_4O)_6$)

Batch Preparation (for 7 g of as-synthesized product)

- (1) [11.00 g water + 3.00 g potassium hydroxide + 1.57 g aluminum hydroxide], heat to boiling until clear, cool to room temperature and correct weight loss due to boiling^a
- (2) [18.63 g water + 0.22 g strontium nitrate + 2.70 g 18-C-6 + 15.00 g silica soil, stir until homogenized
- (3) [(1) + (2)], mix for 30 mm. (forms a thick gel). Transfer to a 120 mL PTFE-lined stainless steel autoclave. Final pH:14

Crystallization

Vessel: PTFE-lined stainless steel autoclave

Time: 120 hours

Temperature: 150°C in a preheated oven

Agitation: none; final pH: approximately 13

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash until pH ~ 10
- (3) Dry at 60°C overnight
- (4) Yield: Total ~ 7 g of as-synthesized KFI-type sample (product contains 18-C-6 as organic template, ~ one molecule per unit cell^b)

Product Characterization

XRD Highly crystalline KFI; can be indexed with cubic symmetry, $a_0=18.671(1)\text{Å}$ ^b

Elemental Analyses: Si/Al = 3.7^b

Crystal Size and Habit: by SEM, the crystals display a cubic morphology; most of them are aggregated and their sizes range from 2 to 4 μm

Reference

[1] T. Chatelain, J. Patarin, R. Farré, O. Pétigny, P. Schulz, *Zeolites* 17 (1996) 328

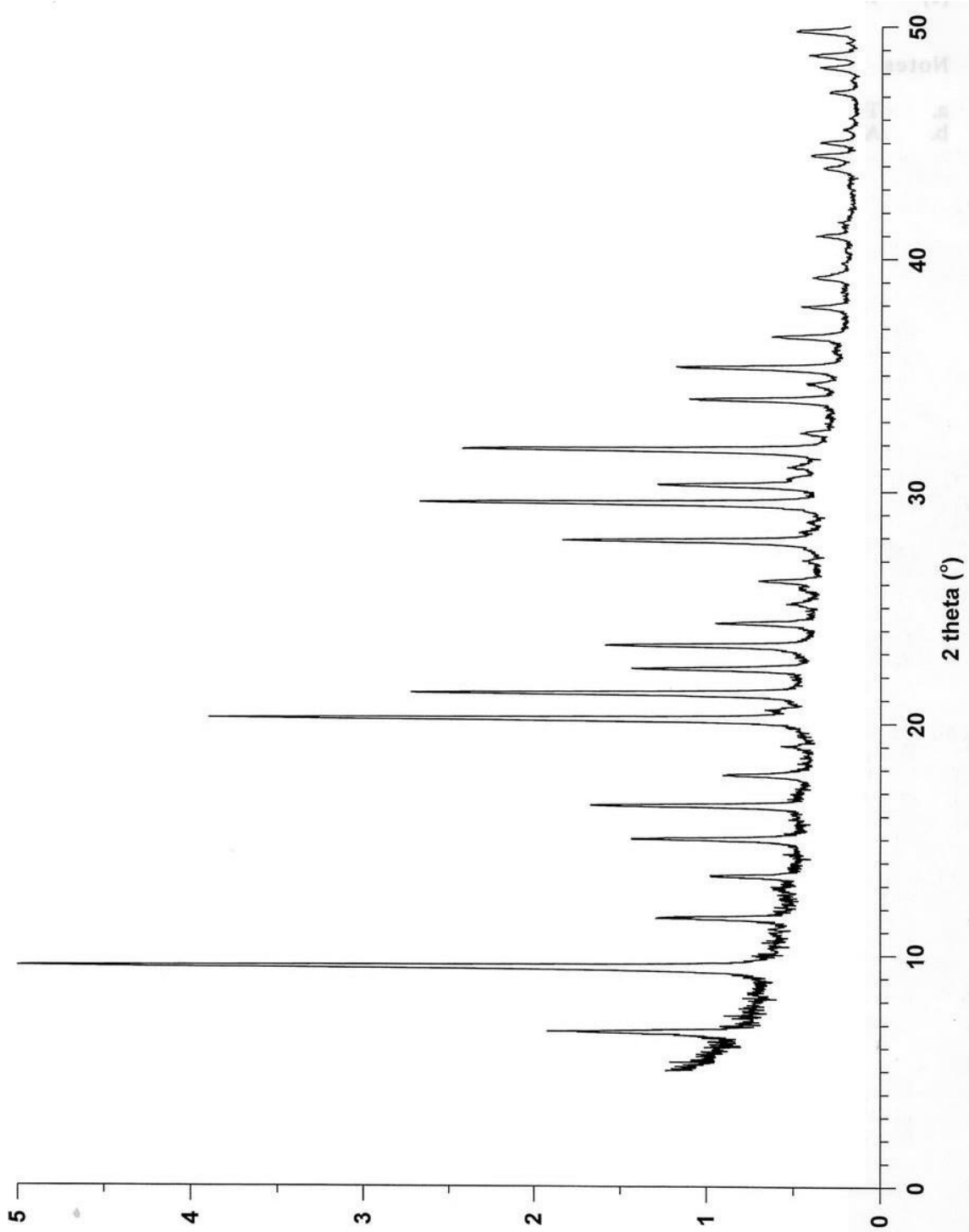
Notes

- a. The starting mixture is prepared in a polyethylene vessel.
- b. According to ref. [1].

KFI

High-Silica KFI

Si(79), Al(21)



Contributed by Giuseppe Bellussi and Angela Carati

Verified by Li Shi and S. B. Hong

Type Material: (Na,H)₅[B₅Si₄₉O₁₀₈] : 8 Q : 5 H₂O^a (Q = Quinuclidine)

Method: R. Millini, A. Carati, G. Bellussi [1]

Batch Composition: 3.0 Q : B₂O₃ : 3.0 SiO₂ : 60 H₂O

Source Materials:

distilled water

quinuclidine (1-azabicyclo[2.2.2.] octane) (Aldrich, 97%)

silica sol (Dupont HS-40, 40% SiO₂, 0.3% Na₂O)

Batch Preparation

- (1) [10 g water + 14.7 g quinuclidine], mix until dissolved
- (2) [61 g water + 10.8 g boric acid + 14.7 g quinuclidine], mix until dissolved
- (3) [39.5 g silica sol + (1)], mix until a uniform gel is obtained
- (4) [(3) + (2)], add solution (2) to gel slowly with vigorous mixing. Final slurry pH – 11

Crystallization

Vessel: Filter to recover solids

Time: 5 days

Temperature: 170°C

Agitation: autoclave is rotated 20 rpm

Product Recovery

- (1) Filter to recover solids
- (2) Wash with distilled water
- (3) Dry at 120°C
- (4) Yield: 90% on SiO₂

Product Characterization

XRD: LEV (only crystalline phase), a = 12.944 Å, c = 21.914 Å

Elemental Analysis: 17 SiO₂ : B₂O₃ : 2.7 Q (dry basis)^b

Crystal Size and Habib: Compact spherical aggregates (4 to 8 μm) of small crystals

Reference

- [1] R. Millini, A. Carati, G. Bellussi, Zeolites 12 (1992) 265

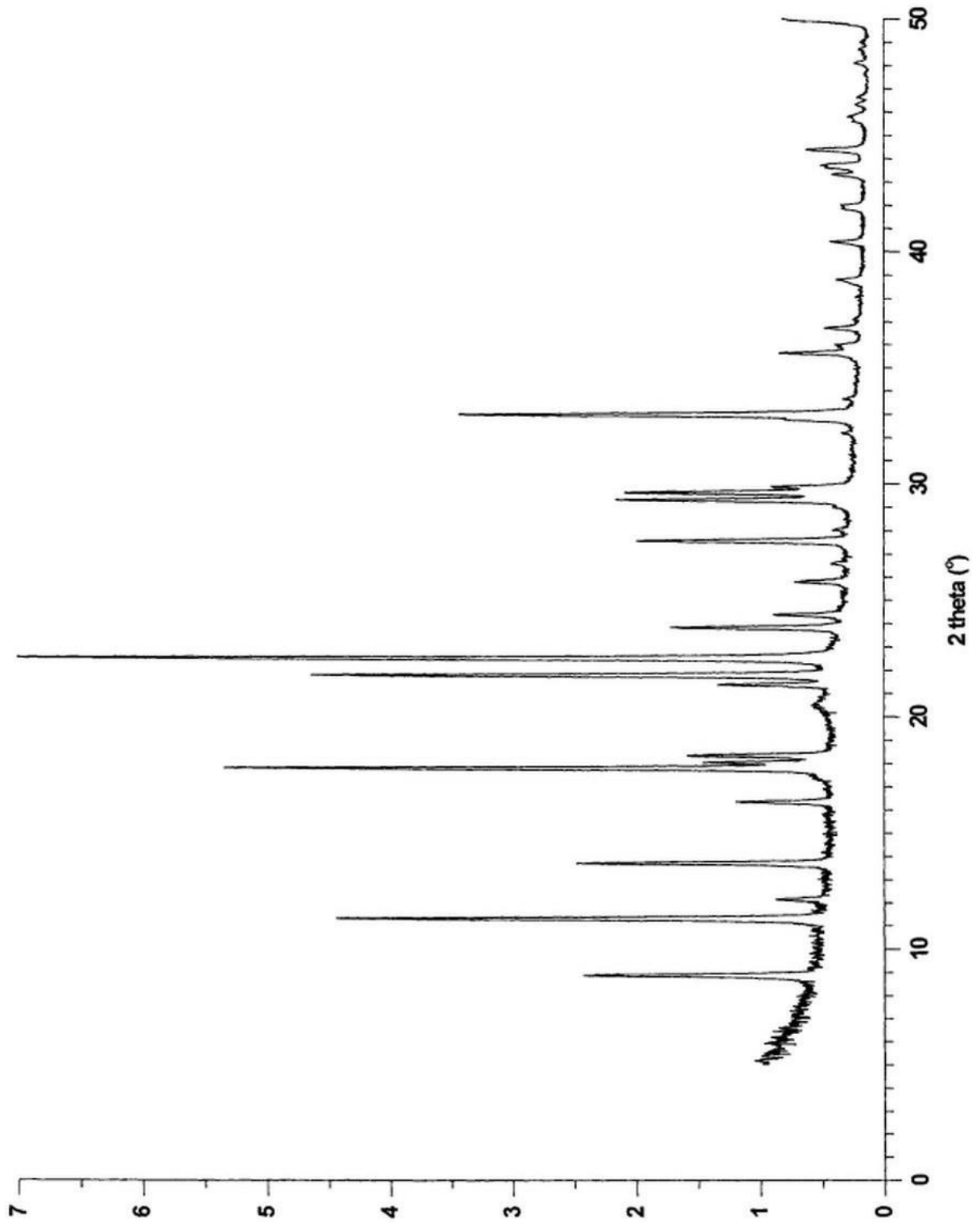
Notes

- a. Protonated quinuclidine (HQ⁺) or Na⁺ (from silica sol) act as counterions for structural boron.
- b. By thermal analysis, organic material adsorbed in extra framework pores is eliminated at 268°C. After treatment at 550°C for a few hours, a limited structure collapse is observed with formation of amorphous material and trigonal BO₃ units.
[1]

LEV

[B]-Levyne

Si(89), B(11)



LTA

Linde Type A

Si(50), Al(50)

Contributed by R. W. Thompson and K. C. Franklin

Verified by B. Subotic, A. Cizmek and K. Hashimoto

Type Material $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] : 27 \text{ H}_2\text{O}$

Method R W. Thompson, M. J. Huber [1]

Batch Composition 3.165 Na_2O : Al_2O_3 : 1.926 SiO_2 : 128 H_2O ^a

Source Materials

deionized water

sodium hydroxide (Fisher Scientific, 99+% NaOH)

sodium aluminate (Fisher Scientific, $\text{NaO}_2 : \text{Al}_2\text{O}_3 : 3 \text{ H}_2\text{O}$)^b

sodium metasilicate (Fisher Scientific, $\text{Na}_2\text{SiO}_3 : 5 \text{ H}_2\text{O}$)

Batch Preparation (for 10 g dry product)

- (1) [80 mL water + 0.723 g sodium hydroxide], mix gently until NaOH is completely dissolved. Divide into two equal volumes in polypropylene bottles
- (2) [One-half of (1) + 8.2 58 g sodium aluminate], mix gently in capped bottle until clear^c
- (3) [Second half of (1) + 15.48 g sodium metasilicate], mix gently in capped bottle until clear^c
- (4) [(2) + (3)], pour silicate solution into aluminate solution quickly; a thick gel should form. Cap tightly and mix until homogenized^d

Crystallization

Vessel: 100-150 mL polypropylene bottle (sealed)

Incubation: none required

Temperature: $99 \pm 1^\circ\text{C}$

Time: 3-4 hours^e

Agitation: stirred or unstirred

Product Recovery

- (1) Remove from heat source and cool to below 30°C
- (2) Filter to recover solids and wash with deionized water until filtrate pH is below 9^f
- (3) Dry product on filter paper and watch glass at $80\text{-}110^\circ\text{C}$ overnight
- (4) Yield: 28.1 g (hydrated) or 10.4 g (dry)

Product Characterization

XRD LTA; characteristic strong reflections at $d = 4.107, 3.714, 3.293$ and 2.987 \AA

Competing phases (if present): SOD (HS), GIS (Pc)

Elemental Analysis: $\text{Na}_2\text{O} . \text{Al}_2\text{O}_3 . 2 \text{ SiO}_2$

Crystal Size and Habit: cubic crystals, $2\text{-}3 \mu\text{m}$ ^g

References

- [1] R W. Thompson, M. J. Huber, J. Cryst. Gr. 56 (1982) 711
- [2] D. W. Breck, Zeolite Molecular Sieves, John Wiley, New York, 1974, p 270
- [3] J. F. Charnell, J. Cryst. Gr. 3 (1971) 291
- [4] H. Neels, W. Schmitz, E.-M. Berger, D. Lutz, Krist. Tech. 13 (1978)1345
- [5] G. Scott, A. G. Dixon, A. Sacco, Jr., R W. Thompson, in Stud. Surf. Sci. Catal. 49, P. A. Jacobs, R. A. Van Santen (eds.), Elsevier, Amsterdam,1989, p 363

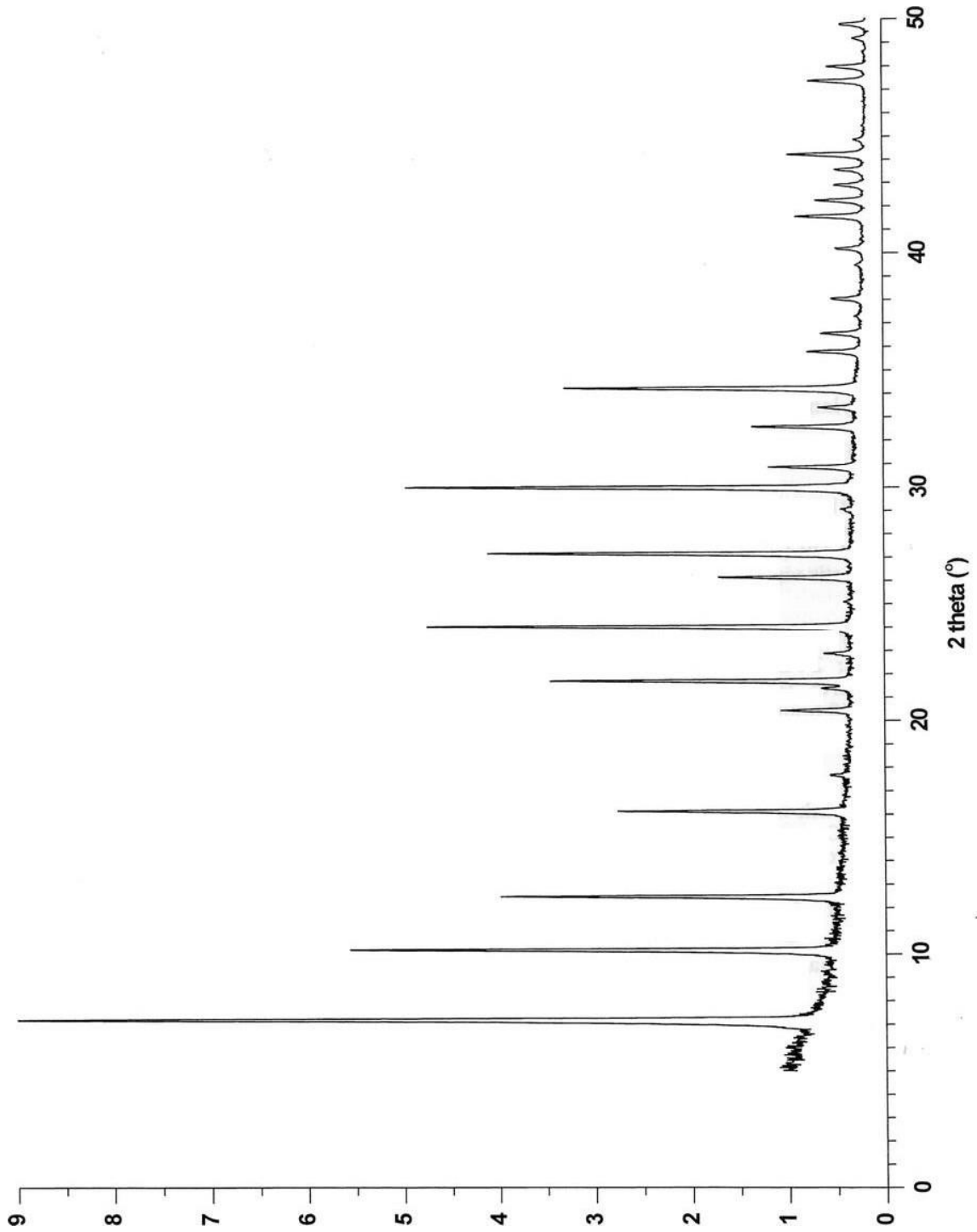
Notes

- a. Zeolite NaA can be synthesized from a wide range of batch compositions as noted in Breck [2] and temperatures other than used in this example, e.g., 60-110°C. Also, it can be made from a variety of alumina and silica source materials other than those used in this example, e.g., pure aluminum powder^h or aluminum wire, fumed silica, sodium disilicate, Ludox, silica gels, etc. The actual weights of these other sources used must be compensated for the presence of water of hydration, Na⁺ ions, etc.
- b. Assumed 100%.
- c. Could take 10-20 minutes.
- d. May be done with laboratory mixer or vigorously by hand for 5-10 minutes.
- e. The turbid gel phase will be observed to diminish in height as the reaction proceeds, accelerating rapidly in the final stages of the crystallization, leaving a clear supernatant above the precipitated crystalline phase.
- f. One-half liter should be sufficient for this preparation.
- g. Zeolite NaA crystals are typically cubic. Dodecahedral crystals have been observed frequently, but there is little fundamental understanding of why this habit forms. Additions of triethanolamine are known to result in larger crystals, but the particle size distribution becomes broader, synthesis times are extended, and the impurity zeolite phases appear with increased abundance. [3-5]
- h. Special care must be taken if powdered aluminum is dissolved in a caustic solution to make the aluminate solution. Since its dissolution is exothermic, the solution can become quite warm and hydrogen evolves.

LTA

Linde Type A

Si(50), Al(50)



Contributed by Moussa Zaarour and Svetlana Mintova

Verified by D. Stosic, D. Wales and X. Zou

Type Material: TMA₉₆ [Al₉₆Si₉₆O₃₈₄] wH₂O (w ~216)

Method: S. Mintova, N. H. Olson, V. Valtchev, T. Bein [1]

Batch Composition: 8 Na₂O : 11.25 SiO₂ : 1.8 Al₂O₃ : 13.4 (TMA)₂O : 721 H₂O

Source Materials

silica sol (SM-30, 30%, Aldrich)

aluminium isopropoxide [Al(OiPr)₃] (Aldrich)

tetramethylammonium hydroxides pentahydrate (TMAOH.5H₂O, 97%, Aldrich)

sodium hydroxide (NaOH, Mallinckrodt, Chesterfield, MO)

distilled water

Batch Preparation

(1) [2.25 g 30% silica sol + 2 g H₂O]

(2) [0.75 g Al(OiPr)₃ + 5 g TMAOH.5H₂O + 0.6 g 1 M NaOH + 7.0 g H₂O]

(3) [(1)+(2)] under stirring^a

Crystallization

Vessel: polypropylene (PP) bottles

Temperature: 40 °C

Time: 7 days

Agitation: orbital shaker (175 rpm)

Product Recovery

(1) Centrifugation (40 000 rpm, 2h), washing till pH=9

(2) Stable colloidal suspension of zeolite crystals in water

(3) Dry solid: freeze drying or conventional oven

Product Characterization

DLS: 40 to 80 nm in diameter

XRD: LTA

HRTEM: Fully crystalline (40 to 80 nm in diameter)

References

[1] S. Mintova, N. H. Olson, V. Valtchev, T. Bein, Science 283 (1999) 958

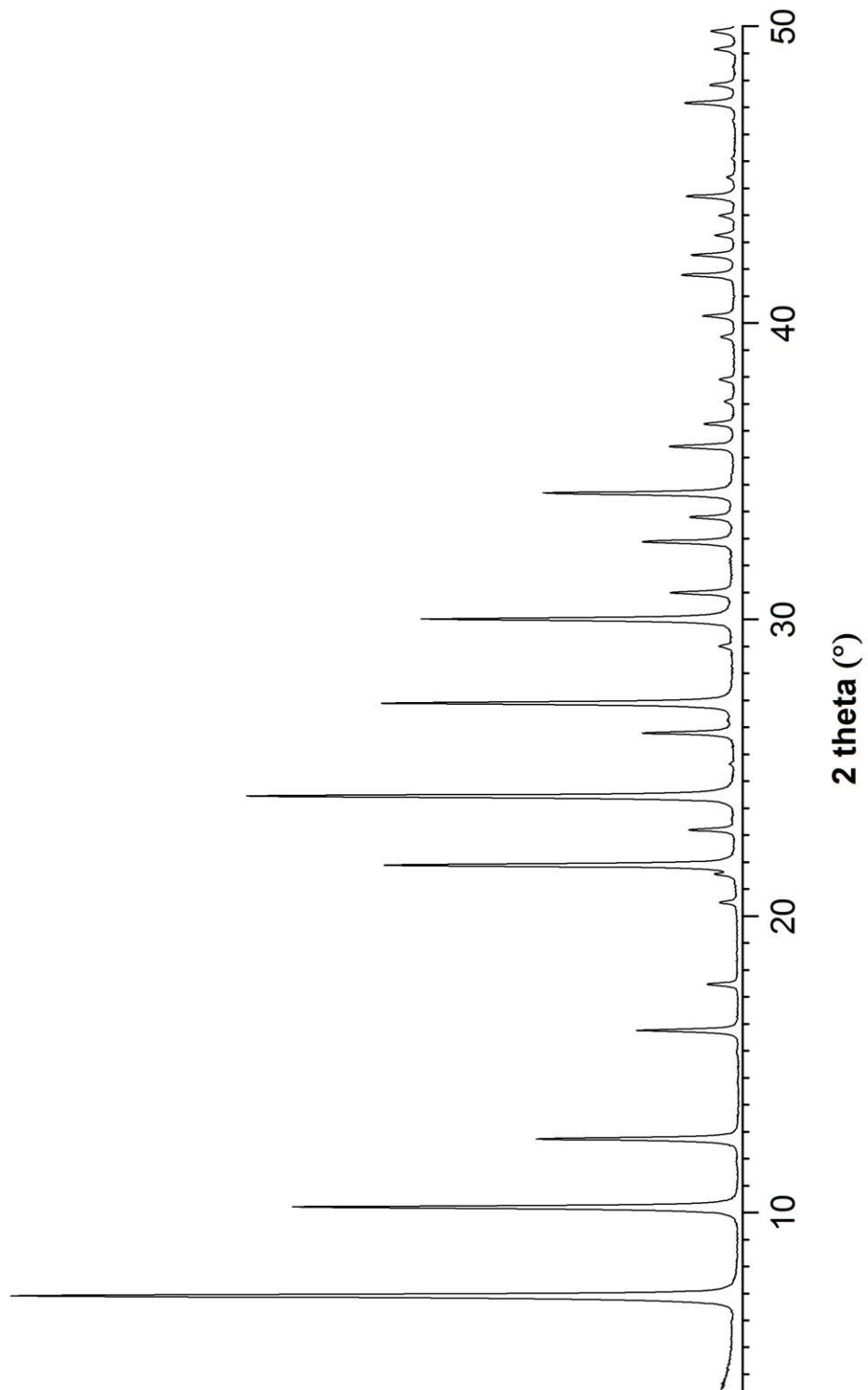
Notes

a. Clear precursor solution is obtained

LTA

Nanosized Linde Type TMA-A

Si(50), Al(50)



LTA

ZK-4

Si(59), Al(41)

Contributed by Don Hopkins

Verified by V. Valtchev, M. Castagnola and G. Kuhl

Type Material $\text{Na}_{9.2}(\text{TMA})_{0.8}[\text{Al}_{10}\text{Si}_{14}\text{O}_{48}]$ (TMA = tetramethylammonium)

Method G. T. Kerr [1]

Batch Composition 1.55 Na_2O : Al_2O_3 : 3.91 SiO_2 : 4.13 $(\text{TMA})_2\text{O}$: 320 H_2O

Source Materials

distilled water

sodium hydroxide (50% solution)

sodium aluminate (~ 46% Al_2O_3 , 31% Na_2O ; Fisher, MC&B, Nalco)

tetramethylammonium hydroxide (TMA-OH, Southwestern Analytical Chemical, 25% aqueous solution)

silica sol (Dupont HS-40 or AS-40, 40% SiO_2)

Batch Preparation (for 34 g product)

- (1) [290 g water + 6.0 g sodium hydroxide solution + 21.5 g sodium aluminate], stir until dissolved
- (2) [292 g TMA-OH (25% solution) + 57.0 g silica sol], stir for approximately 30 minutes
- (3) [(1) + (2)], stir vigorously; gel pH = 14.0 to 14.5

Crystallization

Vessel: Teflon bottle, 1000 mL

Incubation: 24 hours at 25°C (optional)

Temperature: 100°C (oven with efficient air circulation)

Time: 16-48 hours

Agitation: none

Product Recovery^a

- (1) Filter and wash with 0.5 to 1 L water
- (2) Dry at 100°C
- (3) Yield: approximately 34 g (100% on Al_2O_3)

Product Characterization

XRD LTA, $a_0 = 24.38 \text{ \AA}$; competing phases: GIS (long reaction time) and EAB^b

Elemental Analysis (dried at 100°C): 15.7% Al (29.7% Al_2O_3), 23.1% Si (49.4% SiO_2), 12.4% Na (16.7% Na_2O), 2.24% C (3.83% $(\text{TMA})_2\text{O}$)^c

Crystal Size and Habit: cubes (some with penetration twinning) approximately 1.0-1.5 μm on an edge

References

- [1] G. T. Kerr, Inorg. Chem. 5 (1966) 1537

- [2] R. H. Jarman, M. T. Melchior, D. E. W. Vaughan, ACS Symposium Series 218, American Chemical Soc., Washington, D. C., 1983, p 267

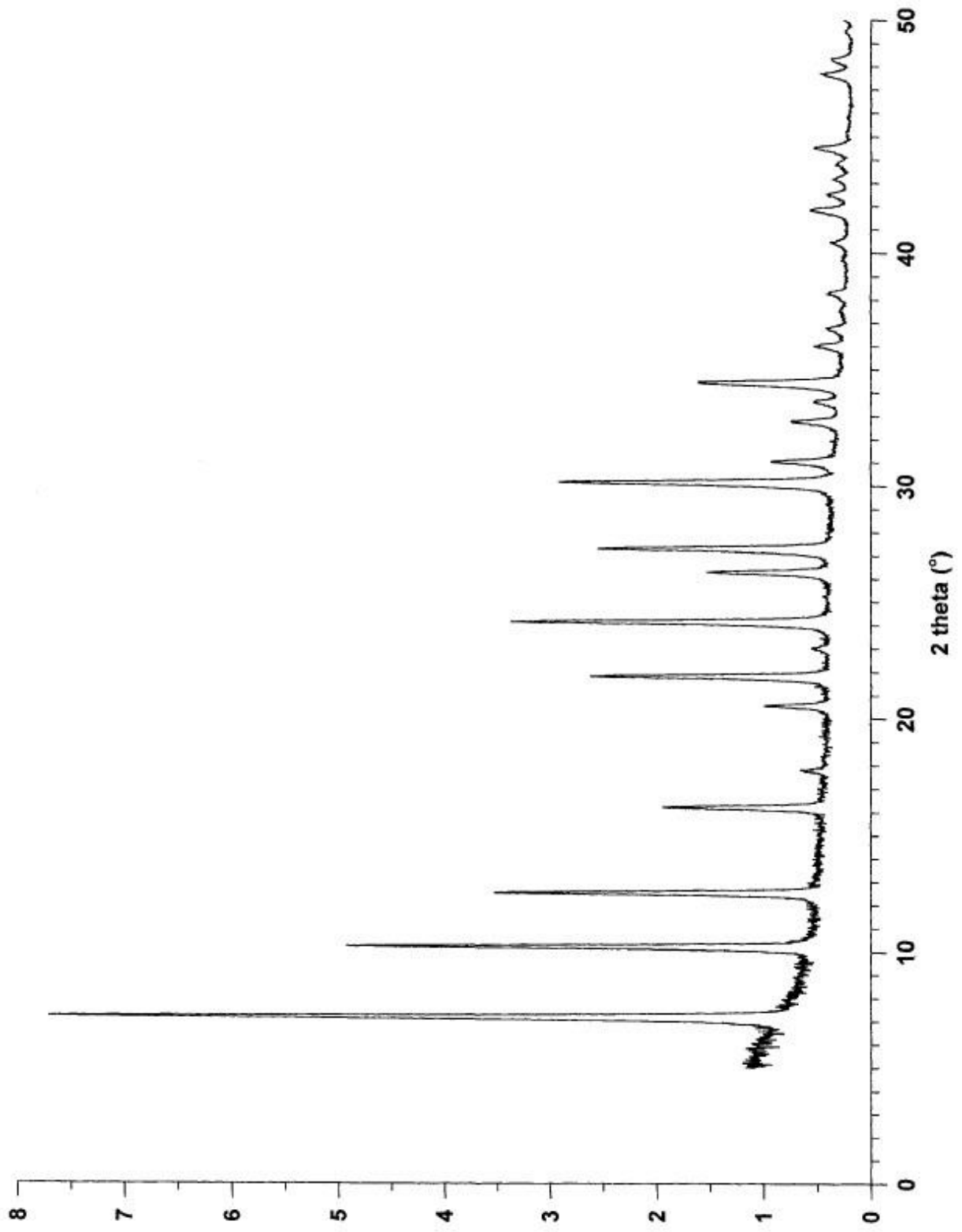
Notes

- a. Although no decomposition of TMA-OH is expected, it is advisable to carry out the crystallization and product work-up in a fume hood. Temperature excursions can produce noxious and toxic by-products, e.g., trimethylamine and methanol.
- b. EAB can co-precipitate with ZK-4 if the TMA-OH is added to solution (1) before the silica sol.
- c. The Si/Al of products by this recipe ranged from 1.39 to 1.43 (average 1.41). Higher and lower Si/Al products have been made using other recipes. [2]

LTA

ZK-4

Si(59), Al(41)



LTA

Zeolite Alpha

Si(75), Al(25)

Contributed by Günter Kühn

Verified by S. Mintova and Zhaolan

Type Material $\text{Na}_4(\text{TMA})_2[\text{Al}_6\text{Si}_{18}\text{O}_{48}]$ (TMA = tetramethylammonium)

Method G. H. Kühn [1]

Batch Composition 1.07 Na_2O : 2.37 $(\text{TMA})_2\text{O}$: Al_2O_3 : 10 SiO_2 : 120 H_2O

Source Materials

distilled water

sodium aluminate (MCB, 28.5% Na_2O , 42.75% Al_2O_3)

tetramethylammonium hydroxide solution (25% TMAOH) ^a

precipitated silica (PPG Corp. Hi-Sil 233, 88% SiO_2) ^b

Batch Preparation (for 36 g product)

- (1) (46.4 g water + 15.6 g sodium aluminate), stir at room temperature until dissolved ^c
- (2) [(1) + 111.7 g tetramethylammonium hydroxide solution], mix
- (3) (2) + 44.5 g precipitated silica, add silica to the aluminate solution gradually with stirring ^d
- (4) Stir or blend for 30 minutes ^d

Crystallization

Vessel polypropylene bottle

Incubation: 48 h at room temperature

Time: 24- 30 hours ^e

Temperature: 90°C

Agitation: none

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter on a dense filter, such as Whatman #5, or separate by decantation, then reslurry sediment, flocculate, ^f and wash with water ^g
- (3) Dry at room temperature or at 110°C
- (4) Yield: 36 g (near 100% on Al_2O_3)

Product Characterization

XRD: LTA (contracted unit cell); competing phase: high-silica sodalite

Elemental Analyses: 0.6 Na_2O : 0.4 $(\text{TMA})_2\text{O}$: Al_2O_3 :6 SiO_2

Crystal size and habit: cubes, <1 μm on edge

Reference

- [1] G. H. Kühn, US Patent 4 191 663

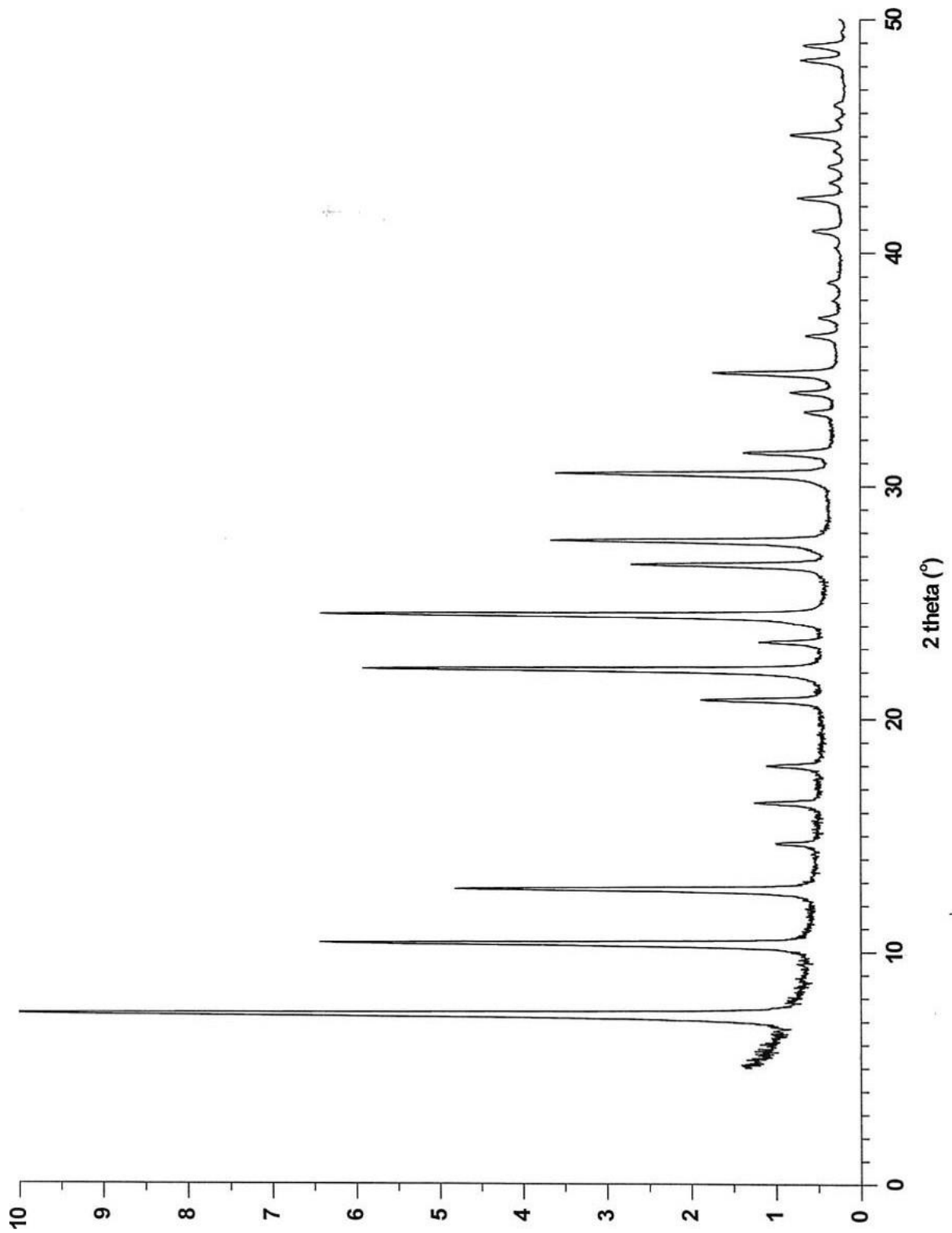
Notes

- a. TMA salts cannot be used because the anions tend to cause nucleation of high-silica sodalite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$).
- b. Hi-Sil 233 has a median particle size of 18-19 μm ; precipitated silica of larger particle size tends to be insufficiently reactive. Ultrasil 320 is an acceptable substitute. If less reactive silica is to be used in this preparation, 10% of the silica should be slurried in the (TMA)OH solution prior to combining the (TMA)OH with the NaAlO_2 solution.
- c. Small amounts of iron may be removed by filtration although this iron does not affect the crystallization. If the sodium aluminate does not dissolve completely, it probably contains $\text{Al}(\text{OH})_3$ and cannot be used.
- d. Slow addition of Hi-Sil is recommended for proper dispersion. Silica-rich gel particles tend to cause nucleation of high-silica sodalite.
- e. The longer crystallization time improves the crystallinity, unless sodalite nuclei are present.
- f. Avoid flocculating in the presence of mother liquor because colloidal silica will coagulate.
- g. Alternatively, use repeated decantation and reslurrying sequences (settling may be accelerated by centrifuging), and optionally, flocculation^h after having removed the bulk of the alkalinity.
- h. See Introductory Article on "Product Recovery."

LTA

Zeolite Alpha

Si(75), Al(25)



Contributed by Henri Kessler and Abdallah Merrouche

Verified by P. Behrens, P. Feng, J. Chen, R. Fricke and C. Ferey

Type Material [Ga₁₂P₁₂O₄₈][(n-C₃H₇)₂NH₂F]₃ · (H₂O)_w (w ~ 6 [1])

Method A. Merrouche, J. Patarin, M. Soulaire, H. Kessler, P. Anglerot [2]

Batch Composition 1 Ga₂O₃ : 1 P₂O₅ : 1 HF : 70 H₂O : 6.5 DPA (DPA = di-n-propylamine)

Source Materials

phosphoric acid (Fluka, 85% H₃PO₄)

distilled water

gallium sulfate hydrate (Strem Chemicals, Ga₂(SO₄)₃ · xH₂O (wt% Ga ~ 18))

hydrofluoric acid (Fluka, 40% HF)

di-n-propylamine (Fluka, 95%)

Batch Preparation (for 1 g dry product)

- (1) [1.16 g phosphoric acid + 2.2 g water + 3.8 g gallium sulfate hydrate + 2.5 g water], stir until dissolved
- (2) [(1) + 0.25 g hydrofluoric acid], mix thoroughly
- (3) [(2) + 3.25 g di-n-propylamine], mix thoroughly. Initial pH = 4 to 4.5

Crystallization

Vessel: PTFE-lined autoclave

Temperature: 140 °C

Time: 24 hours

Agitation: none

Product Recovery

- (4) Filter; wash with distilled water
- (5) Dry at 60 °C
- (6) Yield: approximately 60% with respect to starting oxides

Product Characterization

XRD characteristic strong reflections at d = 12.02, 8.50, 6.94, 6.01 Å

Elemental Analysis (anhydrous form): Ga_{0.49}P_{0.51}O₂(DPA)_{0.13}F_{0.12}

Crystal Size and Habit: cubes (5 - 40 μm)

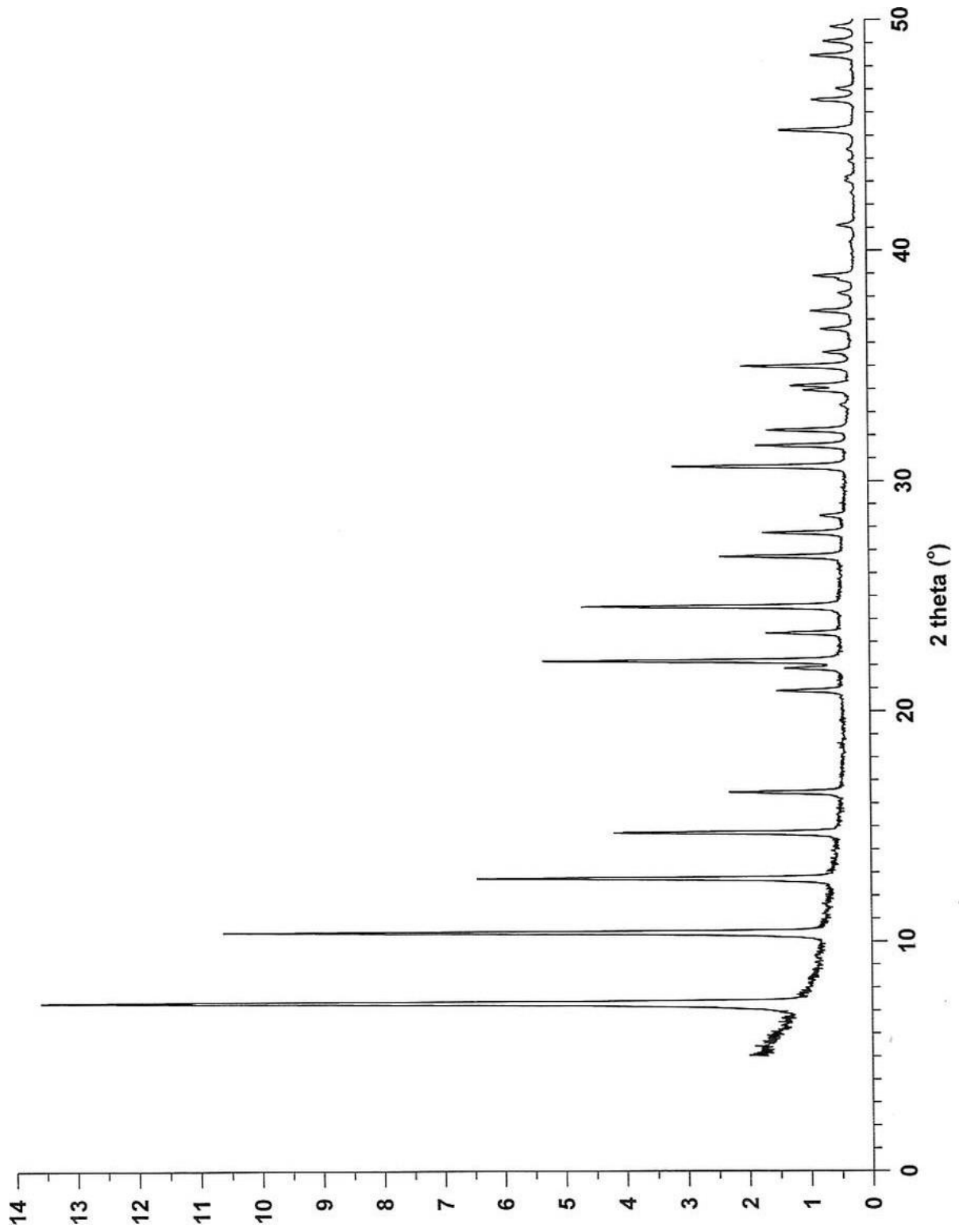
References

- [1] A. Simmen, J. Patarin, C. Baerlocher, in Proceedings of the 9th International Zeolite Conference, Vol. 1, R. Von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Montreal, 1992, Butterworth-Heinemann, Stoneham, 1993, p. 433
- [2] A. Merrouche, J. Patarin, M. Soulaire, H. Kessler, D. Anglerot, in Molecular Sieves, Vol. 1, Synthesis of Microporous Materials, M. L. Occelli, H. F. Robson (eds.), Van Nostrand Reinhold, New York, 1992, p. 384

LTA

GaPO₄

P(50), Ga(50)



LTF

LZ-135

Si(71), Al(29)

Contributed by Qisheng Huo

Verified by E.-P. Ng, S B. Hong, S. Komaty

Type Material $\text{Na}_{26}(\text{TMA})_6[\text{Si}_{76}\text{Al}_{32}\text{O}_{216}]$
(TMA= Me_4N^+)

Method L.B. McCusker, Ch. Baerlocher, S.T. Wilson, and R.W. Broach [1]

Batch Composition 5.0 SiO_2 : 1.0 Al_2O_3 : 2.80 Na_2O : 5.0 TMACl : 5.0 TEABr : 156 H_2O (TEA= Et_4N^+)

Source Materials double distilled water sodium hydroxide (NaOH) sodium aluminate (NaAlO_2) silica sol(Ludox LS, 30%) tetramethylammonium chloride (TMACl) tetraethylammonium bromide (TEABr)

Batch Preparation (for 59 g product)

- (1) [solid sodium hydroxide + solid sodium aluminate + an approximately equivalent weight of water], heat to get a clear solution
- (2) [(1)^a + silica sol (Ludox LS, 30%)], mix for 0.5 min in a blender
- (3) [(2) + TMACl and TEABr in the remaining water], blend at high speed for 4 min

Crystallization

Vessel: PTFE-lined vessel
Temperature: 100° C
Time: 240 hours
Agitation: high speed rotation

Product Recovery

- (1) Filter and wash with water
- (2) Dry at ambient temperature

Product Characterization

XRD: LTF^b; competing phase: no
Elemental analysis: 2.34 Si / 1.0 Al / 0.80 Na / 0.18 TMA / 0.01 TEA

Reference

- [1] L. B. McCusker, Ch. Baerlocher, S.T. Wilson, R.W. Broach, J. Phys. Chem. C 113 (2009) 9838
- [2] B. K. Macus and Brent. M. Lok. U.S. Pat. 4,857,288 (1989)

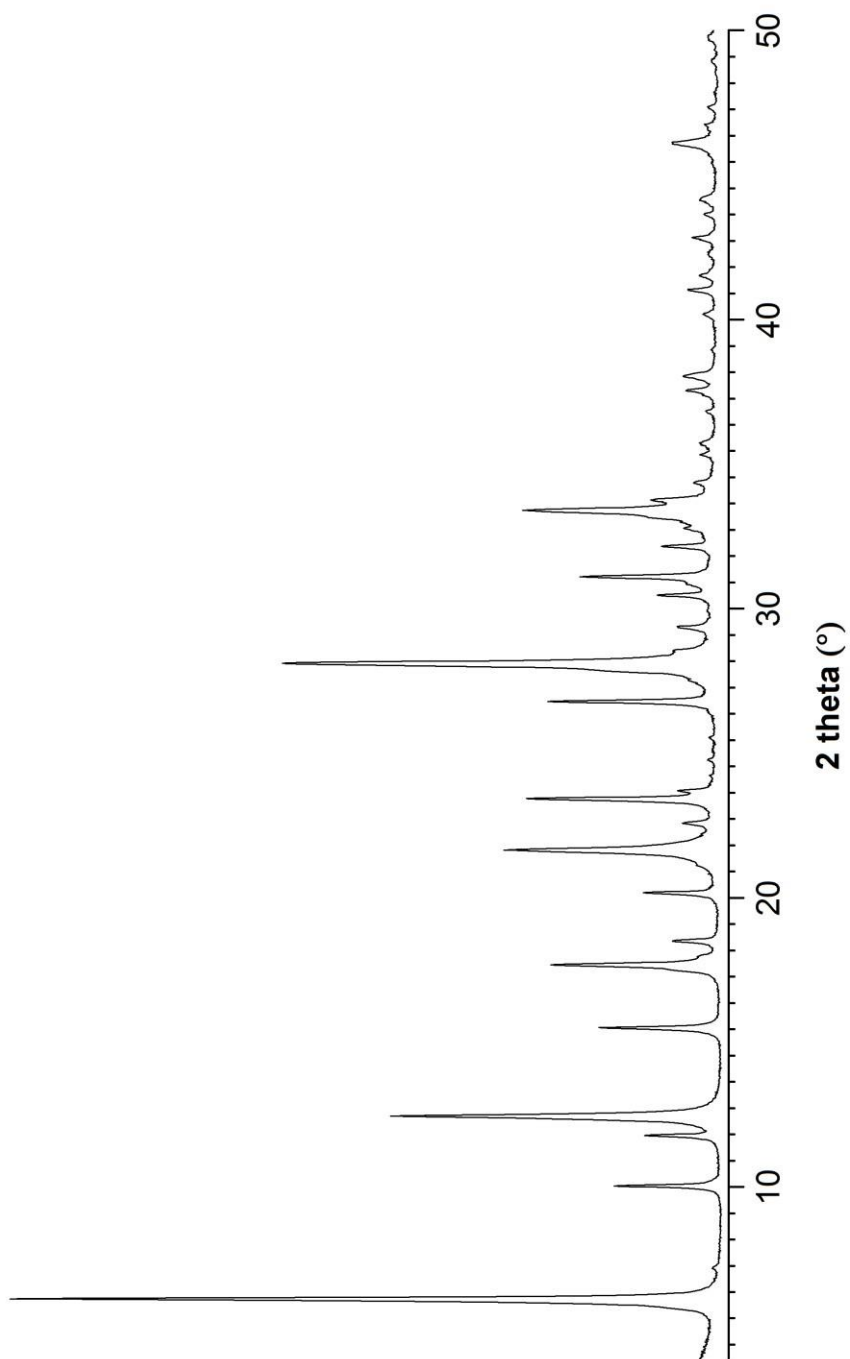
Notes

- a. Warm suspension
- b. Synchrotron powder diffraction data were collected on the UNICAT beamline 33-BM-C at the Advanced Photon Source (APS) at Argonne, Illinois.

LTF

LZ-135

Si(71), Al(29)



LTL

Linde Type L

Si(76), Al(24)

Contributed by J. P. Verduijn

Verified by C. Williams, by M. Uguina, and by J. Warzywoda

Type Material $K_9[Al_9Si_{27}O_{72}] : wH_2O$ (w = 0 to 36)

Method J. P. Verduijn [1]

Batch Composition 2.35 K_2O : Al_2O_3 : 10 SiO_2 : 160 H_2O : trace MgO ^a

Source Materials

deionized water

potassium hydroxide (Baker 0222 pellets, 86.8% KOH)

alumina (Baker 0005, 92.6% $Al(OH)_3$)

silica sol (Dupont Ludox HS-40, 40% SiO_2)

magnesium nitrate (Baker, $Mg(NO_3)_2 \cdot 6 H_2O$)

Batch Preparation (for 59 g product)

- (1) [50.00 g water + 30.39 g potassium hydroxide + 15.82 g alumina], heat to boiling until clear. Cool to room temperature and correct water loss due to boiling
- (2) [150.24 g silica sol + 99.0 g water + 14.5 g $Mg(NO_3)_2$ solution],^b mix until homogeneous (~3 minutes)
- (3) [(1) + (2) + 25.00 g water (rinse)],^c mix until thickening starts (~ 3 minutes) ^d

Crystallization

Vessel: 300 mL stainless steel autoclave ^e

Temperature: 175°C

Time: 48 hours ^f

Agitation: none

Product Recovery

- (1) Cool to room temperature
- (2) Filter and wash (5 times) with 650 mL water. The pH of the last wash water should be ~10
- (3) Dry at 150°C for 16 hours
- (4) Yield: After drying at 150°C, ~ 15.3 wt% based on the weight of synthesis gel in the autoclave (nearly 100% on Al_2O_3)

Product Characterization

XRD: LTL (only crystalline product). Competing phases: MER (without MgO)

Elemental Analysis: 6.2 SiO_2/Al_2O_3 , 1.0 K_2O/Al_2O_3

Crystal Size and Habit: cylindrical, 0.2 to 0.4 μm diameter, 0.4 to 0.7 μm long (L/D ~ 2)

Reference

- [1] J. P. Verduijn, US Patent 5 242 675 (1993)

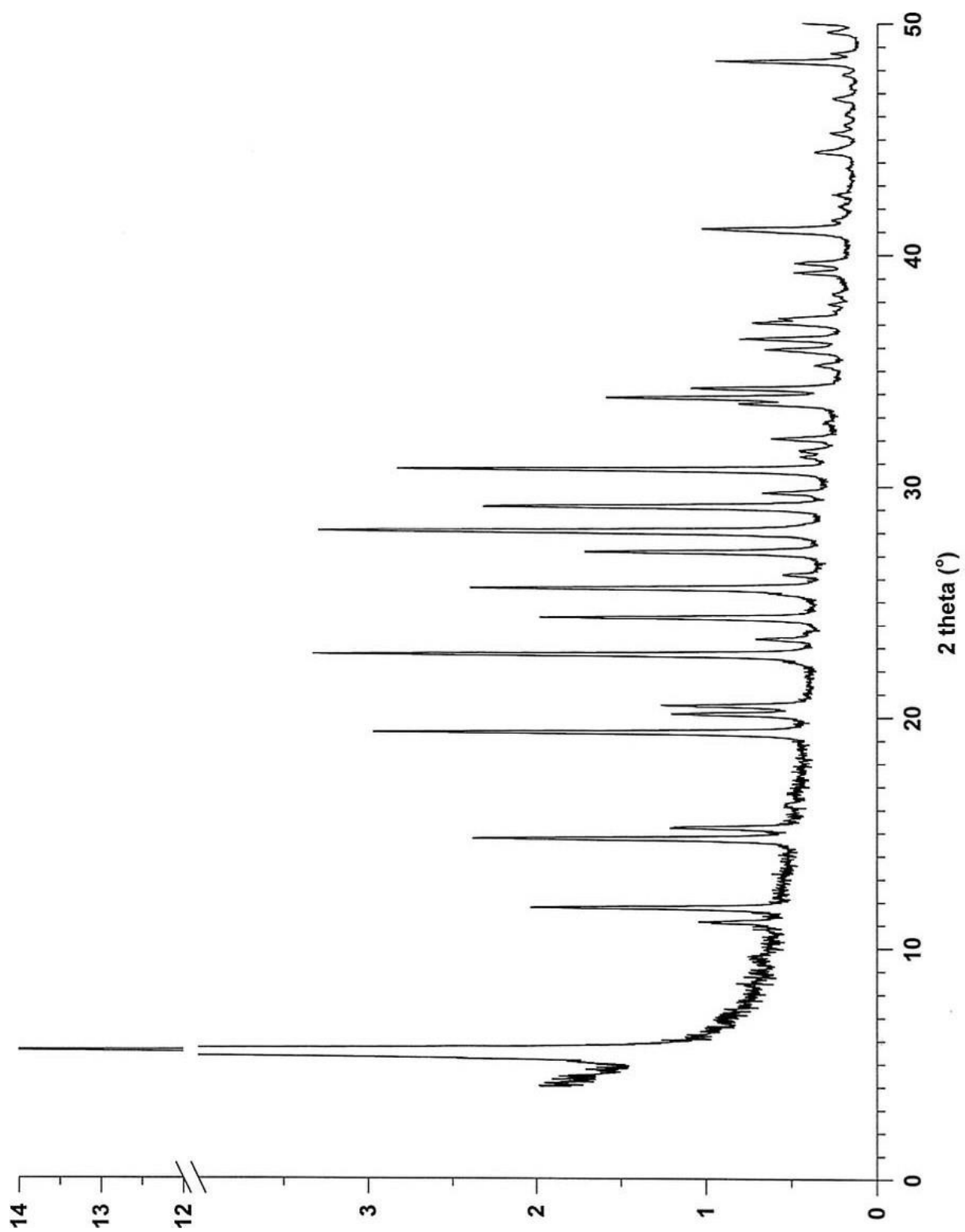
Notes

- a. The synthesis mixture contains 9 wt ppm of added Mg^{2+} species (based on the weight of the synthesis mixture).
- b. $Mg(NO_3)_2$ solution: dissolve 2.5645 g magnesium nitrate ($Mg(NO_3)_2 \cdot 6 H_2O$) in 997.4 g water.
This solution contains 0.24 mg Mg^{2+} /g solution. The function of the Mg^{2+} species is to avoid the formation of byproducts such as MER, and to control the particle size of the LTL product.
- c. This water is used to quantitatively transfer the aluminate solution.
- d. After 3 minutes mixing, the gel is still pourable. Longer mixing is permitted, but the gel then tends to stiffen and is difficult to transfer to the autoclave.
- e. No Teflon liner was used.
- f. Crystallization time is not critical (24 to 72 hours).

LTL

Linde Type L

Si(76), Al(24)



Contributed by Moussa Zaarour and Svetlana Mintova

Verified by G. Rioland, T.J. Daou, J. Patarin, H. Awala, M. Y. Jeon

Type Material: $K_9[Si_{27}Al_{19}O_{72}] : 21 H_2O$

Method: M. Tsapatsis, M. Lovallo, T. Okubo, M.E. Davis, M. Sadakatas [1]
M. Hölzl, S. Mintova, T. Bein [2]

Batch Composition: 5 K_2O : 0.5 Al_2O_3 : 10 SiO_2 : 200 H_2O

Source Materials

aluminium hydroxide (80 wt.% $Al(OH)_3$, 20 wt.% H_2O , Sigma Aldrich)

potassium hydroxide ($\geq 85\%$ KOH, Pellet, Aldrich)

silica sol (Ludox SM-30, 30 wt. % suspension in H_2O , pH = 9.7-10.3, Aldrich)

deionized water (DI)

Batch Preparation

(1) [0.488 g of $Al(OH)_3$ + 5.4 g H_2O + 2.196 g of KOH], stir in a flask^a

(2) [10 g Ludox SM-30+ 5 g H_2O + 1.098 g of KOH], stir in a flask^a

(3) [(1) drop wise + (2)], stir vigorously in a flask cooled in ice bath^a

(4) The white suspension turns to clear after aging for 40 h at RT

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 170 °C

Time: 20 h

Product Recovery

(1) Centrifugation (2000 rpm, 1h) and redispersion in water, washed until pH = 8

(2) Freeze-dry the final product

Product Characterization

XRD: LTL; no competing phase

DLS: monodispersed, average particle size of 40 nm

TEM: cylindrical shape, homogeneous and fully crystalline particles

References

[1] M. Tsapatsis, M. Lovallo, T. Okubo, M.E. Davis, M. Sadakatas, Chem. Mater. 7 (1995) 1734

[2] M. Hölzl, S. Mintova, T. Bein, Stud. Surf. Sci. Cata. A 158 (2005) 11

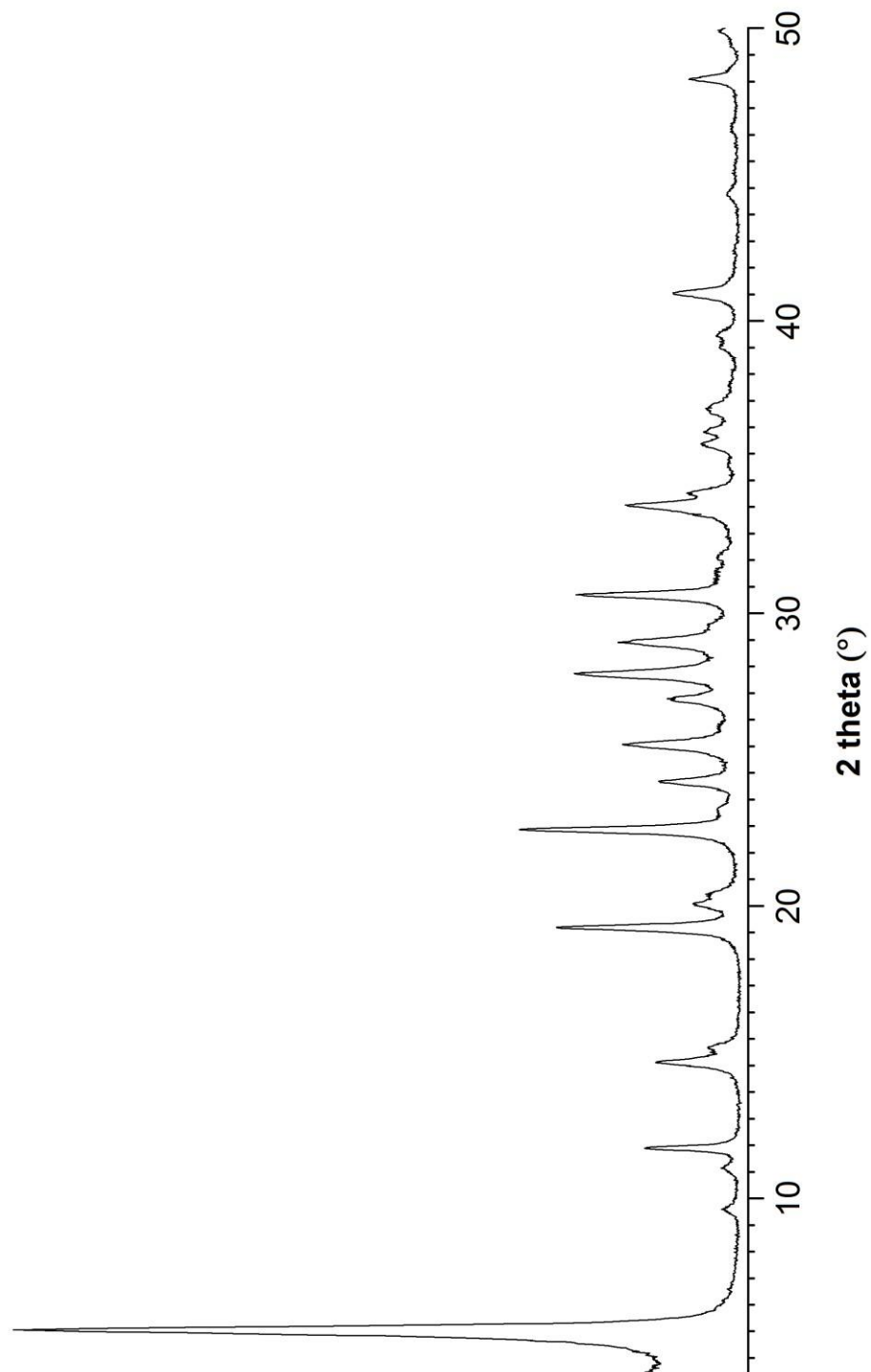
Notes

a. Clear solution is obtained.

LTL

Nanosized Linde Type L

Si(72), Al(27)



MAZ

Mazzite

Si(78), Al(22)

Contributed by David Vaughan and Karl Strohmaier

Verified by S. Yang and A. Navrotsky, C. Williams and C. Round, Hyun-ku Rhee and J. Kornatowski

Type Material $\text{Na}_{73}(\text{TMA}^+)_{0.7}\text{Al}_8\text{Si}_{28}\text{O}_{72} : w\text{H}_2\text{O}$ (TMA = tetramethylammonium)

Method D. E. W. Vaughan [1]

Batch Composition 3.35 Na_2O : 1.24 (TMA)Br : Al_2O_3 : 9.17 SiO_2 : 125 H_2O : 0.66 Na_2SO_4

Source Materials

deionized water

sodium hydroxide (J. T. Baker, ~ 99% NaOH)

alumina (Alcoa C-31, assumed 100% $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$)

sodium silicate (PQ Corp. N brand, 8.9% Na_2O , 28.7% SiO_2)

tetramethylammonium bromide (RSA)

aluminum sulfate (J. T. Baker, $\text{Al}_2(\text{SO}_4)_3 : 17 \text{H}_2\text{O}$)

Batch Preparation (for 112 g dry product)

Preparation of Seed Solution (2)

- (1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
- (2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
- (3) Age for 24 hours at room temperature ^a

Preparation of Crystallization Batch

- (4) [50 g water + 19.6 g NaOH + 25.1 g alumina], reflux until clear. Cool to room temperature and add water to attain the original weight
- (5) [50 g water + 40 g tetramethylammonium bromide], mix until dissolved.
- (6) [396.4 g sodium silicate + 35 g water + 13.9 g (3) + (5)]. Add components sequentially with mixing in a Pyrex one-L reaction kettle with mixing. Heat mixture to 80°C
- (7) [50 g water + 30 g aluminum sulfate], mix until dissolved
- (8) [(6) + (4) + (7)], add sodium alumina to solution followed by alum solution with stirring at 80°C ^b
- (9) Increase temperature to 100°C and stir until homogeneous

Crystallization

Vessel: one-L Pyrex reaction kettle with reflux condenser and stirrer^c

Time: 40+ hours ^d

Temperature: 100°C

Agitation: None, except just prior to sampling

Product Recovery

- (1) Vacuum filter on a Buchner funnel
- (2) Wash to pH < 10
- (3) Dry at 110°C
- (4) Yield near quantitative on Al₂O₃

Characterization

XRD excellent MAZ

Elemental analysis: 0.92 Na₂O : 0.1 (TMA)₂O : Al₂O₃ : 7.14 SiO₂

Crystal size and habit: barrel-shaped aggregates of needle-like crystals (2 to 3 μ long and 0.1 μm dia.)^e

References

- [1] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89
- [2] D. E. W. Vaughan, US Patent 4 178 352 (1979)

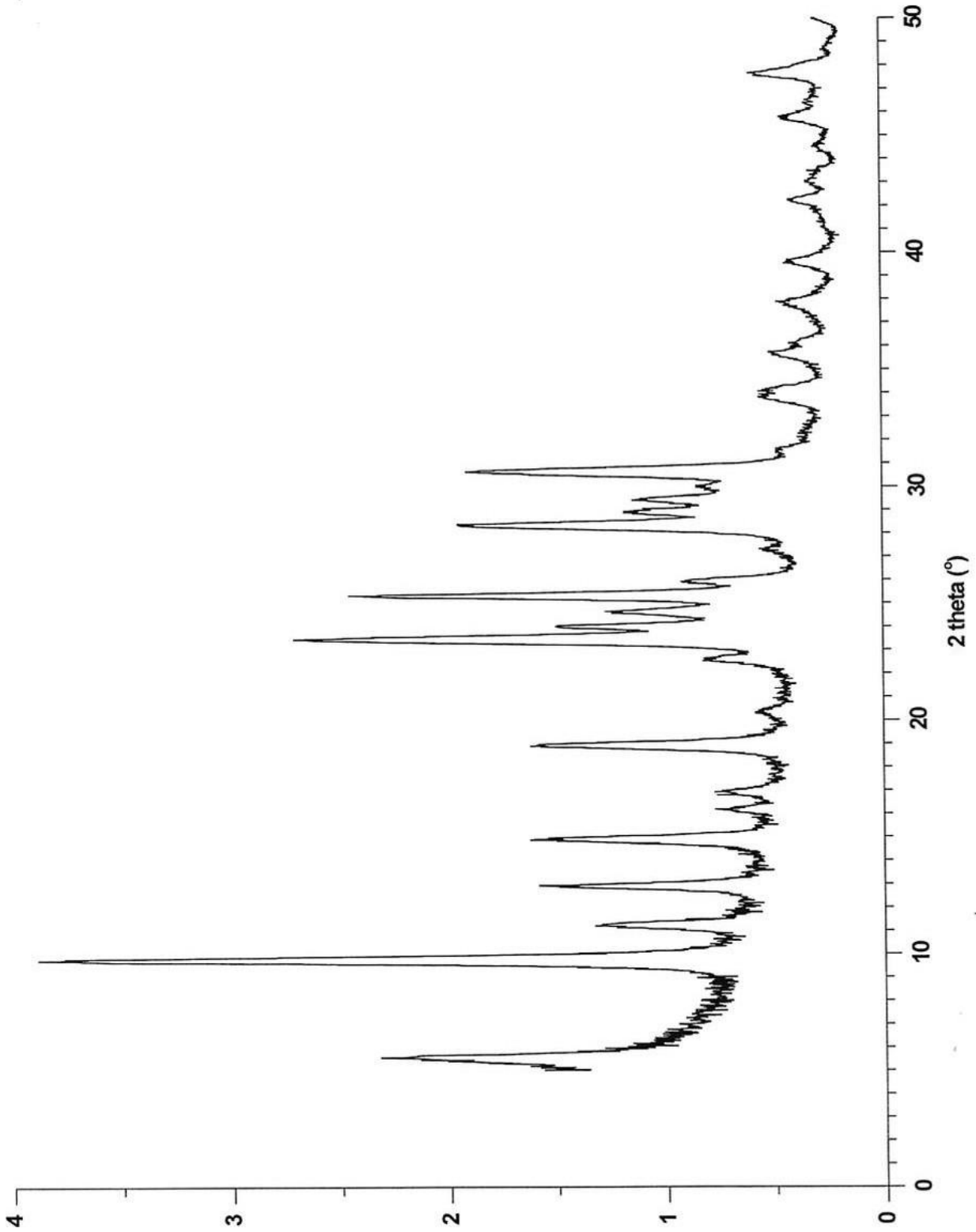
Notes

- a. Stored at room temperature, this seed solution will be stable and usable for several months.
- b. This formulation produces a hard gel when the alum is added making it difficult to fully homogenize. A Hobart or Kitchenaid mixer is better than a blender if available. The gel breaks up at about 80°C.
- c. Alternatively, a one-L Teflon jar (Nalgene) or subdividing the gel between smaller vessels is appropriate.
- d. After about 18 hours, faujasite is fully crystallized (Si/Al = 2.4). Continuing the crystallization for more than 40 hours produces fully crystalline MAZ. It was still pure MAZ after 7 days.
- e. ¹³C NMR shows one site in the GME cage.

MAZ

Mazzite

Si(78), Al(22)



MEL

Nanosized TBA-Silicalite-2

Si(100)

Contributed by Moussa Zaarour and Svetlana Mintova

Verified by D. Stosic, D. Wales, X. Zou

Type Material: [Si₉₆O₁₉₂]

Method: S. Mintova, N. Petkov, K. Karaghiosoff, T. Bein [1]

Batch Composition: SiO₂ : 0.15 TBA₂O : 4.0 EtOH : 17 H₂O

Source Materials

tetraethoxysilane (TEOS) (98%, Aldrich)

tetrabutylammonium hydroxide TBAOH (40%, Aldrich)

distilled water

Batch Preparation

(1) [20 g TEOS + 18.3 g TBAOH], stir in a plastic flask

(2) [(1) + 18.68 g H₂O], mix under vigorous stirring in a plastic flask^a

(3) Aging (hydrolyzation of silica) on orbital shaker at RT for 45 hours

Crystallization

Vessel: polypropylene (PP) bottles

Temperature: 90 °C

Time: 68 h

Product Recovery

(1) Centrifugation (2000 rpm, 1h) and redispersion in water, washed until pH = 8

(2) Freeze-drying

Product Characterization

DLS: monodisperse particles with size of 90-100 nm

XRD: MEL

SEM: spheroidal crystals

Reference

[1] S. Mintova, N. Petkov, K. Karaghiosoff, T. Bein, *Microporous Mesoporous Mater.* 50 (2001) 121

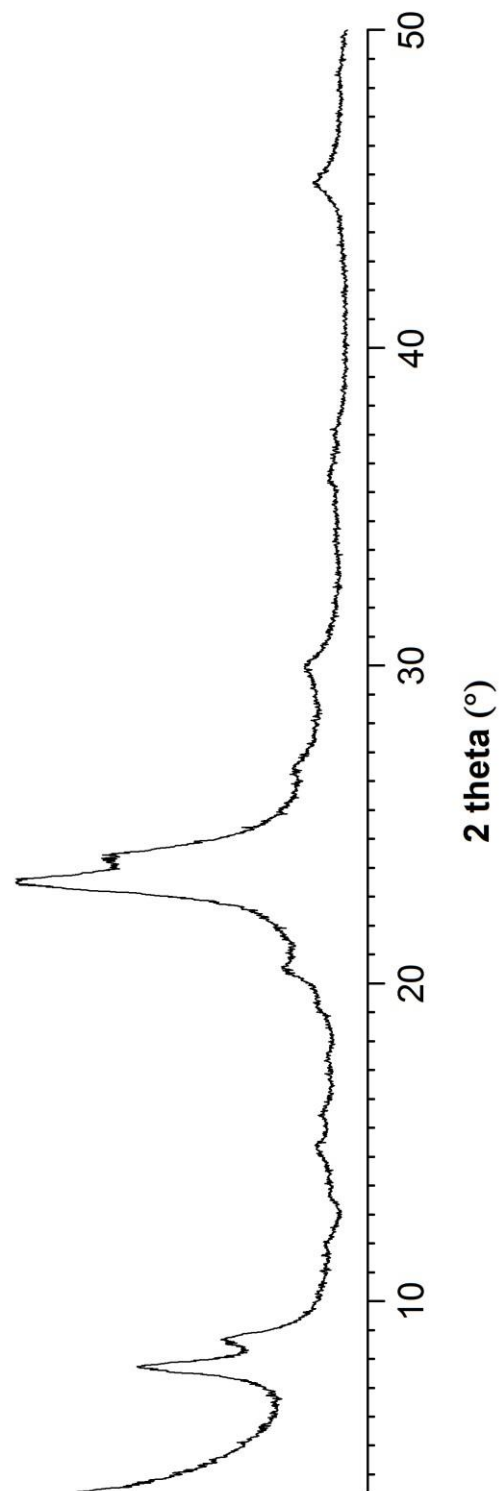
Notes

a. Clear solution is obtained

MEL

Nanosized TBA-Silicalite-2

Si(100)



MER

Linde W

Si(65), Al(35)

Contributed by Karl Strohmaier

Verified by P. Piccione and Huann-Jih Lo

Type Material $K_{11}Al_{11}Si_{21}O_{64} \cdot 20H_2O$

Method R M. Milton [1]

Batch Composition 3 K_2O : 0.05 Na_2O : Al_2O_3 : 5 SiO_2 : 100 H_2O

Source Materials

deionized water

potassium hydroxide (J. T. Baker, 87.6% KOH)

alumina (Alcoa C-31, 65% Al_2O_3)

colloidal silica (duPont Ludox HS-40, 40% SiO_2)^a

Batch Preparation (for 15 g dry product)

- (1) [20 g water + 12.4 g potassium hydroxide + 5.0 g alumina], heat to a gentle boil with stirring until clear. Cool to room temperature and add water to attain the original weight
- (2) [24.2 g colloidal silica + 18.5 g water + (1)]. Add components sequentially with mixing in a beaker^b

Crystallization

Vessel: 125 Teflon-lined autoclave (Parr #4748 acid digestion bomb)

Time: 48 hours

Temperature: 150°C^c

Agitation: None

Product Recovery

- (1) Vacuum filter on a Buechner funnel
- (2) Wash to pH < 10
- (3) Dry at 110°C
- (4) Yield 15 g, near quantitative on Al_2O_3

Characterization

XRD excellent MER, unit cell dimensions (space group $I4/mmm$ - No. 139) $a = 14.15 \text{ \AA}$, $c = 10.03 \text{ \AA}$

Elemental Analyses: K_2O : Al_2O_3 : 3.66 SiO_2

Crystal size and Habit: barbell-shaped aggregates (40-50 μm long and 20-30 μm dia.) of needle-like crystals.

Reference

- [1] R M. Milton, US Patent 3 012 853 (1961)

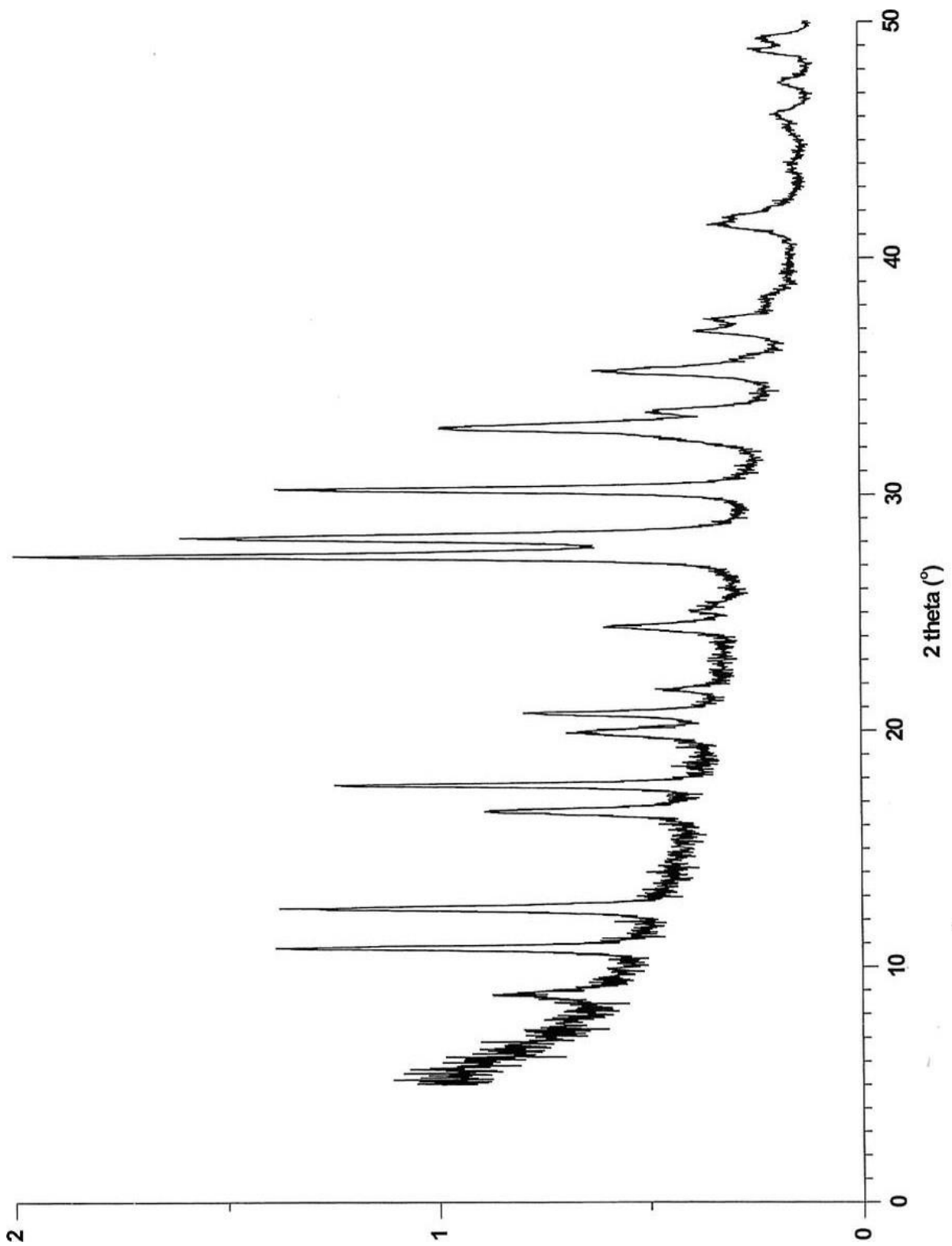
Notes

- a. Available from Aldrich or Alpha.
- b. Solution gels in about 5 minutes.
- c. If mixture is crystallized at 100°C, a mixture of chabazite and Linde W is made.

MER

Merlinoite

Si(65), Al(35)



MFI

High-Al ZSM-5

Si(93), Al(7)

Contributed by Hans Lechert and Ralph Kleinwort

Verified by A. Palmqvist, J. Brendle and H. Kessler

Type Material $\text{Na}_7[\text{Al}_7\text{Si}_{89}\text{O}_{192}] : \text{wH}_2\text{O}$

Method H. Lechert, R. Kleinwort ^a

Batch Composition 3.25 Na_2O : Al_2O_3 : 30 SiO_2 : 958 H_2O (exclusive of seeding gel)

Source Materials

distilled water

sodium hydroxide (Merck, pure)

tetrapropylammonium hydroxide (Fluka, 20% solution)

silicic acid (Merck, technical grade, SiO_2 : 0.5 H_2O)

sodium aluminate (Roth, Al_2O_3 : 1.24 Na_2O : 0.57 H_2O)

Seeding Gel Preparation^b

- (1) [710.3 g water + 13.8 g sodium hydroxide + 117.0 g TPA-OH solution], dissolve and mix thoroughly
- (2) [(1) + 158.9 g silicic acid], add silica in portions under stirring. Shake the resulting mixture for one hour at ambient temperature. Age at 100°C for 16 hours

Synthesis Gel Preparation (for ~87 g product)

- (1) [867.8 g water + 8.8 g sodium hydroxide + 10.3 g sodium aluminate], dissolve and mix thoroughly
- (2) [(1) + 113.1 g silicic acid], add silica in portions under stirring. Shake vigorously for one hour at ambient temperature
- (3) [(2) + 50 g seeding gel],^c shake for one hour

Crystallization

Vessel: 50 mL PTFE-lined stainless steel autoclaves

Temperature: 180°C ^d

Time: 40 hours ^e

Agitation: none

Product Recovery

- (1) Recover product by filtration
- (2) Wash thoroughly with distilled water
- (3) Dry at 105°C for 24 hours
- (4) Pulverize dried product in an agate mortar ^f

Product Characterization

XRD: fully crystalline MFI;^{g,h} competing phase: mordenite (at lower Si/Al ratios in the gel)

Elemental Analysis: Si/Al = 12 to 13.5ⁱ
Crystal Size and Habit: 6 μm crystals

References

- [1] G. Bellussi, G. Perego, A. Carati, U. Gomaro, V. Fatore, in *Innovation in Material Science*, P. J. Grobet, W. J. Mortier (eds.), Elsevier, Amsterdam, 1988
- [2] H. Kacirek, A. Meyer, German Patent 3 402 842 Al
- [3] R. Kleinwort, PhD Thesis, University of Hamburg (1995)
- [4] A. Nastro, C. Coflella, R Aiello, in *Stud. Surf. Sci. Catal. Vol. 24*, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985, p 19
- [5] J. M. Berak, R Mostowcz, in *Stud. Surf. Sci. Catal., Vol 24*, B. Drzaj, S. Hocevar, S. Pejovnik (eds.), Elsevier, Amsterdam, 1985
- [6] W. Schwieger, K. H. Bergk, U. Haedcke, German Patent 2 83 1 26 (1990)
- [7] H. P. Rieck, German Patent OS 3 242 352 (1984)
- [8] P. Chu, F. J. Rosinski, European Patent Appl. 110650 (1983)

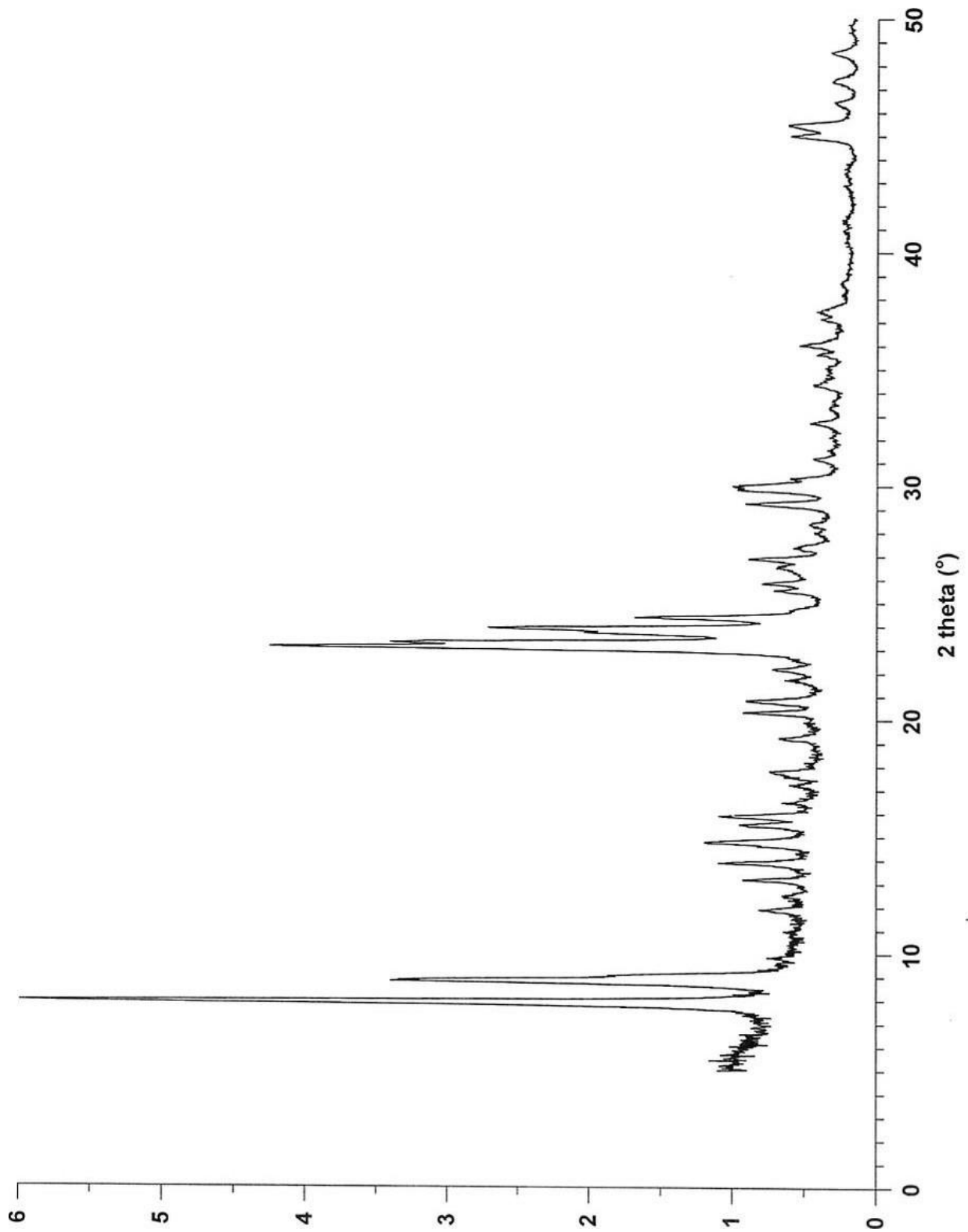
Notes

- a. According to Bellussi, [1] the ZSM-5 structure crystallizes in batches of the composition: $\text{NaAlO}_2 n[\text{Na}_m\text{H}_{4-m}\text{SiO}_4] p\text{H}_2\text{O}$ in the ranges $n = 20$ to 50 , $m = 0.1$ to 0.2 and $p = 400$ to 500 . For $m < 0.1$, generally amorphous products were observed. Above $m = 0.2$, mordenite crystallizes. For $n < 20$, ferrierite was found and above $n = 50$, zeolite Q. The Si/Al ratio in the product was nearly equal to the Si/Al in the batch. Compared to batches with template, those without template usually show a distinctly enhanced crystallization time. The enhancement is especially due to an increased induction period, leading to the conclusion that the crystallization should be carried out with the use of seeds. Another hope of the application of seeds is that the area of the formation of ZSM-5 in the crystallization field can be extended to higher m and lower n by suppressing the formation of mordenite which crystallizes preferably in that region.
- b. A quite active seeding agent is obtained by carefully aging a gel giving silicalite. [2] For this gel, only a small amount of TPA-OH is necessary which does not influence the Si/Al ratio of the final product.
- c. Good results have been obtained using 1-10 wt% seeding gel in the mixture.
- d. Good results have been obtained at temperatures from 145°C to 190°C . At 190°C , the crystallization is finished at about 10 hours.
- e. The crystallization kinetics have been checked by comparison of the crystallinity with an industrial sample by X-ray. [3]
- f. The final products were kept in a desiccator over saturated CaCl_2 solution for 24 hours before further characterization.
- g. The kinetic experiments showed that the described seeding gel led to a drastically reduced induction period of crystallization and to a considerable increase in the crystallinity of MFI. This shows that the area of MFI crystallization can be extended into the range where mordenite or ferrierite has been found.
- h. Crystallinity of the products was determined by comparing the sum of the peak areas between $2\theta = 23.2^\circ$ and 24.5° with that of a well-crystallized industrial sample which was used as a standard throughout the experiments.
- i. For lower Si/Al ratios in the batch, mordenite could not be avoided. For higher Si/Al ratios in the batch, Si/Al of the products increased but remained slightly below Si/Al of the batch. Further information about the crystallization of MFI in template-free systems can be found in references [4-8].

MFI

High-alumina ZSM-5

Si(93), Al(7)



Contributed by Moussa Zaarour and Svetlana Mintova

Verified by G. Rioland, T.J. Daou, J. Patarin, H. Awala, M. Tsapatsis, Z. Qin

Type Material: [Si₉₆O₁₉₂]

Method: A.E. Persson, B.J. Schoeman, J. Sterte, J.-E. Otterstedt [1]
S. Mintova, N.H. Olson, J. Senker, T. Bein [2]^a

Batch Composition: 9 TPAOH : 25 SiO₂ : 480 H₂O : 100 EtOH

Source Materials

tetraethylorthosilicate TEOS (99.99 %, Aldrich)
tetrapropylammonium hydroxide (TPAOH, 1.0 M aqueous solution, Aldrich)
double distilled water

Batch Preparation

[20 g TEOS + 35 g TPAOH + 5.26 g H₂O] hydrolyze for 24 h on a gyratory shaker (180 rpm)^b

Crystallization

Vessel: polypropylene (PP) bottle
Temperature: 90 °C
Time: 30 h

Product Recovery

- (1) Centrifugation (20000 rpm, 1h) and redispersion in water till pH=8
- (2) Drying at 70 °C for 15 hours or freeze-drying
- (3) Calcination: 600 °C for 6h
- (4) Solid product: 2.9 g

Product Characterization

XRD: MFI; DLS: particle size of 80-90 nm; SEM: zeolite nanocrystals with spheroidal shape

References

- [1] A.E. Persson, B.J. Schoeman, J. Sterte and J.-E. Otterstedt, Zeolites 14 (1994) 557
- [2] S. Mintova, N.H. Olson, J. Senker, T. Bein, Angew. Chem. 41 (2002) 2558

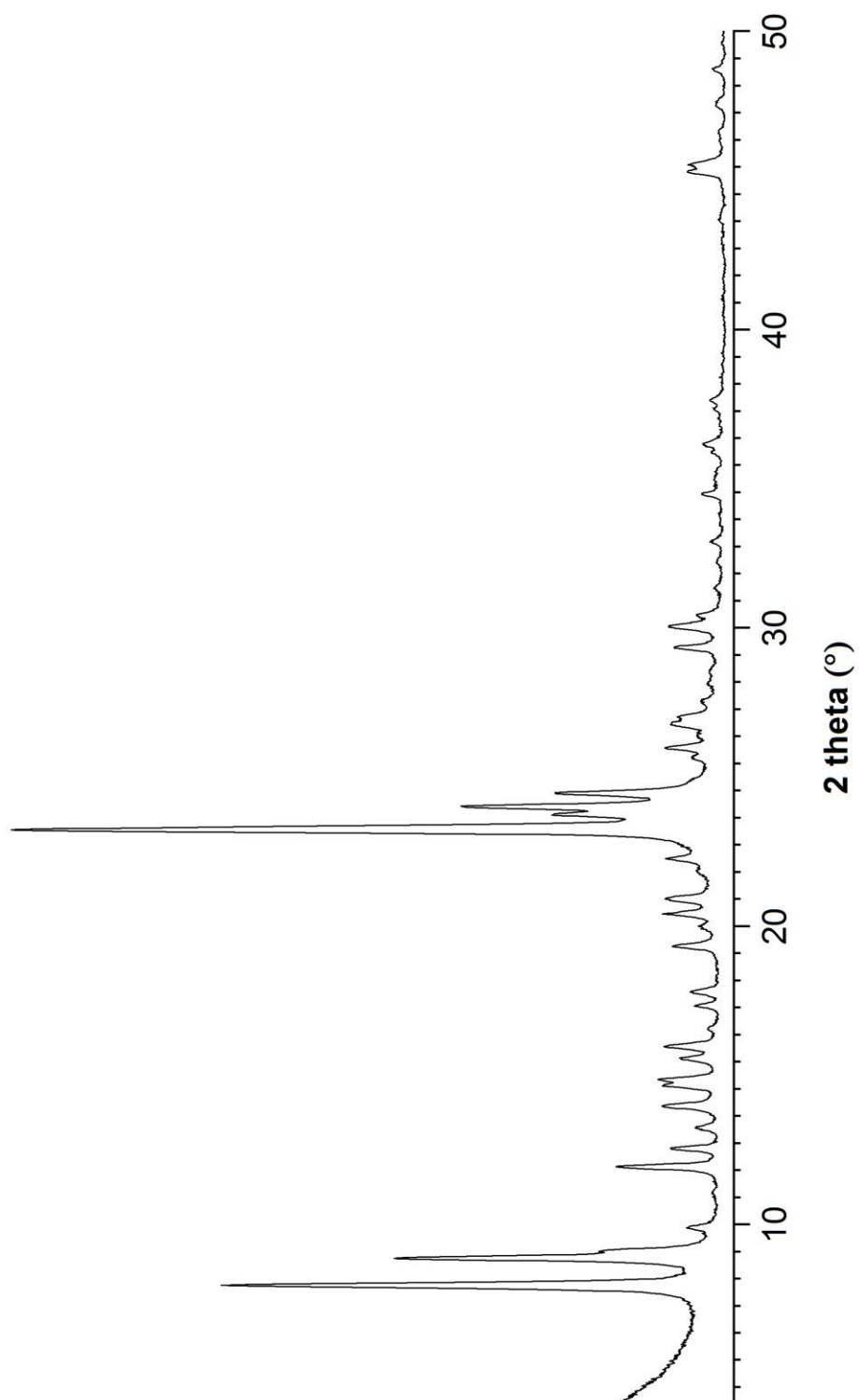
Notes

- a. The procedure reported in [2] is slightly different from [1], but the final product is the same (nanosized TPA-silicalite-1).
- b. Clear precursor solution is obtained.

MFI

Nanosized TPA-silicalite-1

Si(100)



MFI

Template-free ZSM-5

Si(96), Al(4)

Contributed by Wha Jung Kim

Verified by S. B. Hong, E.-P. Ng, J. Shin

Type Material: Na₄[Al₄SiO₉₂] : wH₂O

Method: W.J Kim and S.D. Kim [1]

Batch Composition: 10 Na₂O : 100 SiO₂ : 2 Al₂O₃ : 2250 H₂O

Source Materials

deionized water

10 wt.% NaOH solution prepared from 96 wt.% sodium hydroxide (SAMCHUN Chem. Co.)

sodium aluminate (Junsei Chem. Co., 37 wt.% Al₂O₃ and 31 wt.% Na₂O)

colloidal silica (Dupont Chem. Co., Ludox AS-40)

Batch Preparation

- (1) [60g of silica sol + 21.4g of 10 wt.% NaOH solutions^a], stir in a beaker
- (2) [30g of water + (1)], stir at 200 rpm for 3h
- (3) [57g of water + 1.8 g of 10 wt.% NaOH solutions + 2.2g of NaAlO₂], stir in a beaker for 3h
- (4) [(3) +27g of water]
- (5) [add (4) to (2)], stir for 1h to get a homogeneous solution

Crystallization

Vessel: Teflon-lined stainless steel autoclave equipped with a doubled-stirrer of pitched blade turbine and sampling port.

Temperature: 190° C

Time: 2h

Temperature: 150° C

Time: 35h^b

Agitation: 200 rpm

Product Recovery

- (1) Collect through the sampling port
- (2) Filter and wash with water using membrane filter (Advantec MFS, Inc., pore size of 0.2 μm)
- (3) Dry at ambient temperature or at 100°C

Product Characterization

XRD: fully crystalline MFI; Competing phase: mordenite at lower Si/Al ratios in the gel

Elemental Analysis: Si/Al = 25

Crystal Size and Habit: 2 μm crystals

Reference

- [1] W.J. Kim and S.D. Kim, U.S. Pat. 7,361,328 (2008)
- [2] S.D. Kim, S.H. Noh, K.H. Seong and W.J. Kim, *Micropor. Mesopor. Mater.* 72 (2004) 185
- [3] S.D. Kim, Noh, J.W. Park and W.J. Kim, *Micropor. Mesopor. Mater.* 92 (2006) 181

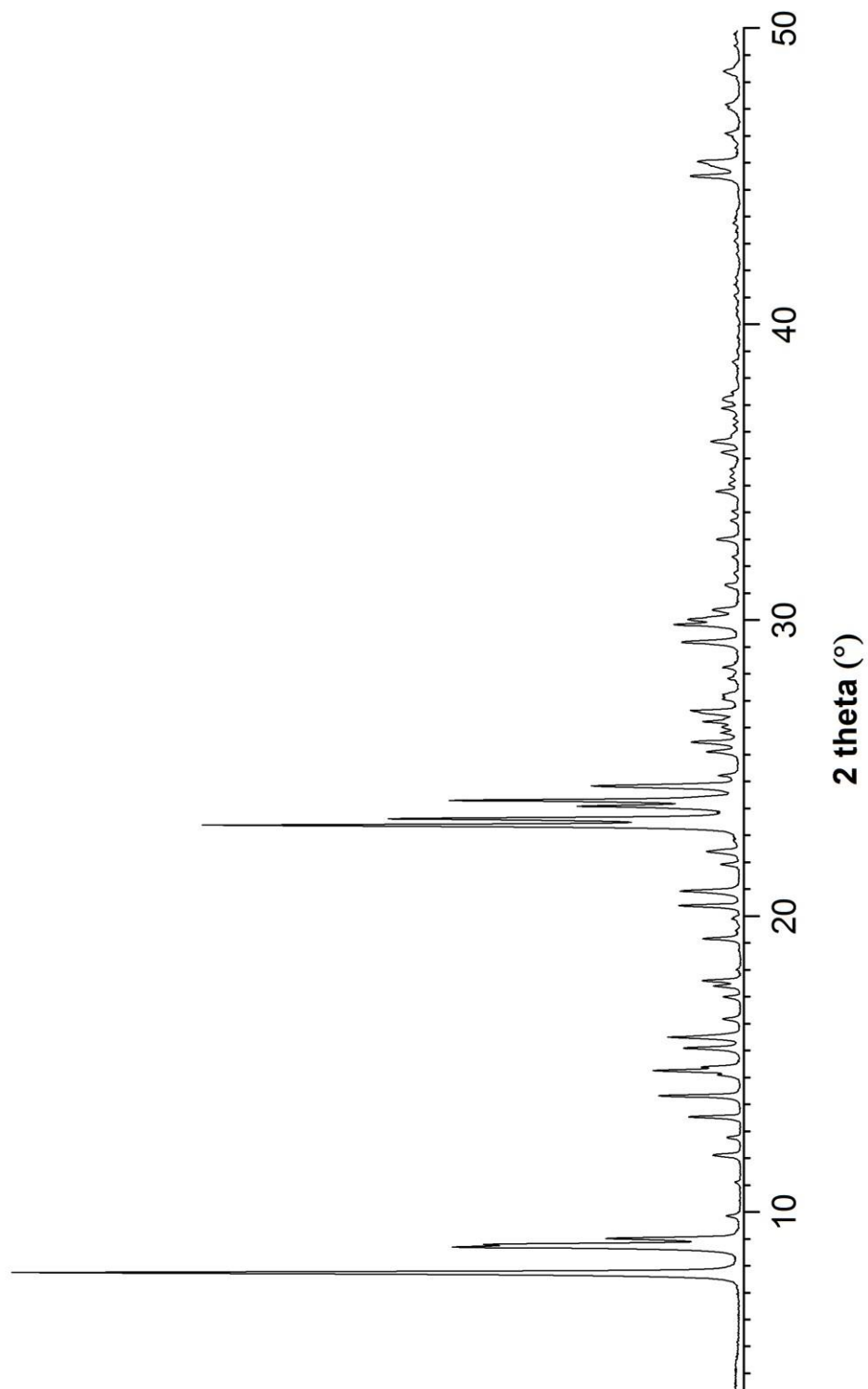
Notes

- a. Slowly added.
- b. The reaction temperature of the resultant mixture was increased up to 190° C while performing stirring at 200 rpm, and maintained for 2 hours. Then, the reaction temperature was decreased to 150° C and maintained for 35 hours.

MFI

Template-free ZSM-5

Si(96), Al (4)



MFI

Silicalite-1

Si(100)

Contributed by A. C. Faust and C. Schott-Daric

Verified by J. Cejka and B. Schoeman

Type Material $\text{Si}_{96}\text{O}_{192}\text{F}_4(\text{TPA})_4$ (TPA = tetra-n-propylammonium)

Method J.-L Guth, H. Kessler, R. Wey [1]

Batch Composition 1 SiO_2 : 0.08 (TPA)Br: 0.04 NH_4F : 20 H_2O

Source Materials

distilled water

tetrapropylammonium bromide (Fluka, 98%)

ammonium fluoride (Fluka, 98%)

silica (Degussa Aerosil 130, 99+%)

Batch Preparation (for 12 g product)

- (1) [72 g water + 4.26 g tetrapropylammonium bromide + 0.296 g ammonium fluoride], stir until dissolved
- (2) [(1) + 12 g silica], mix with a spatula, and then stir until homogenized. Initial pH = 6

Crystallization

Vessel: PTFE-lined autoclave

Time: 15 days ^a

Temperature: 200°C

Agitation: none

Product Recovery

- (1) Filter, wash with distilled water
- (2) Dry at 80°C
- (3) Yield: 12.7 g; near 100% based on silica

Product Characterization

XRD: characteristic strong reflections at $d = 11.01, 3.829, 3.806$ and 3.698 \AA

Elemental Analyses: $\text{Si}_{96}\text{O}_{192}\text{F}_4(\text{TPA})_4$

Crystal Size and Habit: prisms $95 \times 80 \mu\text{m}$

Reference

- [1] J.-L Guth, H. Kessler, R Wey, in Stud. Surf. Sci. Catal., Vol. 28, Y. Murakami, A. Iijima, J. W. Ward (eds.), Kodansha-Elsevier, Tokyo, 1986, p. 121

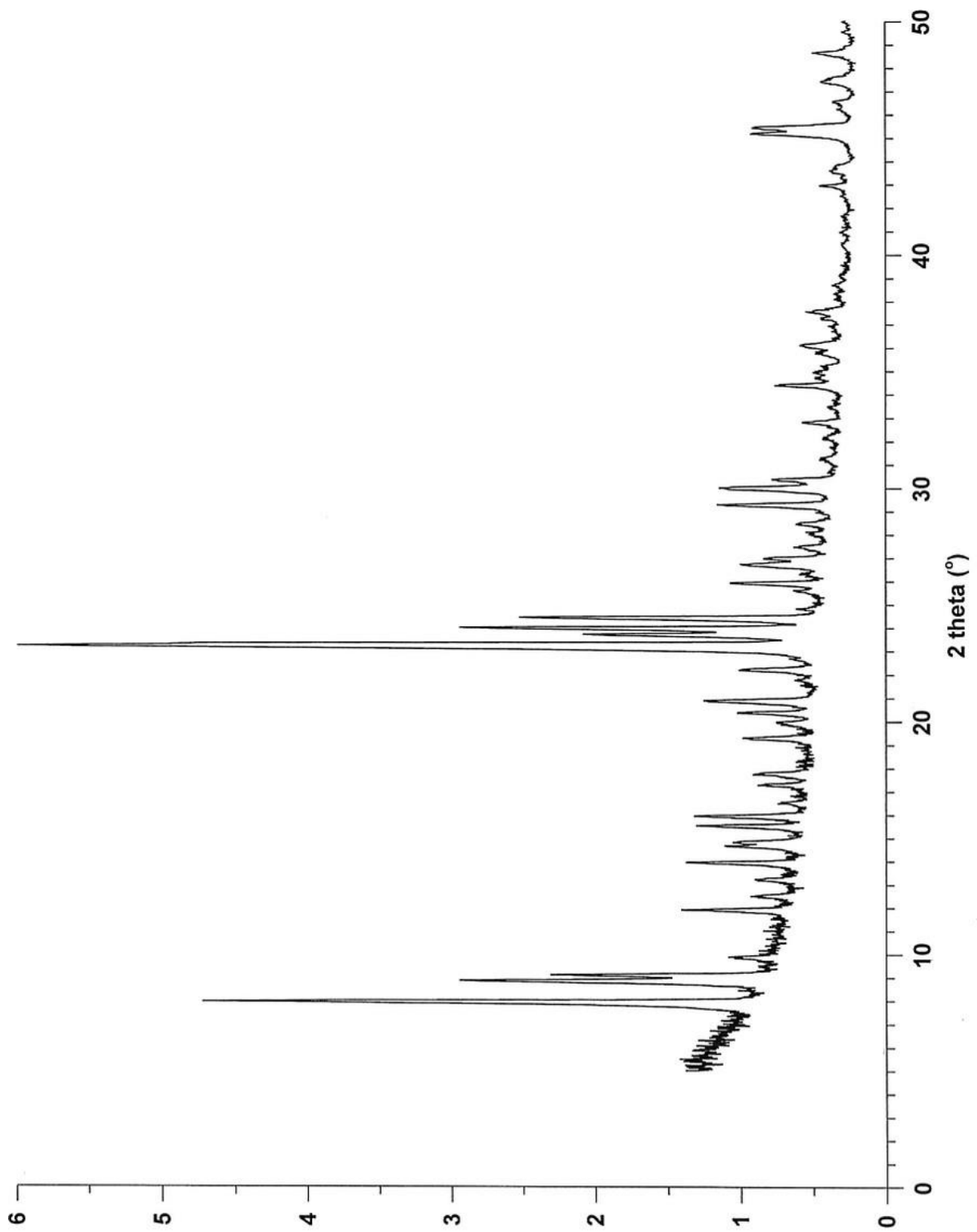
Note

- a. Increasing NH_4F leads to a decrease in crystallization time (2 days for $\text{NH}_4\text{F}/\text{SiO}_2 = 1$).

MFI

Silicalite-1

Si(100)



MFI

[B] ZSM-5

Si(98), B(2)

Contributed by Rob de Ruiter

Verified by Z. Gabelica, U. Deforth and A. Cichocki

Type Material $\text{Na}_{0.4}(\text{TPA})_{0.4}[\text{B}_2\text{Si}_{94}\text{O}_{192}] \cdot w\text{H}_2\text{O}$ (TPA = tetra-n-propylammonium)

Method R de Ruiter, J. C. Jansen, H. van Bekkum [1]

Batch Composition 2.1 Na_2O : B_2O_3 : 2.4 SiO_2 : 4 TPABr: 1050 H_2O

Source Materials

distilled water

silica (Aerosil 200-Degussa)

sodium hydroxide (J. T. Baker, reagent grade)

tetrapropylammonium bromide (TPABr)(CFZ Zaltbommel)

boric acid (Merck p.a.)

Batch Preparation (0.12 to 0.14 g product/35 mL autoclave)

- (1) [280 g water + 2.66 g silica + 3.1 g sodium hydroxide], shake overnight at room temperature
- (2) [(1) + 19.7 g tetrapropylammonium bromide], stir until dissolved
- (3) [90 g water + 2.92 g boric acid], stir until dissolved
- (4) [20 mL of (2) + 5 mL of (3)], mix thoroughly; initial pH ~11

Crystallization

Vessel: Teflon-lined stainless steel autoclave, 35 mL

Time: 5 days

Temperature: 180°C

Agitation: none

Product Recovery

- (1) Filter and wash
- (2) Yield: 60-70% on SiO_2

Product Characterization

XRD: Pure MFI, no extraneous phases

Elemental Analysis: 93.5% SiO_2 , 1.25% B_2O_3 , 2% TPABr, 0.25% Na_2O

Crystal Size and Habit: prismatic to lath morphology depending on boron content, the crystal thickness (in b-direction) decreases with boron content of framework

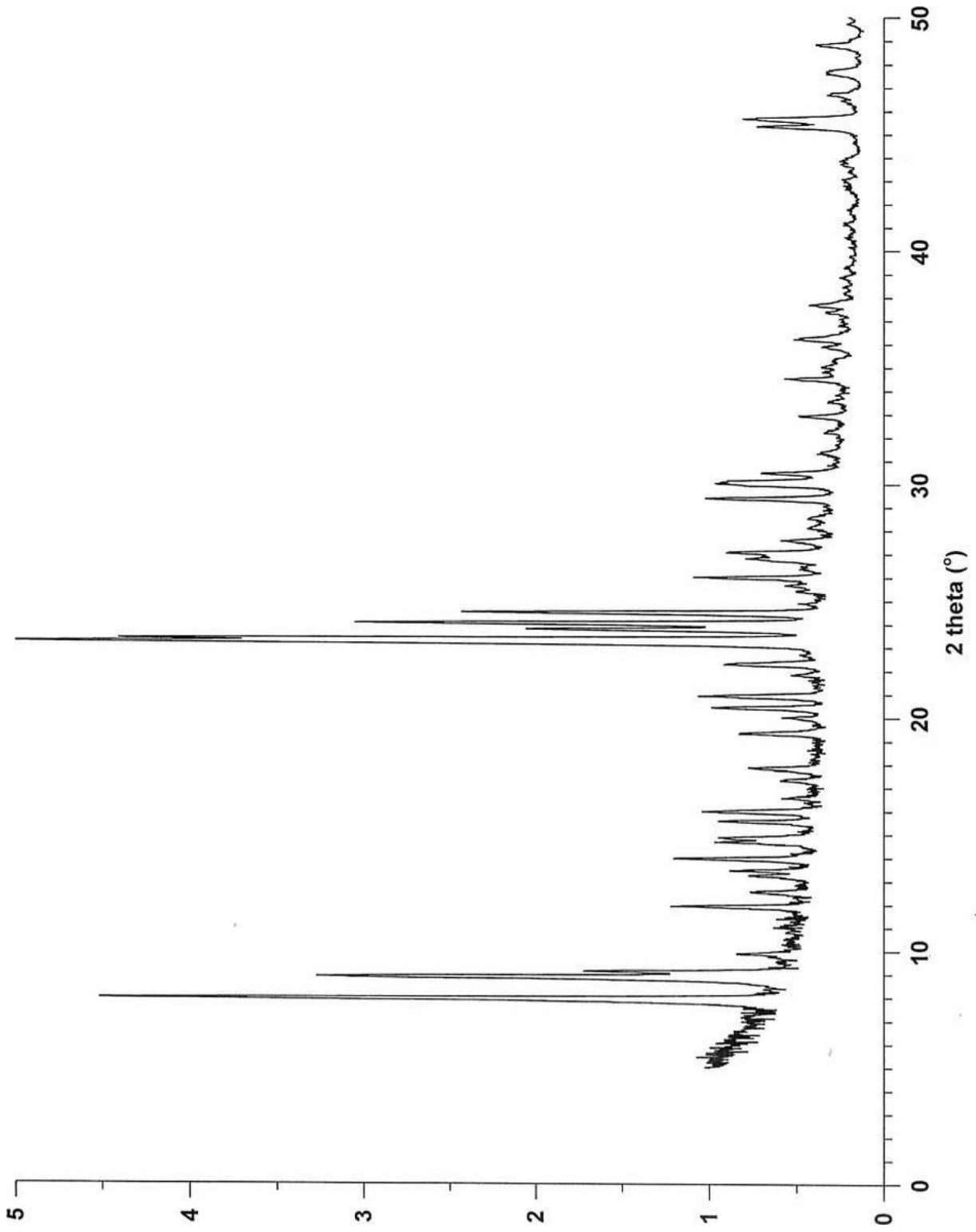
Reference

- [1] R. de Ruiter, J. C. Jansen, H. van Bekkum, in Synthesis of Microporous Materials, Vol. 1, M. L. Occelli, H. F. Robson (eds.), Van. Nostrand Reinhold, New York, 1992, p 167

MFI

[B] ZSM-5

Si(98), B(2)



MFI

[Fe]-ZSM-5

Si(96), Fe(4)

Contributed by Angelika Brückner

Verified by Y. Kiyozumi and P. Fejes

Type Material $\text{Na}_{0.3}(\text{TPA})_{3.7}[\text{Fe}_4\text{Si}_{92}\text{O}_{192}] \cdot w\text{H}_2\text{O}$ (TPA = tetra-n-propylammonium)

Method A. Brückner, R. Lück, W. Wieker, B. Fahlke [1]

Batch Composition 30 Na_2O : Fe_2O_3 : 30 SiO_2 : 1040 H_2O : 5 (TPA)Br : 25 H_2SO_4

Source Materials

distilled water

sulfuric acid (reagent grade, 98% H_2SO_4)

iron(III) sulfate (reagent grade, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$) sodium

metasilicate (reagent grade, $\text{Na}_2\text{SiO}_3 \cdot 9 \text{H}_2\text{O}$)^a

tetrapropylammonium bromide (TPABr) (Fluka, CH-9470 Buchs)

Batch Preparation (for ~20 g volatile-free product)

- (1) [100 g water + 22 g sulfuric acid + 5.62 g iron(III) sulfate], stir until dissolved
- (2) [163.4 g water + 85.26 g sodium metasilicate], stir until dissolved
- (3) [(1) + (2)], add silicate slowly to iron(III) sulfate solution with good mixing
- (4) [(3) + 13.31 g TPABr], mix vigorously until uniform (~ 400 rpm)

Crystallization

Vessel: stainless steel autoclaves

Temperature: 170°C

Time: 72 hours

Agitation: autoclaves are rotated axially

Product Recovery

- (1) After cooling, filter and wash with water several times
- (2) Dry over P_{4010}
- (3) Calcine at 550°C for 4 hours to remove template

Product Characterization

XRD: ZSM-5 (only phase)

Elemental Analysis: 0.07 Na_2O : Fe_2O_3 : 48 SiO_2 : $w\text{H}_2\text{O}$

Crystal Size and Habit: 1-6 μm , snowball-like

Reference

- [1] A. Brückner, R. Lück, W. Wieker, B. Fahlke, Zeolites 12 (1992) 380

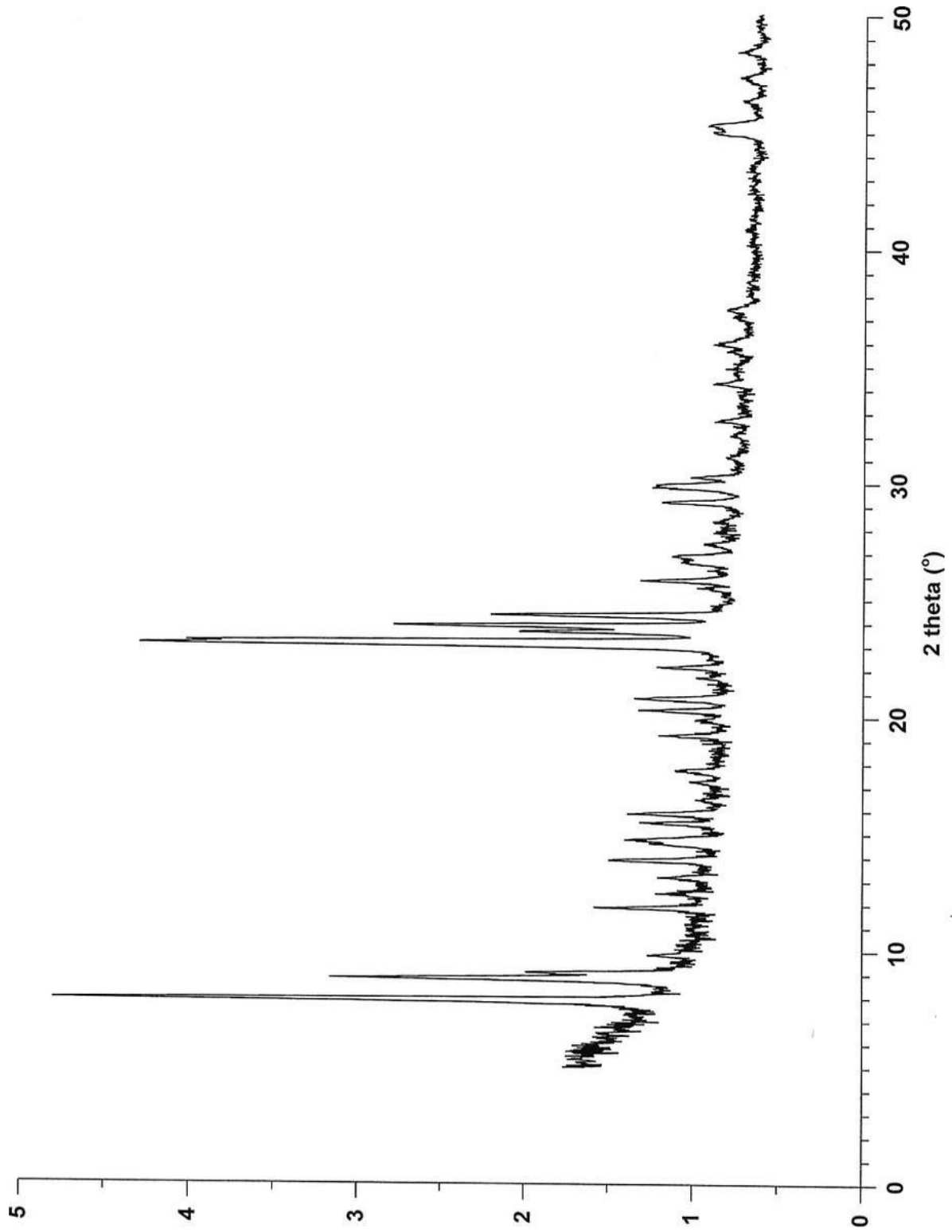
Note

- a. Al(III), a common impurity in silica sources, displaces Fe(III) from T-atom positions in MFI. [1]

MFI

[Fe]-ZSM-5

Si(96), Fe(4)



MFI

[Ti] ZSM-5

Si(98.6), Ti(1.4)

Contributed by Jan H. C. van Hooff and Arjan van der Pol

Verified by D. Serrano and Z. Gabelica

Type Material [Ti_{1.3}Si_{94.7}O₁₉₂] : wH₂O

Method M. Taramasso, G. Perego and B. Notari [1-3]

Batch Composition TiO₂: 70 SiO₂:1980 H₂O : 30 TPA-OH (TPA tetra-n-propylammonium)

Source Materials

distilled water

tetraethylorthosilicate [Si(OC₂H₅)₄] (Merck 800658)

tetraethylorthotitanate [Ti(OC₂H₅)₄] (Merck 821083)

tetrapropylammonium hydroxide (Alfa 17456, 40% solution in water)

Batch Preparation (for 43 g product)

- (1) [163.3 g tetraethylorthosilicate + 2.56 g tetraethylorthotitanate], mix at 35°C
- (2) [(1) + 170 g tetrapropylammonium hydroxide (40% solution)], add slowly at 0°C to prevent hydrolysis
- (3) Heat at 80°C to evaporate ethanol
- (4) Add water to restore initial volume; final pH 12.2

Crystallization

Vessel: 500 mL stirred autoclave

Temperature: 175°C

Time: 2 days

Agitation: 120 rpm

Product Recovery

- (1) Centrifuge to recover solids and wash with water (three times)
- (2) Dry at 120°C
- (3) Heat in air to 550°C (heating rate 5°C/min.) and hold at 550°C for 3 hours
- (4) Yield 90% on SiO₂

Product Characterization

XRD: orthorhombic MFI (only crystalline phase)

Elemental Analysis: 1.37 mol% Ti (72 SiO₂/TiO₂ by AAS) ^a

Crystal Size and Habit: 0.3 μm cubes (SEM)

References

- [1] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501 (1983)
- [2] A. J. H. P. van der Pol, J. H. C. van Hooff, Appl. Catal. 92 (1992) 93
- [3] J. A. Martens, P. Buskens, P. A. Jacobs, A. van der Pol, J. van Hooff, P. J. Kooyman, H. van Bekkum, Appl. Catal. 99 (1993) 71

[4] A. Tuel, Y. Ben Taarit, Zeolites 14 (1994) 272

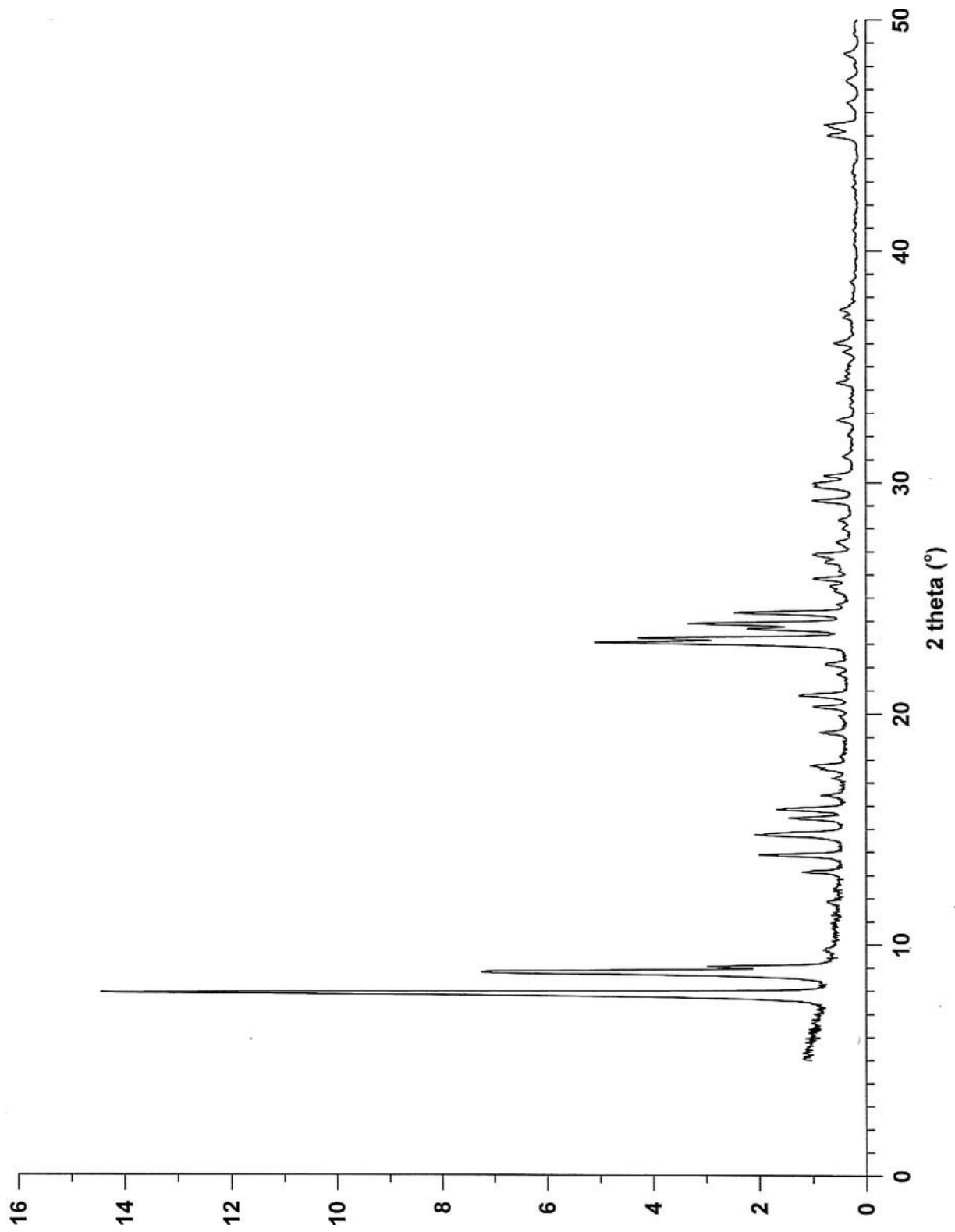
Note

a. No extra-framework TiO_2 can be observed by IR or UV-VIS. No IR bands around 700 cm^{-1} and no UV-VIS bands above 250 nm were observed [4].

MFI

[Ti] ZSM-5

Si(98.6), Ti(1.4)



MFI

[Ti,Al] ZSM-5

Si(97.5), Ti(1.3),Al(1.2)

Contributed by D. P. Serrano, G. Ovejero, R Van Grieken and J. A. Melero

Verified by M. Anderson, J. Rocha and A. Ferreira

Type Material $H_{1.2}[Al_{1.17}Ti_{1.23}Si_{93.6}O_{192}] : w H_2O$

Method G. Ovejero, R. Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero [1]

Batch Composition 1 TiO_2 : 0.25 Al_2O_3 : 40 SiO_2 : 216 H_2O : 7.44 (TPA)OH (TPA tetra-n-propylammonium) ^a

Source Materials

tetraethylorthosilicate [Alfa, $Si(OC_2H_5)_4$]

hydrochloric acid (0.2 N) (reagent grade)

isopropyl alcohol for analysis (Panreac)

aluminum isopropoxide, [Aldrich, $Al(OC_3H_7)_3$]

tetrapropylammonium hydroxide (TPAOH) [Alfa, 40 wt% $(C_3H_7)_4NOH$ in water]

titanium tetrabutoxide [Alfa, $Ti(OC_4H_9)_4$]

Batch preparation (for 2.9 g dried cogel)

A. Acid hydrolysis-condensation

- (1) [8 g tetraethylorthosilicate + 5 g hydrochloric acid (0.2 N)], mix at room temperature for 45 minutes
- (2) [2.5 g isopropyl alcohol + 0.098 g aluminum isopropoxide], mix until dissolved
- (3) [(1) + (2)], add (2) to (1) dropwise. Mix at room temperature for 45 minutes.
- (4) [4 g TPAOH (40 wt%) + 4 g H_2O], mix
- (5) [(3) + 0.75 g (4)], add 20 wt% TPAOH slowly at room temperature. Stir at 0°C for 15 minutes
- (6) [0.327 g titanium tetrabutoxide + 2 g isopropyl alcohol], mix until homogeneous
- (7) [(5) + (6)], add (6) to (5) slowly at 0°C. Stir at 0°C for an additional 20 minutes

B. Basic Gelation:

- (8) [(7) + approximately 1.9 g (4)], add 20 wt% TPAOH slowly at room temperature; mix until gelation
- (9) Dry overnight at 110°C to remove alcohol and water. Grind to give a powdered material
- (10) [(9) + approximately 4.6 g (4)], impregnate the dried and powdered cogel to incipient wetness with 20 wt% TPAOH. Charge to autoclaves

Crystallization

Vessel: Teflon-lined autoclaves (50 mL)

Time: 24 hours

Temperature: 170°C

Agitation: none

Product Recovery

- (1) Centrifuge to recover crystalline product; wash with double-distilled water (three times)
- (2) Dry overnight at 110°C
- (3) Calcme in air at 550°C (heating rate 5°C/minutes and hold at 550°C for 5 hours)
- (4) Yield; 95% on SiO₂

Product Characterization

XRD: MFI structure, orthorhombic

Elemental Analysis: SiO₂/TiO₂ = 76, SiO₂/Al₂O₃ = 160 (by XRF) ^{b,c}

Crystal Size and Habit: 0.4-0.5 μm, cuboid shape

References

- [1] G. Ovejero, R Van Grieken, M. A. Uguina, D. P. Serrano, J. A. Melero, *Catal. Lett.* 41(1996) 69
- [2] G. Bellussi, A. Carati, M. G. Clerici, A. Esposito, *Stud. Surf. 56. Catal.* 63 (1991) 421
- [3] L Forni, M. Pellozi, A. Giusti, G. Fornasari, R Milhini, *J. Catal.* 122 (1990) 44
- [4] A. Thangaraj, R. Kumar, S. Sivasanker, *Zeolites* 12 (1992) 135
- [5] D. Trong On, S. Kaliaguine, L Bonneviot, *J. Catal.* 157 (1995) 235
- [6] F. Geobaldo, S. Bordiga, A Zecchina, E Gianello, G. Leofanti, G. Petrini, *Catal. Lett.* 16 (1992)109

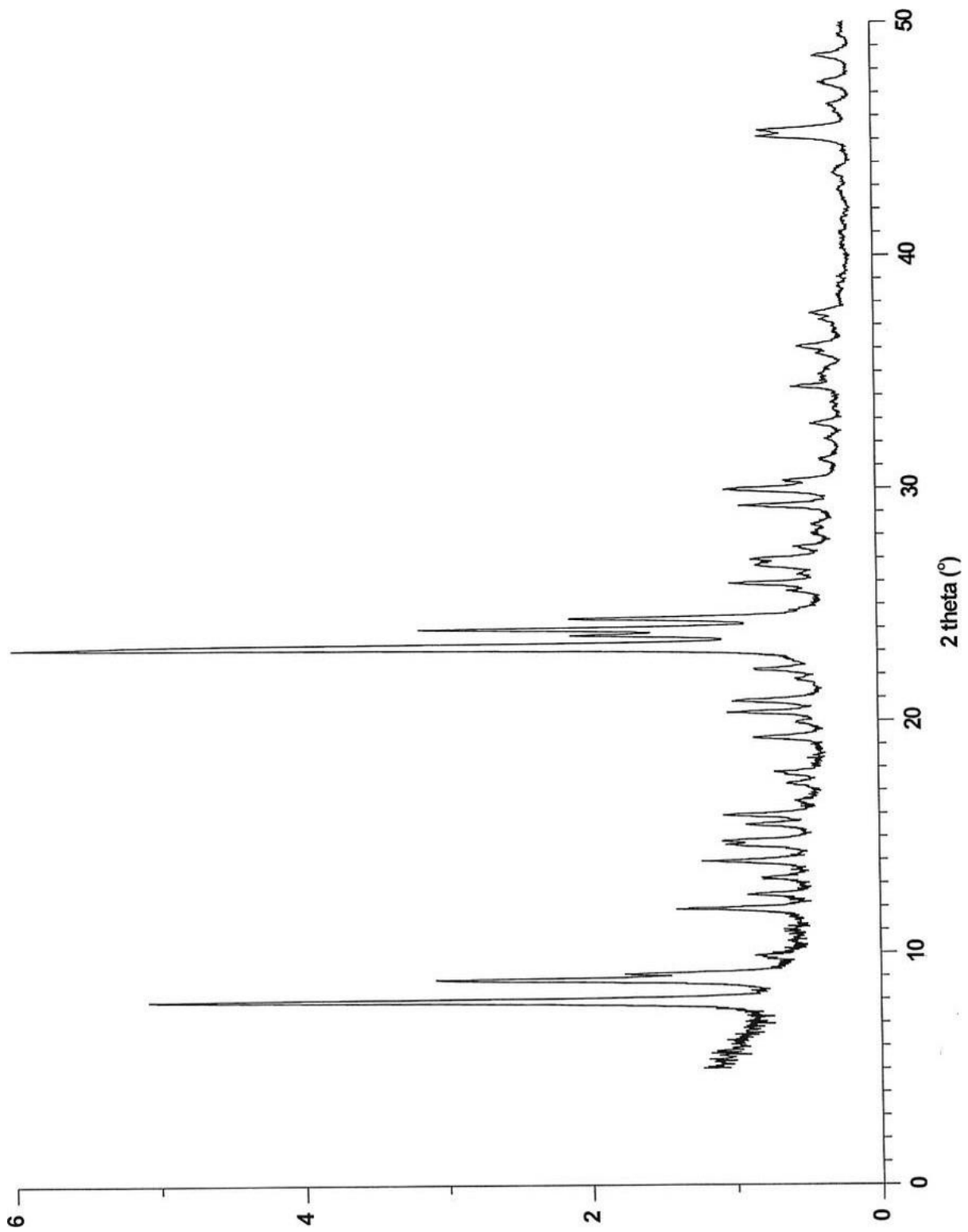
Notes

- a. Ti and trivalent metal ions, Al⁺³, Ga⁺³, Fe⁺³ and B⁺³, can be co-incorporated into ZSM-5 by conventional methods based on hydrothermal crystallization of a liquid gel obtained from respective alkoxides hydrolyzed in basic medium. [2-5]
- b. By DR UV-VIS, adsorption around 330 nm is not detected either in the sample or in the cogel, showing the absence of bulk TiO₂ phases. [6]
- c. By ²⁹Si and ²⁷Al MAS-NMR, atoms are located in tetrahedral environments in the starting cogel and in the synthesized sample.

MFI

[Ti,Al] ZSM-5

Si(97.5), Ti(1.3),Al(1.2)



MFS

ZSM-57

Si(98), Al (2)

Contributed by Tracy M. Davis and Christopher M. Lew

Verified by J. Cejka, F. Rey, A. Khartchenko

Type Material: $H_{1.5}(AlO_2)_{1.5}(SiO_2)_{34.5}$ ^[1]
(SDA = N,N,N,N',N',N'-hexaethyl-(1,5-pentanediammonium) dibromide)

Method: Similar to references [2-5]

Batch Composition: 1 SiO₂ : 0.017 Al₂O₃ : 40 H₂O : 0.1 (SDA²⁺)O : 0.5 NaO

Source Materials deionized (DI)

water fumed silica

(Cabosil M-5)

aluminum hydroxide (Reheis F2000, 5.20 mmol Al₂O₃/g)

sodium hydroxide (Fisher, 1N)

N,N,N,N',N',N'-hexaethyl-(1,5-pentanediammonium) dibromide (made in-house; purity confirmed by NMR)

Batch Preparation (for 0.61 g dry product)

(1) Combine 2.37 g DI water, 0.43 g SDA, and 5.1 g sodium hydroxide to a 23 mL Teflon liner; mix.

(2) Add 0.619 g fumed silica and 0.032 g aluminum hydroxide; mix with a spatula to homogenize.

(3) Cover and stir for 12 hours at room temperature.^a

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 160° C

Time: 7 days

Agitation: 43 rpm (tumbling oven)

Product Recovery

(1) Remove reactor from oven and quench

(2) Filter (with glass-frit funnel) to recover solids

(3) Wash product with ~300 mL DI water

(4) Air dry overnight while pulling vacuum on frit

(5) Dry at ambient temperature or at 80°C

(6) Yield: 0.47 g

Product Characterization

XRD: MFS

Elemental analysis: 42.7 SiO₂ : 1 Al₂O₃^b

Crystal size and habit: disks of aggregated nano-sized crystallites

Micropore volume of the proton-form is 0.15 cc/g by nitrogen adsorption

Reference

- [1] J.L. Schlenker, J. B. Higgins, E.W. Valyocsik, *Zeolites* 10 (1990) 293
- [2] S. Ernst, J. Weitkamp, in: G. Ohlmann (Ed.), *Catalysis and Adsorption by Zeolites*, Elsevier Science Publishers B.V., Amsterdam, 1991, p. 645
- [3] S.-H. Lee, D.-K. Lee, C.-H. Shin, W.C. Paik, W.M. Lee, S.B. Hong, *J. Catal.* 196 (2000) 158
- [4] S.-H. Lee, C.-H. Shin, G.J. Choi, T.-J. Park, I.-S. Nam, B. Han, S.B. Hong, *Microporous Mesoporous Mater.* 60 (2003) 237
- [5] E.W. Valyocsik, N.M. Page, C. T.-W. Chu, US Patent 4 873 067, to Mobil Oil Corporation

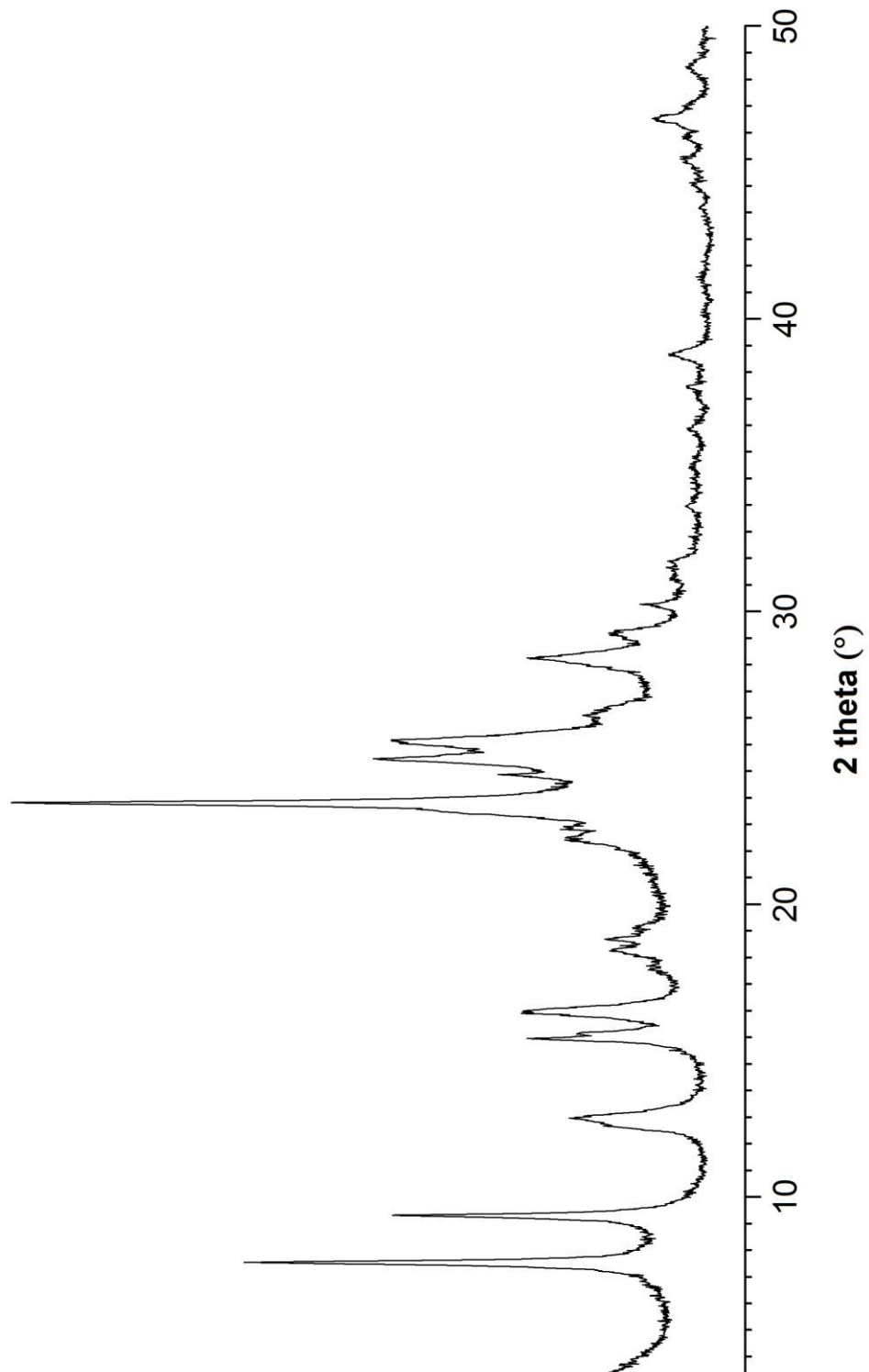
Notes

- a. pH of the final gel after crystallization is 12.35
- b. as-synthesized; organic content not specified

MFS

ZSM-57

Si(98), Al (2)



MOR

Mordenite

Si(90), Al(10)

Contributed by Wha Seung Ahn

Verified by G. Price, K. Satya Narayana Reddy, and Yan Sun

Type Material $\text{Na}_5[\text{Al}_5\text{Si}_{43}\text{O}_{96}] : w \text{ H}_2\text{O}$

Method G. J. Kim, W. S. Ahn [1]

Batch Composition 6 Na_2O : Al_2O_3 : 30 SiO_2 : 780 H_2O

Source Materials

distilled water

sodium hydroxide (Junsei Co., 95% NaOH)

sodium aluminate (Junsei Co., 32.6% Na_2O , 35.7% Al_2O_3)

silica powder (Zeosil from Kofran Co., 91.8% SiO_2 , 8.2% H_2O)^a

Batch Preparation (for 56 g dry product)

- (1) [40 g water + 19 g sodium hydroxide], stir until dissolved
- (2) [(1) + 14.3 g sodium aluminate], stir until dissolved
- (3) [(2) + 645 g water], mix
- (4) [(3) + 98.2 g silica], stir for 30 minutes

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Incubation: none^b

Temperature: 170 °C

Time: 24 hours^c

Product Recovery

- (1) Filter and wash to pH < 10
- (2) Dry at 100 °C
- (3) Yield: near 100% on Al_2O_3

Product Characterization

XRD: 100% mordenite, characteristic peaks at $d = 3.45, 3.97, 9.02, 3.27$ and 3.21

Å competing phases: quartz, analcime, gismondine

Elemental Analysis: $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 17.2 \text{ SiO}_2$

Crystal Size and Habit: irregular spherical to prismatic, $\sim 5 \mu\text{m}$ ^d

Reference

- [1] G. J. Kim, W. S. Ahn, Zeolites 11(1991) 745

Notes

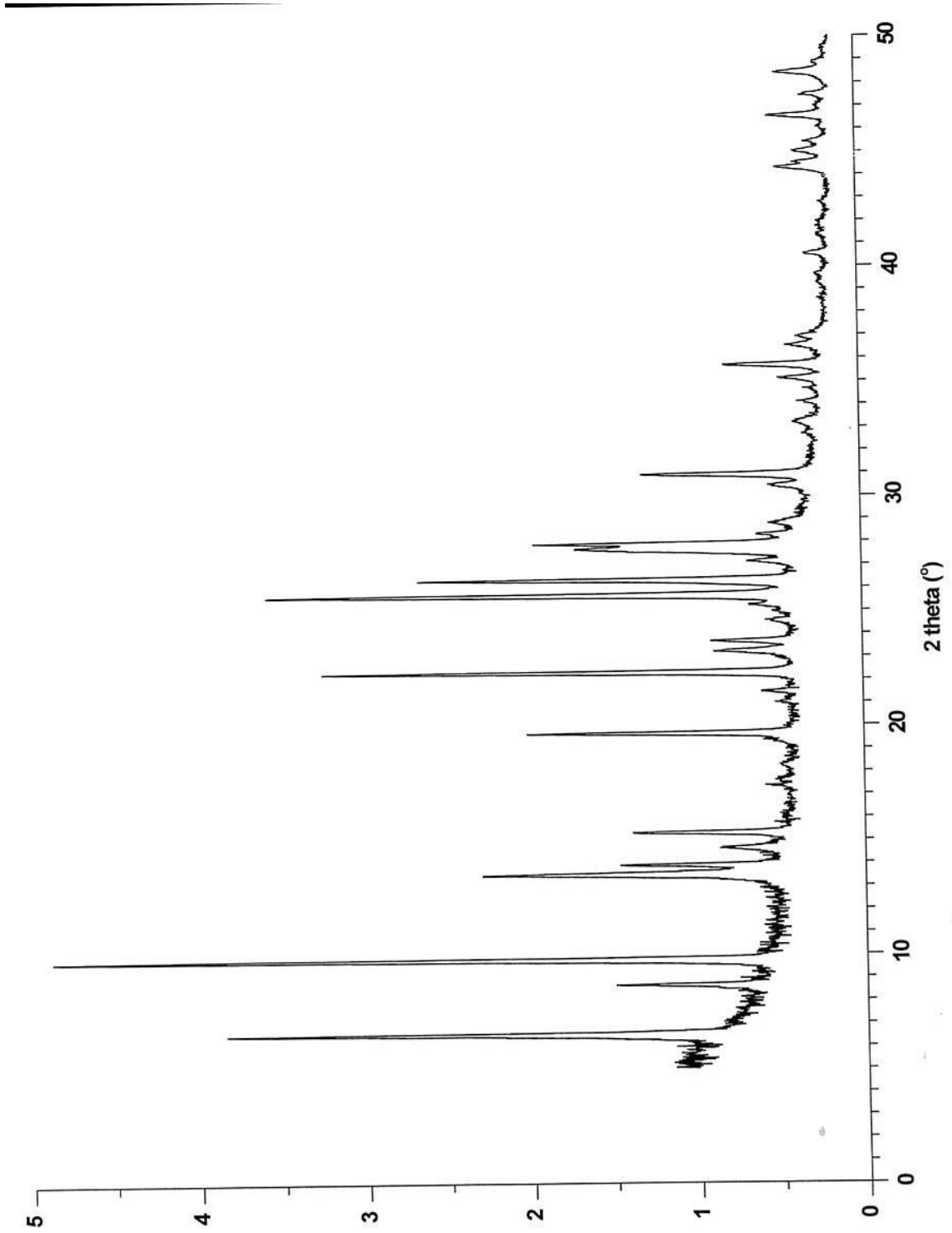
- a. Sodium silicate can also be used as a silica source, but crystallization rates are lower.

- b. Incubation is not required when using silica powder as SiO₂ source; aging at room temperature resulted in larger crystals but lower crystallization rates.
- c. Seeding with 5 wt% mordenite in the reaction batch substantially improved the crystallization rate.
- d. Typically needle-shaped crystals, but siliceous crystals can be plate or flat prismatic shape.

MOR

Mordenite

Si(90), Al(10)



MOZ

ZSM-10

Si (88), Al (12)

Contributed by Tracy M. Davis and Christopher M. Lew

Verified by N. Benavent, J. Cejka, A. Khartchenko

Type Material: $K_{24}Al_{24}Si_{84}O_{216} \cdot xH_2O \cdot yR^{[1]}$
(SDA = 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane dihydroxide)

Method: J.B. Higgins and K.D. Schmitt [1]

Batch Composition: 1 SiO₂ : 0.068 Al₂O₃ : 29.5 H₂O : 0.06 (SDA²⁺)O : 0.365 K₂O

Source Materials

deionized water (MilliQ quality from Millipore)
fumed silica (Aldrich)
aluminum hydroxide (Reheis F2000, 5.20 mmol Al₂O₃/g or from Aldrich, 57% Al₂O₃)
potassium hydroxide (Aldrich, 90 wt.% diluted with water to 20 wt%)
1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane dihydroxide (made in-house; 10 wt% or 1.135 N; purity confirmed by NMR and CHN)

Batch Preparation (for 1.351 g dry product)

- (1) Combine 10.535 g MilliQ water, 8.176 g potassium hydroxide (20 wt.%), and 0.487 g aluminum hydroxide in a 50 ml polypropylene closed vial. The mixture was stirred using a magnetic bar for 15 min.
- (2) Add 2.402 g fumed silica; magnetically mixed to homogenize.
- (3) Add 4.227 g SDA solution; magnetically mixed to homogenize.
- (4) Cover and magnetically stir for 3 days at room temperature.^a

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 100° C
Time: 15 days
Agitation: 60 rpm (tumbling oven)

Product Recovery

- (1) Remove reactor from oven and quench
- (2) Filter (with glass-frit funnel) to recover solids
- (3) Wash product with ~300 mL DI water
- (4) Dry in an oven at 100°C
- (5) Yield: 1.351 g

Product Characterization

XRD: MOZ
Elemental analysis: 7.5 SiO₂ : 1 Al₂O₃ °
Crystal size and habit: Aggregates of poorly faceted nano-sized crystallites
Micropore volume of calcined potassium-form is 0.12 cc/g by nitrogen adsorption

Reference

[1] J.B. Higgins, K.D. Schmitt, *Zeolites* 16 (1996) 236-244.

Notes

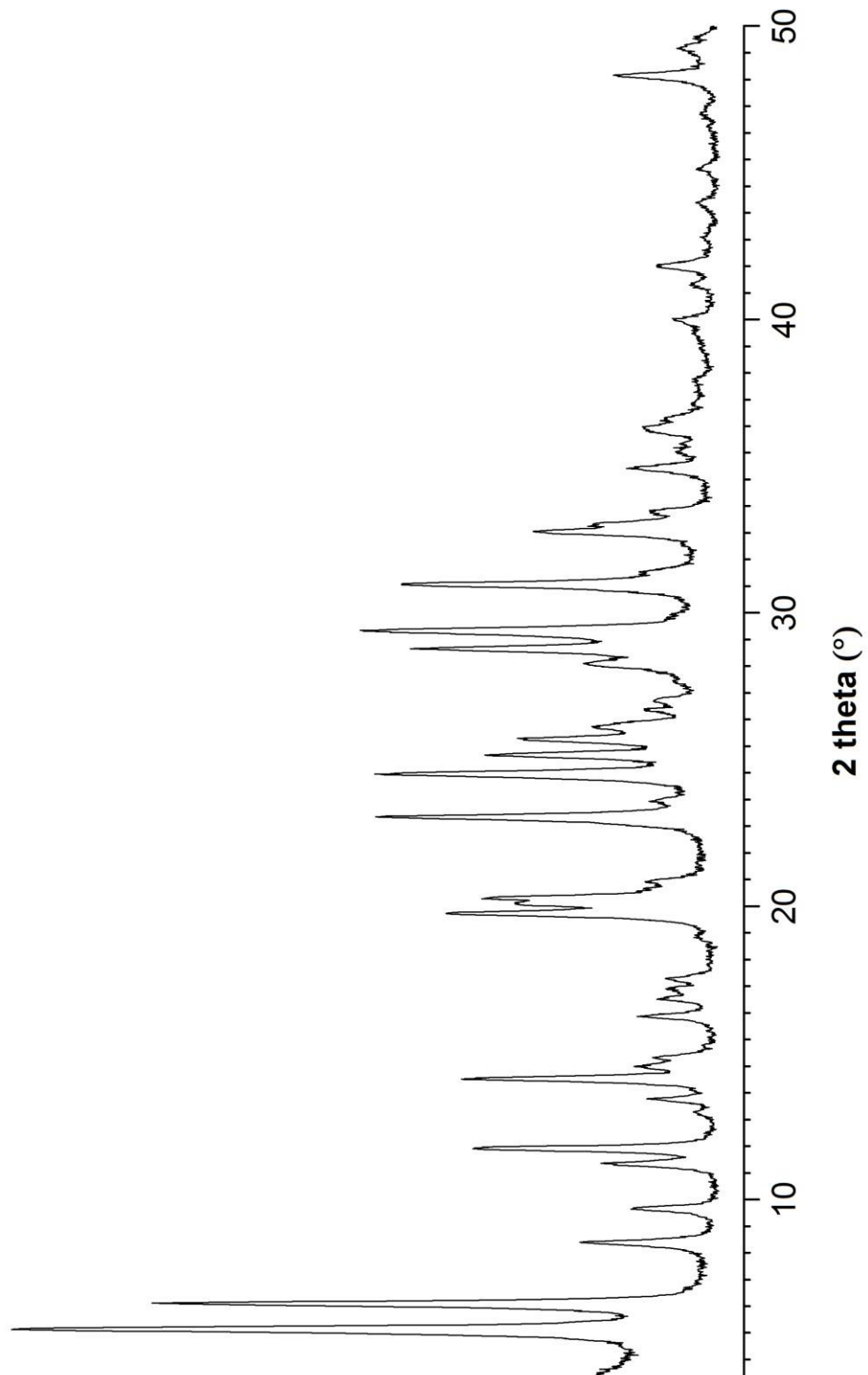
a. pH of the initial gel is 13.1 and the pH of the final gel after crystallization is 12.7.

b. as-synthesized; organic content not specified.

MOZ

ZSM-10

Si (88), Al (12)



Contributed by Yoshihiro Kubota

Verified by J.-L. Paillaud, C. Xia, F. Gao and X. Zou

Type Material: Si_{101.6}Al_{11.4}O₂₂₄

(SDA = TEBOP²⁺(I⁻)₂ = *N,N'*-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidine diiodide)

Method: D. L. Dorset, S. C. Weston, S. S. Dhingra [1]

Batch Composition: 1.0 SiO₂ : 0.1 Al(OH)₃^a : 0.375 KOH : 0.1 TEBOP²⁺(I⁻)₂ : 30 H₂O

Source Materials

colloidal silica (Ludox HS 40)

aluminum hydroxide (50 wt.%)

deionized water (DI)

8 mol/L potassium hydroxide aqueous solution (titrated as 5.93 mmol/g)

TEBOP₂⁺(I⁻)₂ synthesized from bicyclo[2.2.2]oct-7-ene-2,3:5,6- tetracarboxylic anhydride (Aldrich)

Batch Preparation (for ca. 6 g as-synthesized dry product)

- (1) [15.0 g Ludox HS-40 + 40.0 g DI water + 0.78 g aluminum hydroxide], stir for 10 min in a Teflon beaker
- (2) [(1) + 6.32 g potassium hydroxide aqueous solution 5.93 mmol/g]; stir for 30 min
- (3) [(2) + 5.58 g TEBOP₂⁺(I⁻)₂]; stir for 4 h at room temperature

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 160 °C

Time: 16 days

Agitation: 0 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 80 °C
- (4) Yield: 6.0 g
- (5) Calcination conditions to remove SDA: 600°C for 10 h in air

Product Characterization

XRD: MSE

Crystal size: smaller than 100 nm

Reference

- [1] D. L. Dorset, S. C. Weston, S. S. Dhingra, J. Phys. Chem. B 110 (2006) 2045
- [2] S. Inagaki, Y. Tsuboi, Y. Nishita, T. Syahylah, T. Wakihara, Y. Kubota, Chem. Eur. J. 19 (2013) 7780

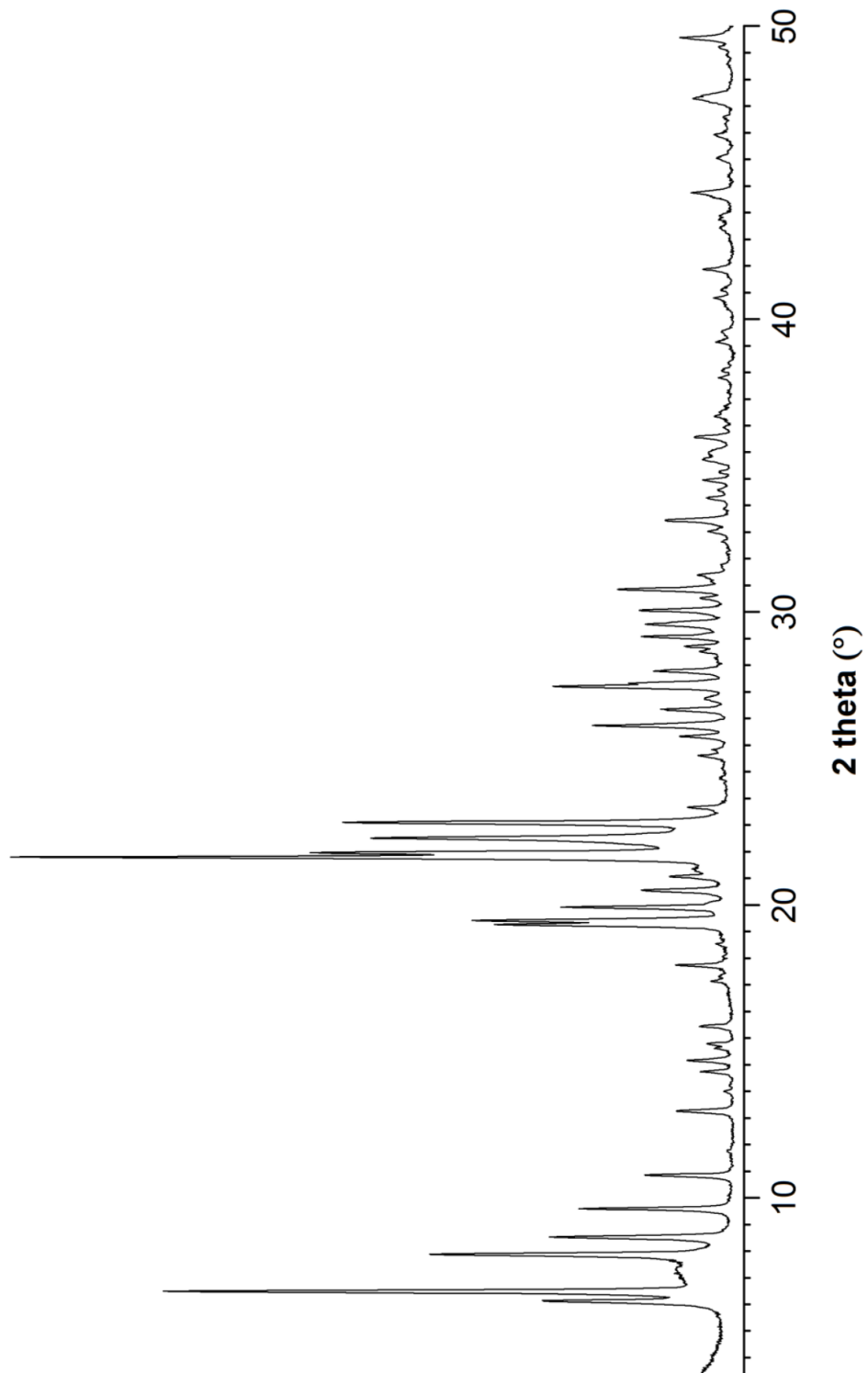
Notes

- a. Al(OH)₃ source is important. The brand should be Pfalz and Bauer or Aldrich.

MSE

MCM-68

Si (101.6), Al (11.4)



Contributed by Valentin Valtchev

Verified by S. Ernst and A. Iwasaki

Type Material (SiO₂)₁₃₆ q R. q » 10, (R = TMA⁺ and TrMA) ^a

Method I. Vergilov, V. Valtchev [1]

Batch Composition 15 Na₂O:16 TrMA:16 (TMA)Cl : 55 SiO₂ : 3387 H₂O: 10 H₂SO₄ ^{b,c}

Source Materials

bidistilled water

sodium silicate (Riedel de Haen, 63% SiO₂, 18% Na₂O, 18% H₂O)

sulfuric acid (98% H₂SO₄)

trimethylammonium (TrMA) chloride (Merck, 98% TrMA·HCl)

tetramethylammonium (TMA) chloride (Merck, > 98% (TMA)Cl)

Batch Preparation (for 30 g dry product)

- (1) [300 g water + 52.5 g sodium silicate], heat and stir until dissolved ^d
- (2) [150 g water + 10.7 g sulfuric acid]
- (3) [(1) + (2)], mix thoroughly
- (4) [15.29 g trimethylammonium chloride + 17.54 g tetramethylammonium chloride + 150 g water], mix thoroughly
- (5) [(3) + (4)], mix thoroughly; pH 9.2 to 9.5

Crystallization

Vessel: stainless steel or Teflon jar

Time: 12 to 14 days

Temperature: 200°C

Agitation: none

Product Recovery

- (1) After crystallization, pH 10.5
- (2) Filter to recover solids, and wash with hot water
- (3) Dry at ambient temperature (drying at 90-110°C acceptable)
- (4) Yield: 88% based on silica

Characterization

XRD: MTN only crystalline phase, ^e a₀ = 19.39 Å, single crystal structure refinement [2];

competing phases: NU-1 (when gel contains aluminum), quartz (when pH of starting gel >11.5)

Elemental Analysis: 0.0018 Na₂O. SiO₂ ^f

Crystal Size and Habit octahedral morphology, 100 to 200 nm dia. [1]

References

- [1] I. Vergiov, V. Valtchev, *Zeolites* 11 (1991) 387
- [2] J. Macicek, V. Valtchev, G. Kirov, in *Collected Abstracts, 14th Congress and General Assembly Int. Union of Crystallography*, H. C. Freeman (ed.), Lamb Printers, Perth, Australia, 1987, C-134

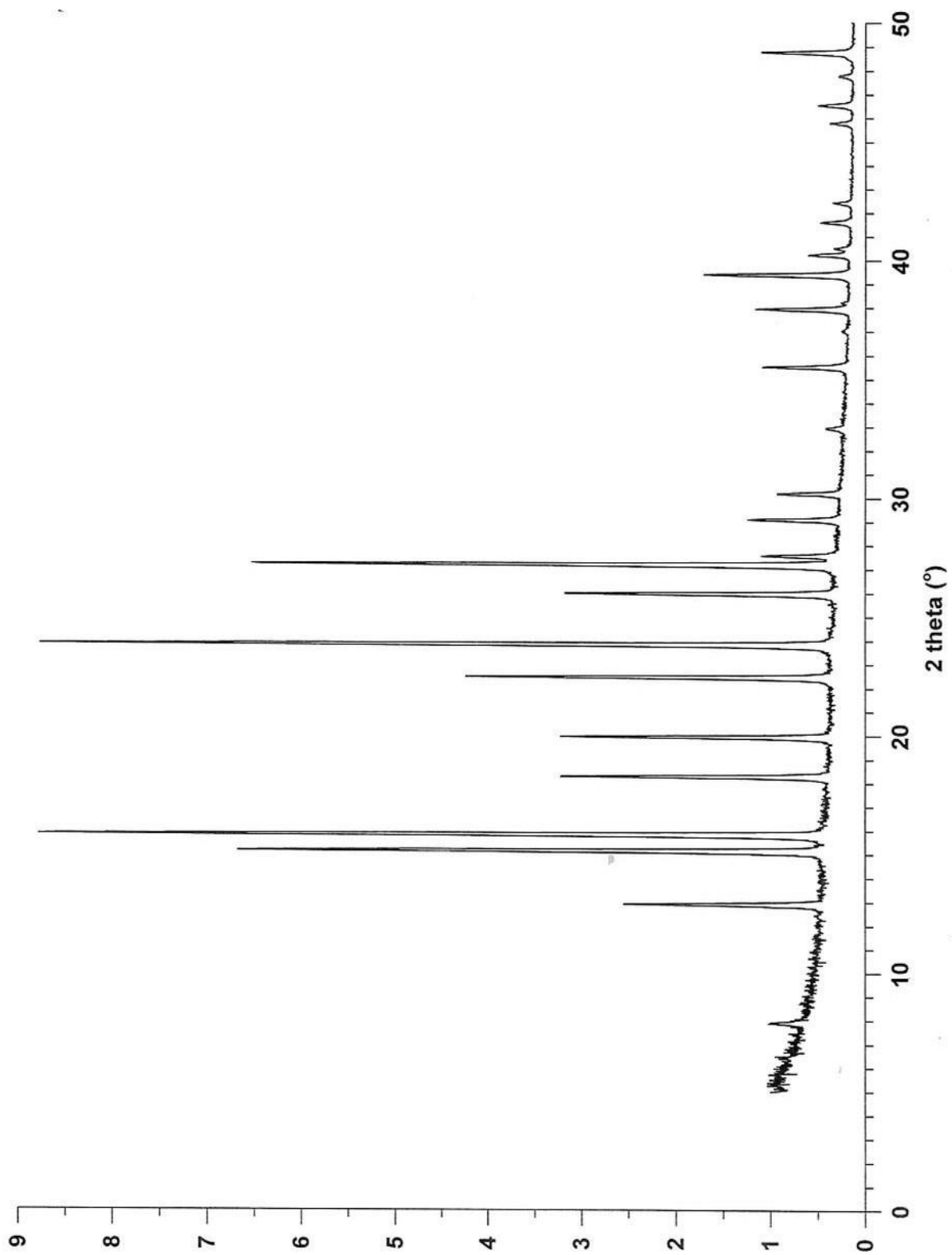
Notes

- a. Crystalline product is 7.4 wt% TMA⁺ and TrMA by thermal analysis.
- b. With TMA⁺ only, complex crystal twins are formed.
- c. H₂O includes water from sodium silicate, sulfuric acid and added water.
- d. Sodium silicate solution must be heated and stirred until converted to a clear solution.
- e. XRD patterns of as-synthesized product and product after 600°C calcination do not differ significantly.
- f. Analysis of ZSM-39 calcined for 1 hour at 950°C in air gave 94.7% SiO₂, 0.17% Na₂O, and a remainder, probably consisting of carbonaceous material and water.

MTN

ZSM-39

Si(100)



Contributed by Mohamed H.M. Ahmed, Oki Muraza

Verified by G. Rioland, T.J. Daou, J. Patarin, H. Awala

Method S.I Zones [1-5]

Batch Composition 0.02 K₂O : 0.0045 Al₂O₃ : 0.16 SiO₂ : 0.04 SDA : 6.07 H₂O
(SDA = isobutylamine)

Source Materials

deionized water
potassium hydroxide (98+% Aldrich)
aluminium hydroxide (r.g., Al(OH)₃ 77 %, Alfa Aesar)
colloidal silica solution (Ludox HS 40, Aldrich)
isobutylamine (99 %, Aldrich)

Batch Preparation

- (1) [1.87 g KOH + 33.3 ml of deionized water] stir until all the pellets are dissolved.^a
Amount of all reactants divided by 4:
- (2) [(1) + 45.94 ml of deionized water + 0.715 g Al(OH)₃] stir at 500 rpm until the mixture becomes homogenous.^a
- (3) [(2) + 20.425 g of colloidal silica] added dropwise after 10 min of stirring.^a
- (4) [(3) + 3.38 ml of isobutylamine] dropwise; leave the gel stirring for 6 h at rate of 500 rpm. The gel is not dense.

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 170 °C
Time: 6 days
Vertical rotation: 35 rpm

Product Recovery

- (1) Dilute crystalline gel with water.
- (2) Filter and wash with water.
- (3) Dry at 105 °C for 12 h.
- (4) Yield: 8 g.
- (5) Calcination: heating to 500 °C for 3h, then static heating 3h at 500 °C

Product Characterization

XRD : MTT; pure SSZ-32 phase. Competing phase: MFI
SEM : Crystal size and habit: rod-like shape crystals with less than 100 nm size.

References

- [1] S.I. Zones, Zeolite SSZ-32 Google Patents (1991)
- [2] S.I. Zones, Zeolite SSZ-32 Google Patents (1993)

- [3] D.L. Holtermann, R.A. Innes, D.S. Santilli, J.N. Ziemer, S.I. Zones, Hydrocarbon conversion process using zeolite SSZ-32 as catalyst Google Patents (1994)
- [4] Y. Nakagawa, S.I. Zones, Preparation of zeolites using organic template and amine, Google Patents (1998)
- [5] S.I. Zones, B. Lee, L.-T. Yuen, T.M. Davis, J.N. Ziemer, A. Ojo, Method for preparing small crystal SSZ-32 Google Patentes (2013)

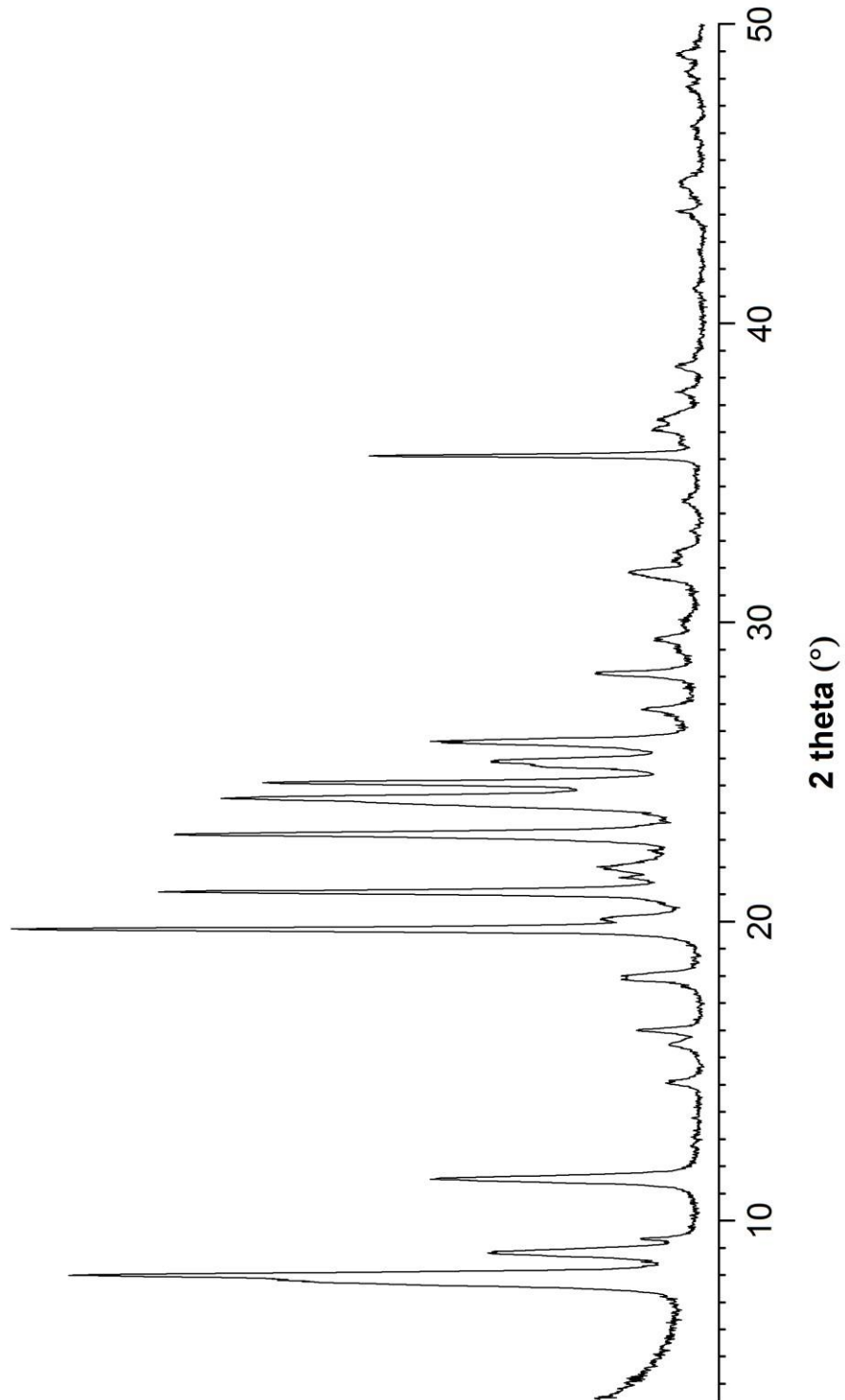
Notes

- a. Clear solution is obtained.
- b. SDA used for synthesizing SSZ-32 is isobutylamine which gives small crystals size.
- c. The source of Si is colloidal silica instead of fumed silica that was used in previous works.
- d. The above procedure is the first time tested in a rotational oven.
- e. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ in this procedure is 30, within the range which favors the producing SSZ-32 over ZSM-23.

MTT

SSZ-32

Si(x), Al(x)



MTT

ZSM-23

Si(97), Al(3)

Contributed by Stefan Ernst

Verified by R Ravishankar and Wha-Seung Ahn

Type Material Na[AlSi₂₃O₄₈] · wH₂O (w » 4)

Method S. Ernst, R Kumar, J. Weitkamp [1]

Batch Composition 20.6Na₂O : Al₂O₃: 100SiO₂ : 4610H₂O: 46.2Pyrr: 18.8 H₂SO₄

Source Materials

demineralized water

sodium hydroxide, reagent grade (Riedel-de Haen)

pyrogenic silica (Cab-o-Sil M5)^a

pyrrolidine (Pyrr), (Fluka)

aluminum sulfate (Al₂(SO₄)₃ · 18H₂O, Fluka)

sulfuric acid (96 wt% H₂SO₄, Fluka)

Batch Preparation (for 14 g product)^b

(1) [195.8 g water + 4.40 g sodium hydroxide], mix until dissolved

(2) [(1) + 16.5 g silica], add silica to solution (1) over the course of ~5 minutes under continuous stirring

(3) [24.4 g water + 8.81 g pyrrolidine + 1.79 g aluminum sulfate], mix until dissolved

(4) [(2) + (3)], add solution (3) to solution (2) with good mixing

(5) [(4) + 4.33 g sulfuric acid], add acid dropwise with stirring; final gel pH = 12.6

Crystallization

Vessel: stainless steel autoclave (300 mL)^c Temperature: 180°C Time: 50 hours Agitation: autoclaves are rotated ~30/minutes

Product Recovery

(1) Cool and filter

(2) Wash extensively with demineralized water

(3) Dry at 100¼C for 16 hours

(4) Yield: approx. 14 g

Product Characterization

XRD: MTT (only crystalline phase), competing phases: MFI (contaminated autoclave) cristobalite (occasional overheating, or pH too high)

Elemental Analysis: SiO₂/Al₂O₃ = 78 (AFS/ICP)^d

Crystal Size and Habit: bundles of needles^e

Reference

[1] S. Ernst, R Kumar, J. Weitkamp, in Zeolite Synthesis, Am. Chem. Soc. Symposium Series 398, M. Ocelli, H. Robson (eds.), 1989, pp 560-573

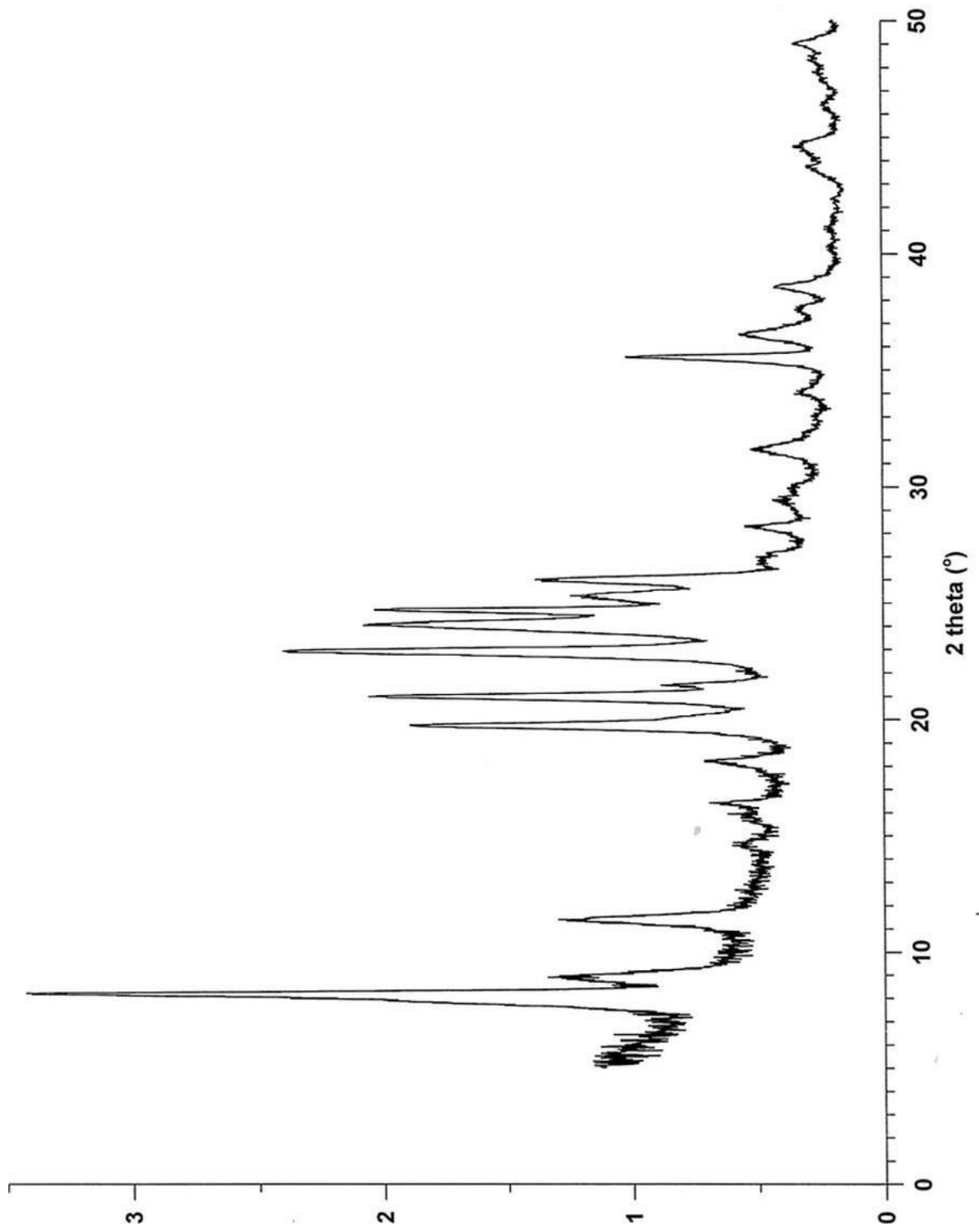
Notes

- a. Cab-O-Sil M5 must be used; other silica sources, such as silica sol or sodium silicate, lead to different products.
- b. The synthesis has been successfully scaled up to a 5 liter autoclave (stirring rate: 120/minutes, yield: 250 g).
- c. The crystallization vessels have to be cleaned very thoroughly in order to avoid seeding effects from residual crystallites of ZSM-5, for example.
- d. With pyrrolidine as template, the molar ratio can be varied between 70 and 150.
- e. Platelet-like ~1 um can be synthesized using C₇diquat [(CH₃)₃N-(CH₂)₇-N(CH₃)₃]Br₂ as template. [1]

MTT

ZSM-23

Si(97), Al(3)



MTW

ZSM-12

Si(97), Al(3)

Contributed by Girolamo Giordano

Verified by Nguyen Huu Phu, A. Souza de Araujo and G. Kuhl

Type Material $\text{Na}_{0.5}(\text{MTEA})_{1.3}[\text{Al}_{0.8}\text{Si}_{27.2}\text{O}_{56}] : 0.6 \text{ H}_2\text{O}$ (MTEA = methyltriethylammonium)

Method S. Ernst, P. A. Jacobs, J. A. Martens, J. Weitkamp [1], P. Chu, G. H. Kuhl [2]

Batch Composition 10 Na_2O : Al_2O_3 :100 SiO_2 :2000 H_2O : 20 MTEABr

Source Materials

distilled water
sodium hydroxide (Carlo Erba RPF, 99+% NaOH)
aluminum hydroxide hydrate $[\text{Al}(\text{OH})_3]$ (Aldrich)
methyltriethylammonium bromide [MTEA Br] (Fluka)
precipitated silica (BDH, 99+% SiO_2)

Batch Preparation (for ~2.5 g product)

- (1) [9 g distilled water + 0.4 g sodium hydroxide + 0.078 g aluminum hydroxide hydrate], stir until dissolved
- (2) [9 g distilled water + 1.96 g MTEA Br], stir until dissolved
- (3) [(1)+ (2)], stir until homogenized
- (4) [(3) + 3 g precipitated silica], stir for 1 hour at room temperature and seal in the reactor

Crystallization

Vessel: Teflon-lined autoclave, 20 mL
Time: 6 days
Temperature: 140°C
Agitation: none

Product Recovery

- (1) Cool to room temperature and filter to recover solids
- (2) Wash with distilled water until filtrate pH = 9
- (3) Dry at 105°C

Product Characterization

XRD: MTW only crystalline phase; competing phases: MFI (high alumina), cristobalite (high temperature or high pH)
Elemental Analyses: 0.66 Na_2O : Al_2O_3 : 66.7 SiO_2 : 1.5 H_2O : 1.58 $(\text{MTEA})_2\text{O}$
Crystal Size and Habit: rice-grain shaped, length 5 μm

References

- [1] S. Ernst, P. A. Jacobs, J. A. Martens, J. Weitkamp, Zeolites 7 (1987) 458
- [2] P. Chu, G. H. Kuhl, US Patent 4452 769 (1983)
- [3] A. Katovic, G. Giordano, Chem. Express 6 (1991) 969

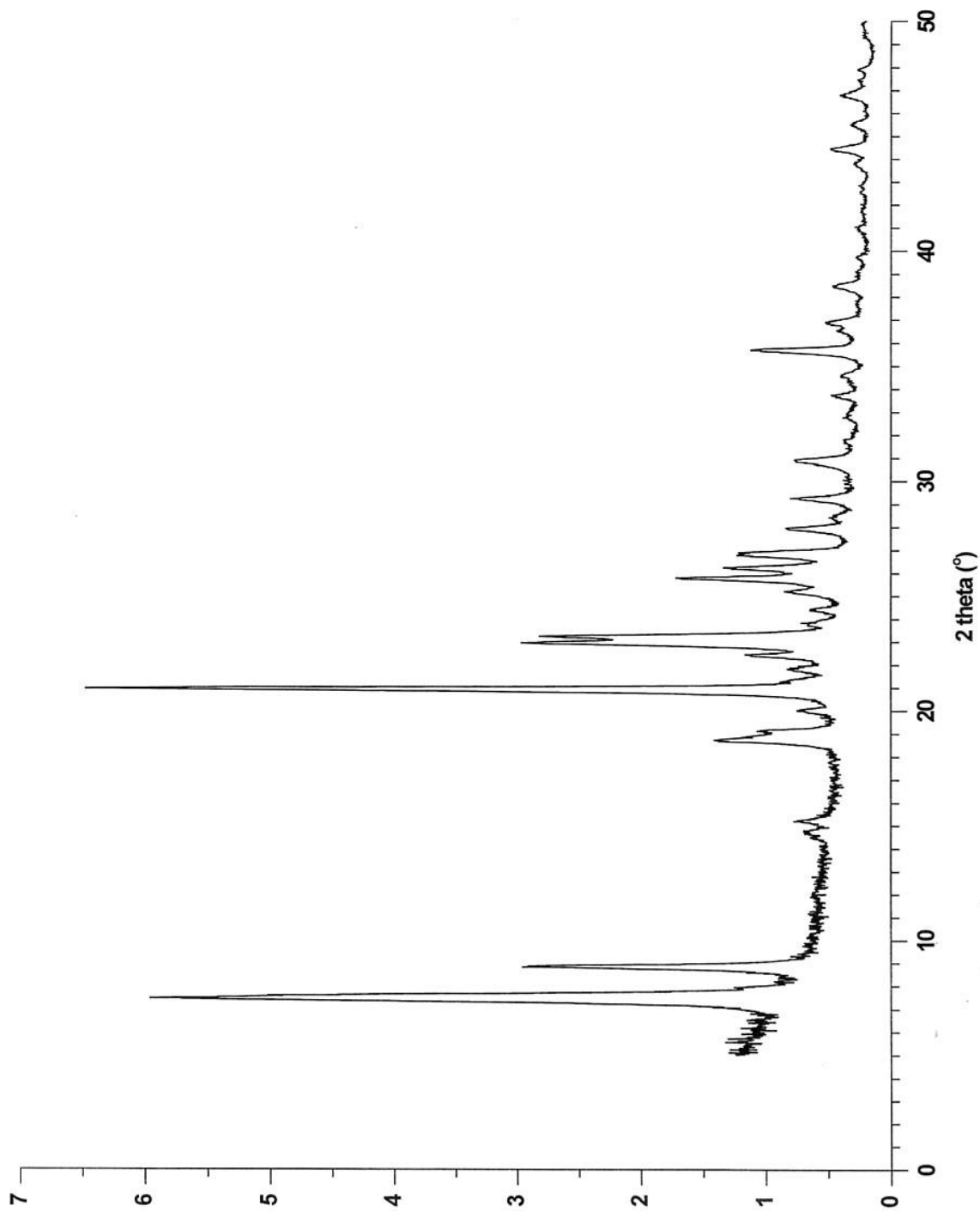
Note

- a. MTW zeolite can also be obtained when tetraethylammonium bromide (TEA Br) substitutes for MTEA Br in the hydrogel described in the Batch Composition section. In this case spheroidal crystals of about 0.6 μm diameter are obtained. [3]

MTW

ZSM-12

Si(97), Al(3)



MTW

[Ga] ZSM-12

Si(93), Ga(7)

Contributed by Susan Lambert

Verified by K. Reddy and M. Mertens

Type Material $\text{Na}_2[\text{Ga}_2\text{Si}_{26}\text{O}_{56}] : 4 \text{ H}_2\text{O}$

Method S. L Lambert [1]

Batch Composition 4.5 Na_2O : Ga_2O_3 : 52.4 SiO_2 : 13.7 TEMA Br : 867 H_2O (TEMA = triethylmethylammonium)

Source Materials

deionized water

sodium hydroxide (Mallinkrodt dry pellets, > 98.5% NaOH)

gallium oxide (Alfa, 99.99%)

triethylmethylammonium bromide (TEMA Br) (Fluka, purum)

silica sol (Dupont Ludox AS-40, 40% SiO_2)^a

Batch Preparation (for 13 g dry product)

- (1) [21.72 g NaOH + 37.04 g water + 11.37 g Ga_2O_3], heat in a closed pressure vessel (Teflon-lined Parr acid digestion bomb) at 110°C for 23 hours
- (2) [4.65 g of solution (1) + 29.22 g water + 10.78 g TEMA Br], stir until dissolved
- (3) [(2) + (31.47 g silica sol + 11.63 g H_2O)], add diluted silica sol to (2) with stirring using an eye dropper over course of 15 min. Batch pH 13-14^b

Crystallization

Vessel: two Teflon-lined Parr acid digestion bombs (125 mL)

Time: 20 days^c

Temperature: 150°C

Agitation: none

Product Recovery

- (1) Supernatant liquid pH 12.5
- (2) Filter and wash with 600 mL distilled water
- (3) Dry at 100°C
- (4) Yield: 13.64 g white solids (12.25 g volatile free), 91% recovery on SiO_2 or 87% on Ga_2O_3

Product Characterization

XRD: MTW framework by comparison to ZSM- 12 crystallinity reference, best is [Al] MTN.

Minor impurity: cristobalite; no other phases present

Elemental Analyses (volatile-free): 93.4% SiO_2 , 5.35% Ga_2O_3 , 0.62% Na_2O , 0.14% Al_2O_3 .

Loss on ignition at 900°C: 10.17%^d

Molar Composition: 0.35 Na₂O : 0.05 Al₂O₃ : Ga₂O₃: 54.4 SiO₂ : 22 H₂O^e

Reference

- [1] S. L Lambert in Proceedings of the 9th international Zeolite Conference, R. von Ballmoos, J. B. Higgins, M. M. J. Treacy (eds.), Butterworth-Heinemann, London, 1993, P. 223

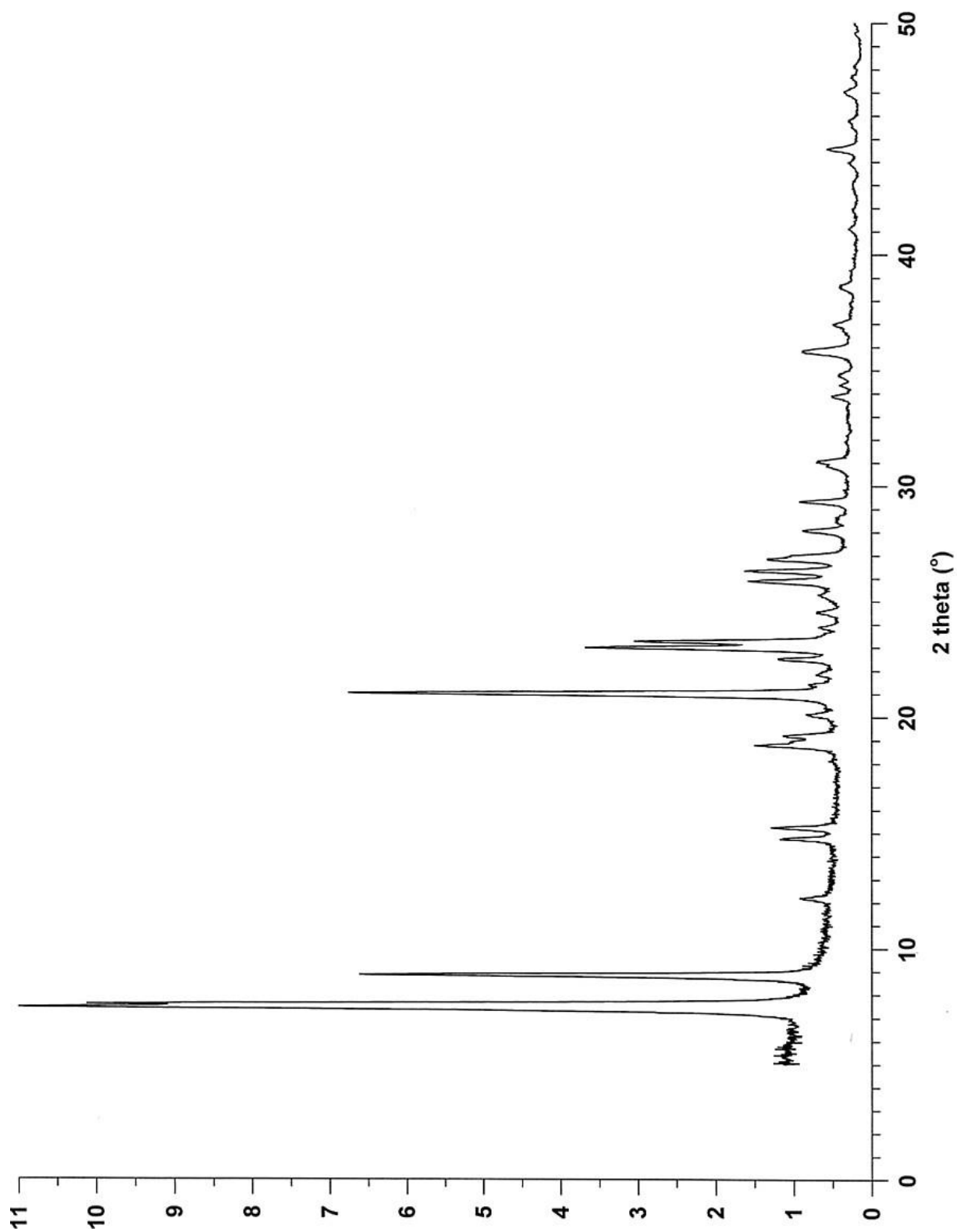
Notes

- a. Dupont's Ludox HS-40 is an acceptable substitute.
- b. pH values were measured with ColorpHast pH indicator paper (range 5-10 or 7.5-14, from E. M. Science, Gibbstown, NJ, USA)
- c. Crystallinity vs. (Al) ZSM-12 reference: 70% after 16 days, 88% after 18 days, 90% after 20 days. The crystallization proceeds more rapidly as the amount of gallium in the synthesis batch is reduced.
- d. Template burnout occurs at 460°C in air.
- e. By ²⁹Si MAS NMR, Si/(Ga + Al) = 14; excess SiO₂ by elemental analysis is attributed to amorphous silica. ⁷¹Ga static NMR one symmetrical Ga line at 158.5 ppm (ref. Ga(NO₃)₃).

MTW

[Ga] ZSM-12

Si(93), Ga(7)



Contributed by Avelino Corma

Verified by J. Weitkamp and N. Kumar

Type Material $\text{Na}_{0.08}[\text{Al}_4\text{Si}_{68}\text{O}_{144}] : (\text{C}_6\text{H}_{12}\text{NH})_{10.8}$ [1]^a

Method A. Corma, C. Corell, J. Pérez-Pariente [1]

Batch Composition 2.7 Na_2O : Al_2O_3 : 30 SiO_2 : 1347 H_2O : 15 HMI^b (HMI = hexamethyleneimine)

Source Materials

deionized water

sodium aluminate (Carlo Erba, 56% Al_2O_3 , 37% Na_2O)

sodium hydroxide (98% NaOH)

hexamethyleneimine $\text{C}_6\text{H}_{12}\text{NH}$ (Aldrich, 99% HMI)

silica (Degussa, Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 12.8 g dry product)^c

- (1) [124.20 g water + 0.92 g sodium aluminate + 0.60 g sodium hydroxide], stir until dissolved^d
- (2) [(1) + 7.61 g hexamethyleneimine], mix thoroughly^e
- (3) [(2) + 9.23 g silica], mix thoroughly^f

Crystallization

Vessel: PTFE-lined stainless steel autoclaves

Time: 7 days

Temperature: 150°C

Agitation: 60 rpm

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash with distilled water
- (3) Dry at 100°C overnight
- (4) Yield; 99% based on alumina

Product Characterization

XRD: MCM-22 [2]; competing phases: FER (when crystallized under static conditions), ZSM-5 (when gel $\text{SiO}_2/\text{Al}_2\text{O}_3 > 100$), ZSM-12 (when gel $\text{SiO}_2/\text{Al}_2\text{O}_3 > 200$)

Elemental Analysis: 0.02 Na_2O : Al_2O_3 : 34 SiO_2

Crystal Size and Habit: small thin platelets occasionally forming spherical aggregates of 6-8 μm ^g

References

- [1] A. Corma, C. Corell, J. Pérez-Pariente, Zeolites 15 (1995) 2
- [2] M. K. Rubin, P. Chu, US Patent 4 954 325 (1990)

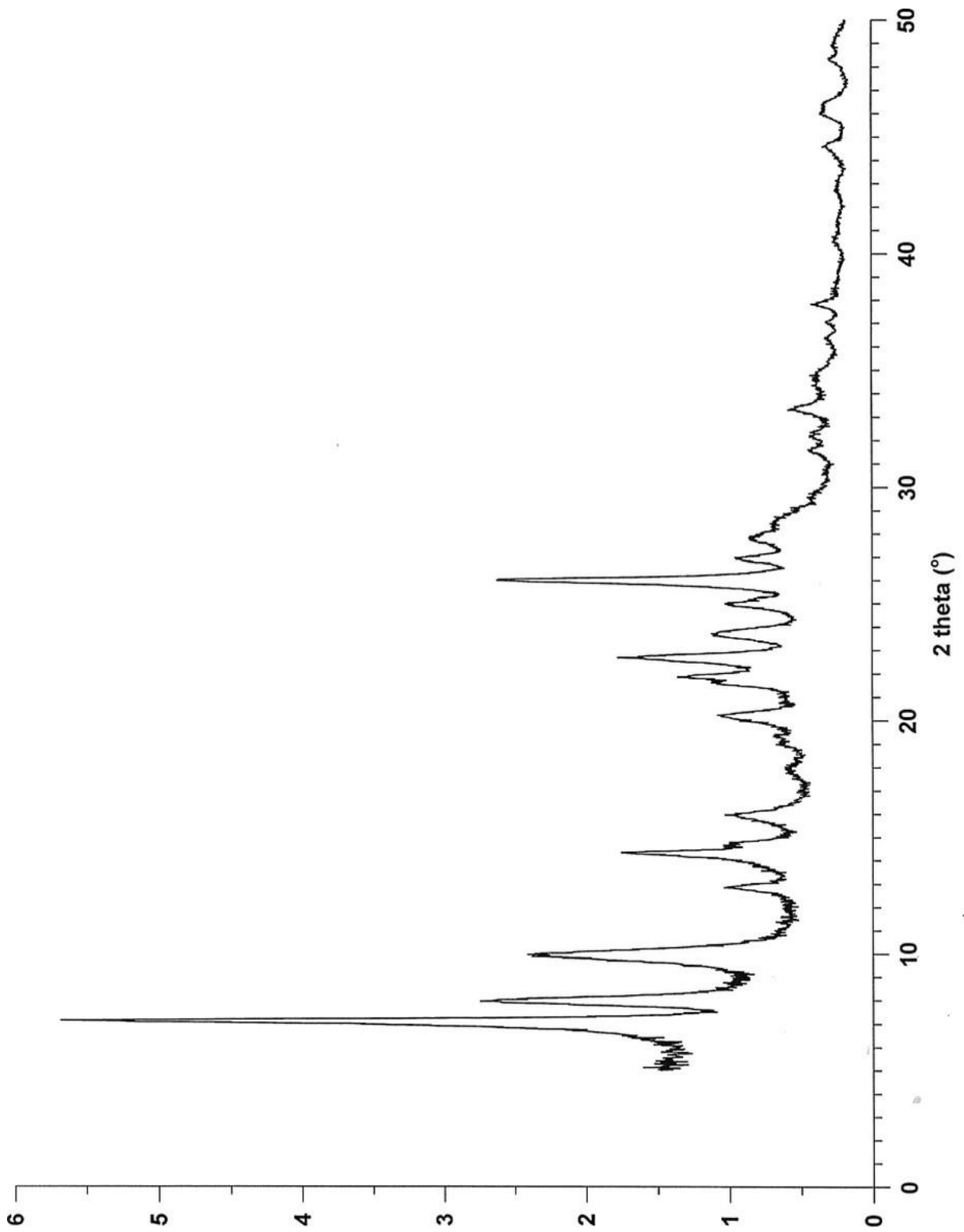
Notes

- a. Missing cations assumed to be protonated HMI.
- b. H₂O includes water from sodium aluminate and added water.
- c. Use polypropylene vessel and vigorous stirring for 30 minutes.
- d. Clear solution
- e. Slightly yellow clear solution
- f. White and fluid gel
- g. Toluene sorptive capacity at 0.1 KPa, 42°C : 10.07 mmol/g. The sample was heated in oxygen flow (30 cm³/min⁻¹) up to 500°C and outgassed overnight at 500°C in a vacuum better than 1 mPa.

MWW

MCM-22

Si(94), Al(6)



NAT

[Ga] Natrolite

Si(62), Ga(38)

Contributed by Mario Occelli

Verified by I. Buhl and by R Aiello

Type Material (NaK₈R₆)[Ga₁₅Si₂₅O₈₀] · wH₂O (R = benzyl trimethylammomum (BTMA))

Method M. L Occelli, E. Goldish, H. Eckert [1]

Batch Composition 5.30 Na₂O : 2.21 K₂O : 2.12 R₂O : Ga₂O₃ : 12.54 SiO₂ : 298 H₂O : 31.4 CH₃OH

Source Materials

deionized water

sodium hydroxide, reagent grade (~97% NaOH)

potassium hydroxide, reagent grade (85% KOH)

gallium oxide (99.99% Ga₂O₃)

sodium silicate (PQN-brand, 29,9% SiO₂, 10.0% Na₂O)

benzyl trimethyl ammonium hydroxide (Excel Co., 40% in methanol)

Batch Preparation

- (1) [50 g water + 9.92 g sodium hydroxide + 29.0 g potassium hydroxide] mix until dissolved
- (2) [(1) + 18.7 g gallium oxide], stir at the boiling point until the solution clears
- (3) [(2) +50 g water], mix and cool to ambient temperature
- (4) [(3) + 167.2 g BTMA. OH solution]
- (5) [251.3 g sodium silicate + 274.3 g water] mix for 4 hours
- (6) [(5) + (4)], add gallate mixture dropwise to the vigorously stirred, diluted sodium silicate; stir for 10 hours at ambient temperature

Crystallization

Vessel: Teflon-lined, stirred autoclave

Incubation: 10 h at ambient temperature with stirring

Temperature: 125 ± 2 °C

Time: 7 days

Agitation: 100 rpm

Product Recovery

- (1) Filter and wash to pH<10
- (2) Dry at 110 °C
- (3) Yield: near 100% on Ga₂O₃

Product Characterization

XRD: NAT; no other crystalline phases or amorphous material observed

Elemental Analyses: Ga₂O₃ : 3.28 SiO₂ : 0.11 Na₂O : 0.56 K₂O : 0.39 (BTMA)₂O

Crystal Size and Habit: Anisotropic columns 10-20 μm long with an almost square cross section often bounded at both ends by pyramids. Twinning and intergrowths are common

Reference

- [1] M. L. Occelli, L. Goldish, H. Eckert, in *Stud. Surf. Sci. Catal.* 84, J. Weitkamp, H. G. Karge, H. Pfeifer, W. Holderich (eds.), 1994, p. 597

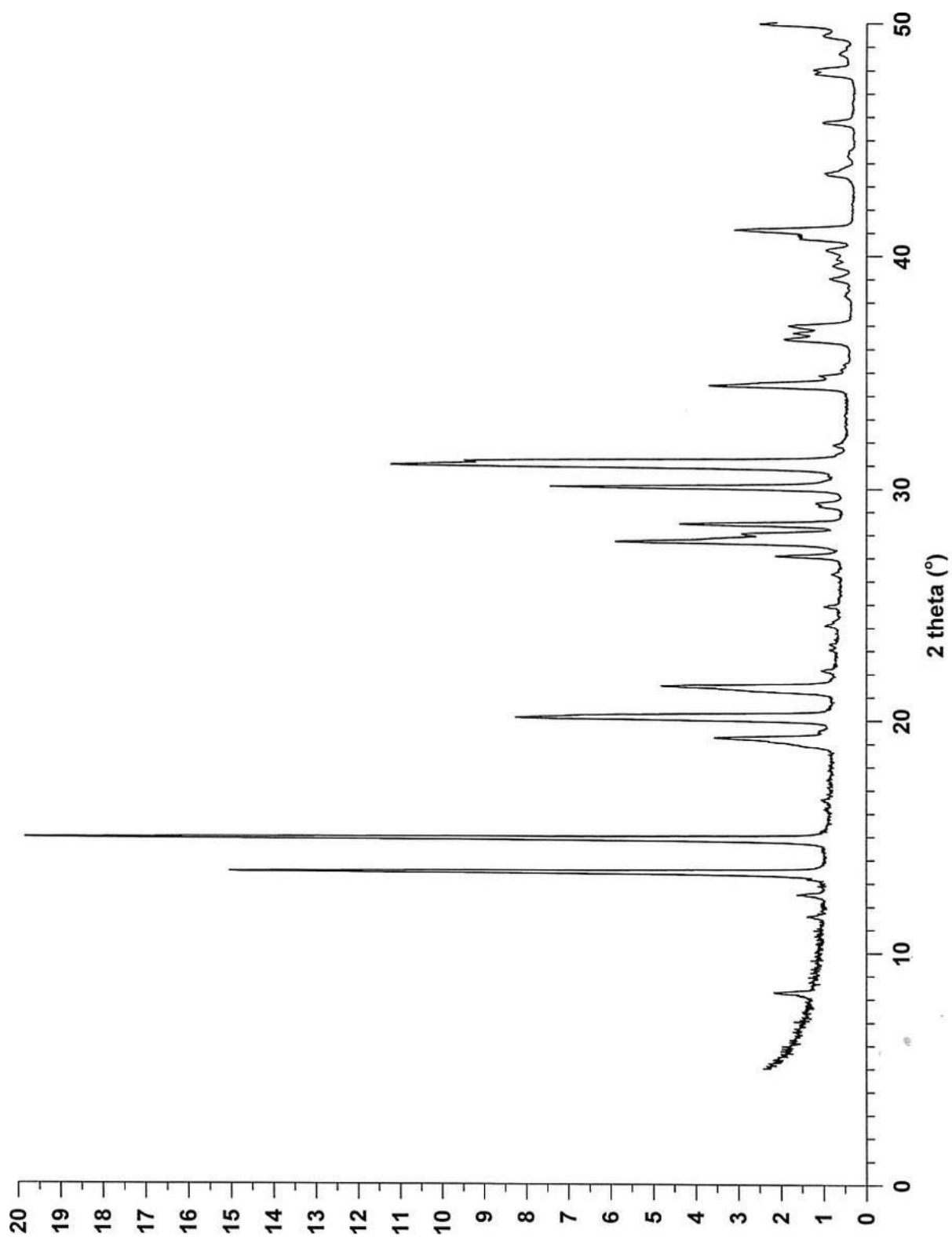
Note

- a. Diluted gallate solution must be clear.

NAT

[Ga] Natrolite

Si(62), Ga(38)



OFF

Linde Type T

Si(78), Al(22)

Contributed by Andrzej Cichocki

Verified by S. Khvoshchev, M. Shubaeva, J. Warzywoda, J. Parise, M. Kleinsorge, S. Park and C. Liu

Type Material $\text{Na}_{2.9}\text{K}_{5.4}[\text{Al}_{8.3}\text{Si}_{27.7}\text{O}_{72}] \cdot w\text{H}_2\text{O}$ (w ~7)

Method A. Cichocki, P. Koscielniak [1, 2]

Batch Composition 4.18 Na_2O : 1.25 K_2O : Al_2O_3 : 16.5 SiO_2 : 175 H_2O

Source Materials

distilled water
sodium hydroxide (97% NaOH)
potassium hydroxide (86% KOH)
silica sol (Rudniki Chemical Works, 29.5% SiO_2 , 0.2% Na_2O)
sodium aluminate solution (26.6% Al_2O_3 19.6% Na_2O) = NaAlO_2

Batch Preparation (for 14 g dry product)

- (1) [9.57 g water + 4.67 g sodium hydroxide + 3.24 g potassium hydroxide], dissolve and cool to room temperature
- (2) [67.0 g silica sol + (1)], mix in a porcelain mortar and stir for 2 minutes ^a
- (3) [(2) + 7.64 g sodium aluminate solution], add NaAlO_2 drop by drop to the stirred silicate over a 10 min. interval and continue stirring for 20 minutes

Crystallization

Vessel: stainless steel autoclave, 120 cm^3 capacity
Aging: 24 h at room temperature
Temperature: 140°C
Time: 7 days
Agitation: none

Product Recovery

- (1) Cool; transfer the reaction mixture to a mortar and grind
- (2) Filter and wash in a Buechner funnel until pH of the filtrate is 10
- (3) Dry at 110°C
- (4) Equilibrate in laboratory air for a few days
- (5) Yield: near 95% on Al_2O_3 and 41.5% on SiO_2 ^b

Product Characterization

XRD pure OFF ^c competing phases: PHI, CHA, LTL ^d
Elemental Analysis: 0.35 Na_2O : 0.65 K_2O : Al_2O_3 : 6.65 SiO_2

Crystal Size and Habit: rods and "bones" type crystals ~9 μm long on average (longest ~22 μm)

References

- [1] A. Cichocki, P. Koscielniak, M. Michalik, M. Bus, *Zeolites* 18 (1997) 25
- [2] A. Cichocki, P. Koscielniak, *Micropor. Mesopor. Mater.* 29 (1999) 369
- [3] A. Cichocki, *Zeolites* 11(1991) 758
- [4] R. Aiello, R. M. Barrer, *J. Chem. Soc.* 1970 (A), 1470

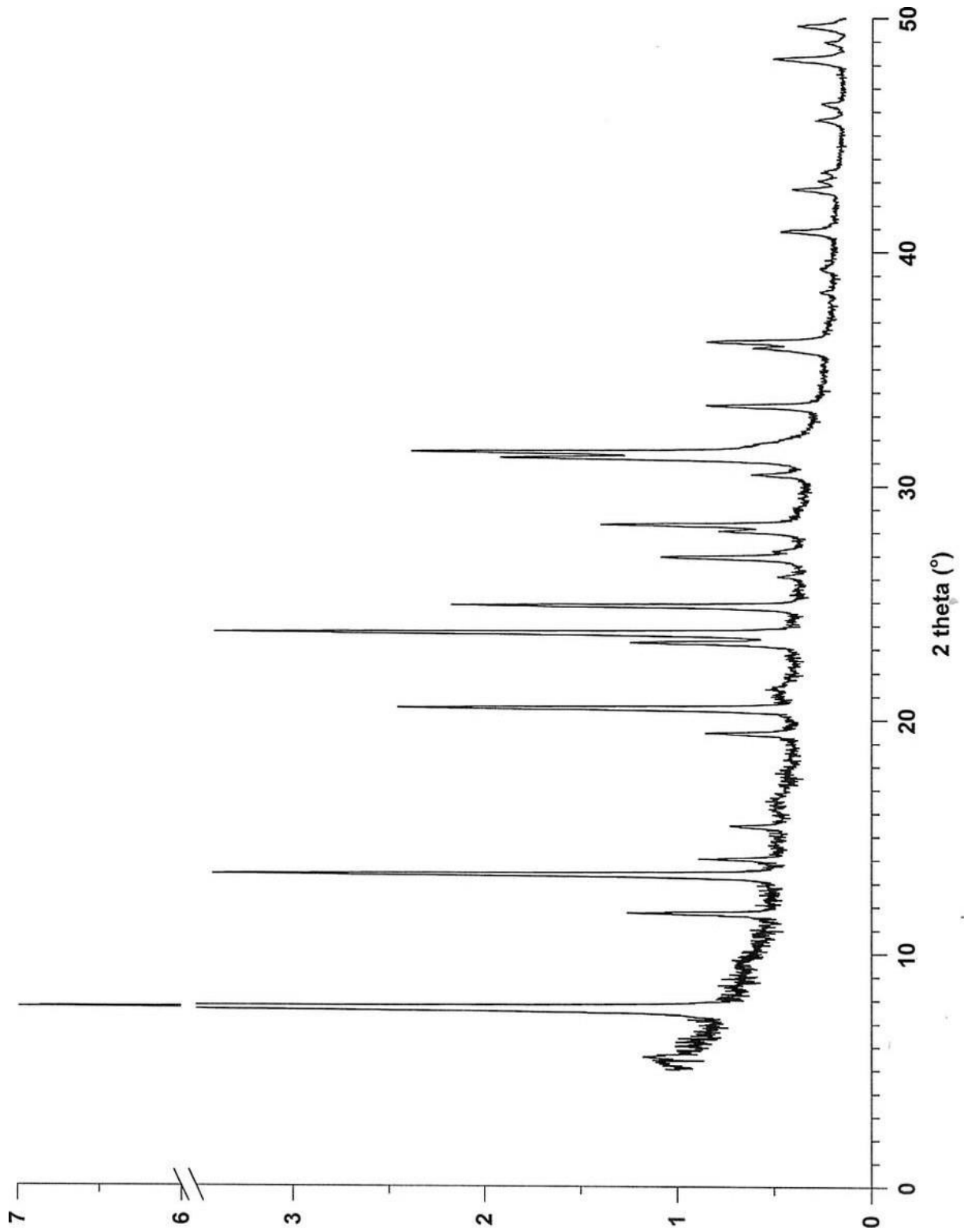
Notes

- a. The use of a porcelain mortar gives a good mix of the reagents, particularly aluminate and silica sol.
- b. 39.9% of the sum of Na₂O, K₂O, Al₂O₃ and SiO₂ masses introduced into the reaction mixture. Synthetic Erionite with SiO₂/Al₂O₃= 6.55 forms from a reaction mixture of composition 8.09 Na₂O : 2.38 K₂O : Al₂O₃ : 27.0 SiO₂ : 448 H₂O when crystallization is carried out in a stainless steel autoclave at the temperature 373 K and time 7 days, but the yield is reduced to 22.5%. This composition differs slightly from that given in ref. [3] where NaOH and KOH were assumed 100%.
- c. The Na/K-system synthetic product shows domains of erionite and offretite in a single crystal. The XRD pattern agrees with natural offretite (PDF), but the product shows adsorption properties erionite. Unfaulted erionite crystallized in the Na/Me₄N-system. [41
- d. Formation of PHI is favored by decreasing relative alkalinity (OH⁻/SiO₂). Decreasing the temperature of crystallization favors CHA. Increasing relative alkalinity leads to formation of LTL.

OFF

Linde Type T

Si(78), Al(22)



OFF

Offretite

Si(79), Al(21)

Contributed by Hans Lechert

Verified by M. Mertens and R Russu

Type Material $\text{Na}_{0.2}\text{K}_{0.9}[\text{Al}_4\text{Si}_{14}\text{O}_{36}] : w\text{H}_2\text{O}^{\text{a}}$

Method H. Lechert, H. Weyda [1]

Batch Composition 3.0 Na_2O : 1.0 K_2O : Al_2O_3 : 20.8 SiO_2 : 1.73 (TMA)Cl : 324 $\text{H}_2\text{O}^{\text{b}}$
(TMA tetramethylammonium)

Source Materials

distilled water

sodium hydroxide, reagent grade (99+% NaOH)

aluminum tri-isopropylate $[\text{Al}(\text{OC}_3\text{H}_7)_3]$

potassium hydroxide, reagent grade (87% KOH)

silica (Merck, precipitated and dried, 87% SiO_2)

tetramethylammopaum chloride [Merck, $\text{N}(\text{CH}_3)_4\text{Cl}$]

Batch Preparation (for 64 g dry product)

- (1) [28.1 g water + 16.8 g sodium hydroxide], mix until dissolved
- (2) [(1) + 42.5 g aluminum tri-isopropylate], stir at 100°C and evaporate to reduce to 42.0 g
- (3) [(2) + 58 g water], stir and cool to ambient temperature; dilute to 100 g total
- (4) [379.3 g water + 8.4 g sodium hydroxide + 13.4 g potassium hydroxide], mix until dissolved
- (5) [(4) + 149.4 g silica], mix for 30 minutes
- (6) [(5) + (3)], mix for 30 minutes
- (7) [(6) + 126.4 g water], mix for 30 minutes
- (8) [(7) + 19.7 g tetramethylammonium chloride], mix for 30 minutes

Crystallization

Vessel: Teflon-lined autoclave

Temperature: 160°C

Time: 20 hours

Agitation: none

Product Recovery

- (1) Centrifuge
- (2) Wash to near neutrality
- (3) Dry at 100°C
- (4) Yield: near 100% on Al_2O_3

Product Characterization

XRD: Strong OFF, no extraneous phases; competing phases: erionite,^c Zeolite P (GIS), analcime Elemental Analysis: 0.10 Na_2O : 0.46 K_2O : Al_2O_3 : 7.72 SiO_2^{d}
Crystal Size and Habit: "rice grains", length 5-10 μm^{e}

Reference

[1] H. Lechert, H. Weyda, in *Synthesis of Microporous Materials*, Vol. I, M. L. Occelli, H. Robson (eds.), Van Nostrand Reinhold, New York, 1992, P. 77

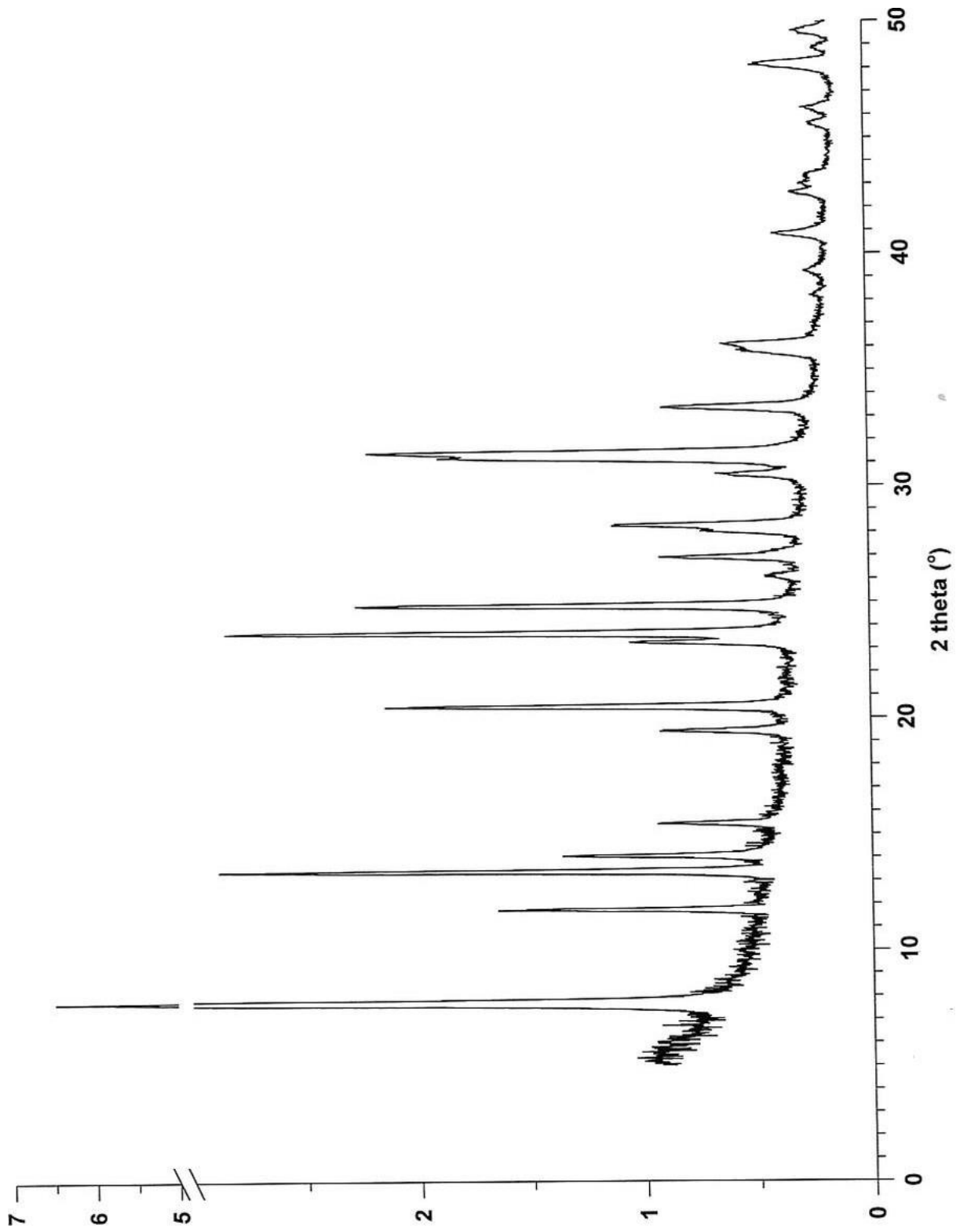
Notes

- a. Missing cations assumed to be TMA⁺ or (after calcination) H⁺.
- b. OFF can be obtained without template in the temperature range 87-107°C with a gel (6.2 Na₂O 3.5 K₂O : Al₂O₃ : 25 SiO₂ : 390 H₂O), but slight deviations from this composition give appreciable amounts of erionite or gismondine. At higher temperatures Zeolite P (GIS) and analcime co-crystallize with offretite.
- c. ERI can be distinguished from OFF in the XRD pattern by lines at $d = 9.13, 5.37, 4.60, 4.17, 3.28, \text{ and } 2.82 \text{ \AA}$.
- d. The template content of the product is quite low (less than one TMA⁺ per UC).
- e. At 190°C, pure erionite can be obtained from a batch composition: 8.0 Na₂O : 1.7 K₂O : Al₂O₃ : 24 SiO₂ : 1.7 TMACl : 410 H₂O. At this temperature the offretite is needles of about 1 μm diameter x 25 μm long. At crystallization times longer than 4 hours at 190°C, an increasing amount of analcime is observed.

OFF

Offretite

Si(79), Al(21)



OFF

[Ga] Offretite

Si(65), Ga(35)

Contributed by Mario Occelli

Verified by F. Machado and S. Iwamoto

Type Material $K_{2.2}Na_{0.1}(TMA)_{4.1}Ga_{6.4}Si_{11.6}O_{36} : wH_2O$ (TMA = tetramethylammonium)

Method M. L. Occelli [1]

Batch Composition 2.25 K_2O : 1.61 Na_2O : 0.5 $(TMA)_2O$: Ga_2O_3 : 11.7 SiO_2 : 250 H_2O : 1.0 HCl

Source Materials

deionized water
sodium hydroxide, reagent grade (~97% NaOH)
potassium hydroxide, reagent grade (~87% KOH)
gallium oxide (99.99%)
silica sol (Dupont HS-40, 39% SiO_2 , 0.5% Na_2O)
tetramethylammonium chloride [99+% (TMA)Cl]

Batch Preparation

- (1) [50 g water + 12.0 g sodium hydroxide + 29.0 g potassium hydroxide], mix until dissolved; heat to boiling
- (2) [(1) + 18.7 g gallium oxide], stir at boiling point until a clear solution is obtained
- (3) [(2) + 30 g water], mix and cool to ambient temperature ^a
- (4) [20 g water + 11.0 g (TMA)Cl], mix until dissolved
- (5) [(3) + (4)], mix thoroughly
- (6) [180.3 g silica sol + 234.8 g water], mix for 4 hours
- (7) [(6) + (5)], add gallate mixture dropwise to the vigorously-stirred diluted silica sol. Continue stirring in a round-bottomed flask for 10 hours

Crystallization

Vessel: 1000 mL round bottomed flask with agitator and reflux condenser
Incubation: 10 h at ambient temperature with stirring
Temperature: 98°C ^b
Time: 3 days ^c
Agitation: Continue stirring until temperature reaches 98°C, then discontinue stirring for balance of crystallization period

Product Recovery

- (1) Filter and wash with deionized water until pH < 10
- (2) Dry at 110°C
- (3) Yield: near 100% on Ga_2O_3

Product Characterization

XRD: OFF, no other crystalline products or amorphous material detected
Elemental Analyses: 49.5% SiO_2 , 42.2% Ga_2O_3 , 7.2% K_2O , 1.1% Na_2O ^d

References

- [1] M. L Occelli, US Patent 5 133 951 (1992)
- [2] M. L Occelli, H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, *Micropor. Mater.* 10 (1997) 123-135
- [3] M. L Occelli H. Eckert, C. Hudalla, A. Auroux, P. Ritz, P. S. Iyer, in *Proceedings of the 11th International Zeolite Conference*, Seoul, Korea, Hakze Chon, Son-Ki Ihm (eds.), Elsevier, Amsterdam, 1997, p 1981
- [4] M. L Occelli, H. Eckert, P. S. Iyer, P. Ritz, in *Synthesis of Porous Materials*, M. L Occelli, H. Kessler (eds.), Marcel-Dekker (1997), p. 283

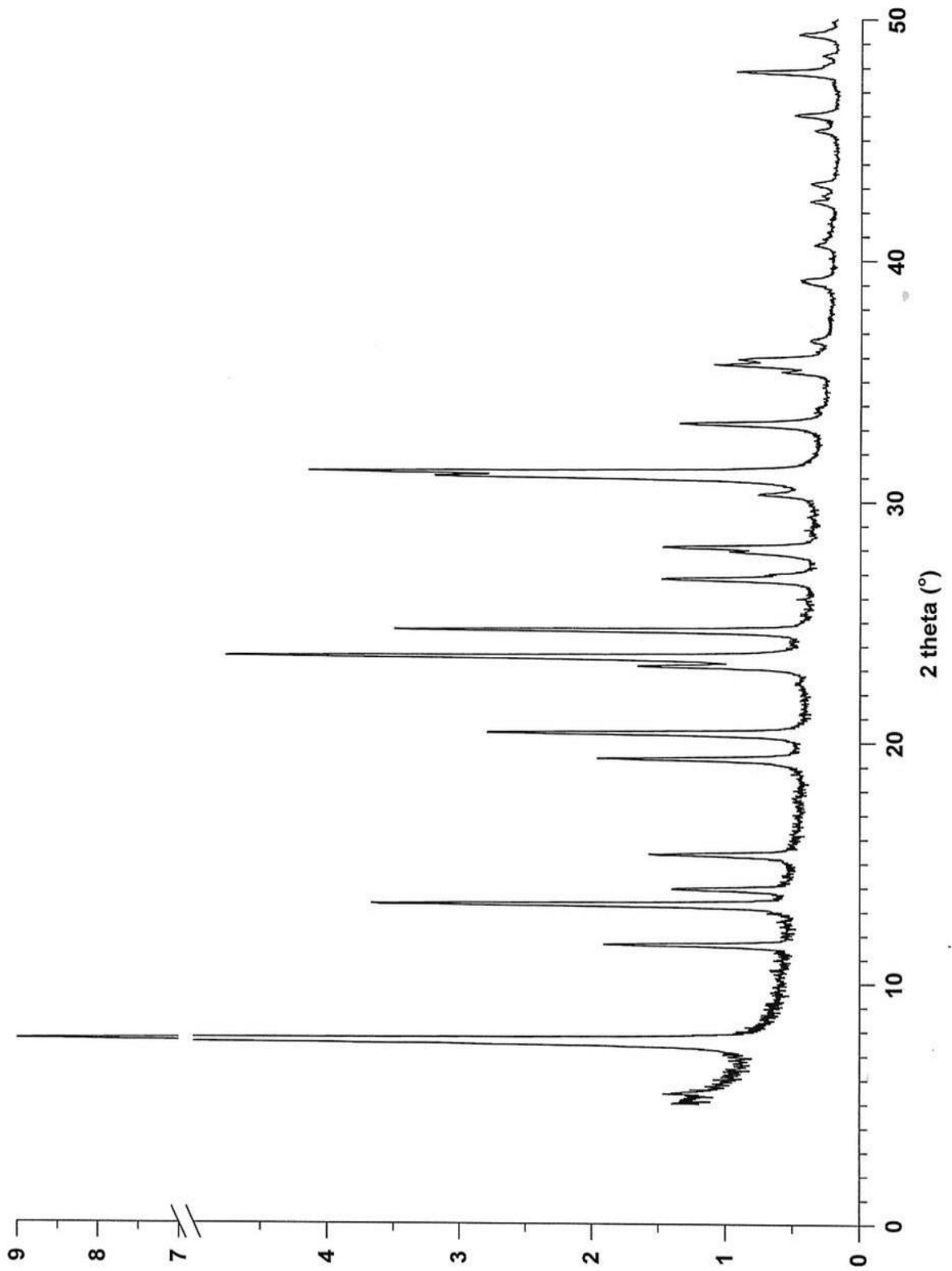
Notes

- a. Diluted Na,K gallate solution must be clear.
- b. Stirring is continued as temperature is increased to 98°C, then discontinued for the remainder of the crystallization treatment.
- c. Methods to reduce crystallization time are given in ref. [1].
- d. After calcination in nitrogen for 2 hours at 500°C followed by calcination in air for 10 hours at 550°C; the BET surface area was 404 m²/g. Characterizations of similar gallium offretites are given in references [2-4].
- e. XRD: OFF, no other crystalline products or amorphous material detected
Elemental Analyses: 49.5% SiO₂, 42.2% Ga₂O₃, 7.2% K₂O, 1.1% Na₂O^d

OFF

[Ga] Offretite

Si(65), Ga(35)



Contributed by David Vaughan

Verified by P. Piccione and B. Subotic

Type Material (Na₈₂K₆₆TEA₁₆)[Al₁₆₄Si₅₀₈O₁₃₄₄] : wH₂O (TEA = tetraethylammomum)

Method D. E. W. Vaughan, K. G. Strohmaier [1,2]

Batch Composition 0.4 K₂O : 0.6 Na₂O : 1.4 (TEA)₂O : Al₂O₃ : 9 SiO₂ : 0.3 Na₂SO₄ : 140 H₂O

Source Materials

deionized water

potassium hydroxide (J. T. Baker, >99% KOH. 0.5 H₂O)

sodium hydroxide (J. T. Baker, ~99% NaOH)

alumina (Alcoa C-31, >99% Al₂O₃· 3 H₂O)

silica sol (Dupont HS-40, 40% SiO₂, 0.4% Na₂O)

tetraethylammonium hydroxide (SACHEM, 35% N(C₂H₅)₄OH)

aluminum sulfate (reagent grade, > 99% Al₂(SO₄)₃· 17H₂O)

Batch Preparation (for 20 g dry product)

- (1) [8.0 g water + 1.79 g potassium hydroxide + 2.8 g sodium hydroxide + 5.1 g alumina], reflux until a clear solution is obtained; cool to room temperature. Replace water lost by evaporation
- (2) [10 g aluminum sulfate + 10 g water], mix and warm if necessary to make a solution
- (3) [49.7 g silica sol + 43.3 g tetraethylammonium hydroxide + (1) + 5.29 g (2) + 19 g water], add sequentially with mixing in a beaker

Crystallization

Vessel: 125 mL Teflon jar (Nalgene)

Incubation: 3 days at room temperature

Time: 12 to 16 days^a

Temperature: 100°C

Agitation: none

Product Characterization

XRD: excellent PAU

Elemental Analysis: 0.4 K₂O : 0.5 Na₂O : 0.1 (TEA)₂O : Al₂O₃ : 6.2 SiO₂ : H₂O

Crystal size and Habit: spherical aggregates (1 to 10 μm) of submicron crystals (<0.1 to 0.2 μm)^b

References

- [1] D. E. W. Vaughan, K. G. Strohmaier, U. S. Patent 5 013 536 (1991)
- [2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233

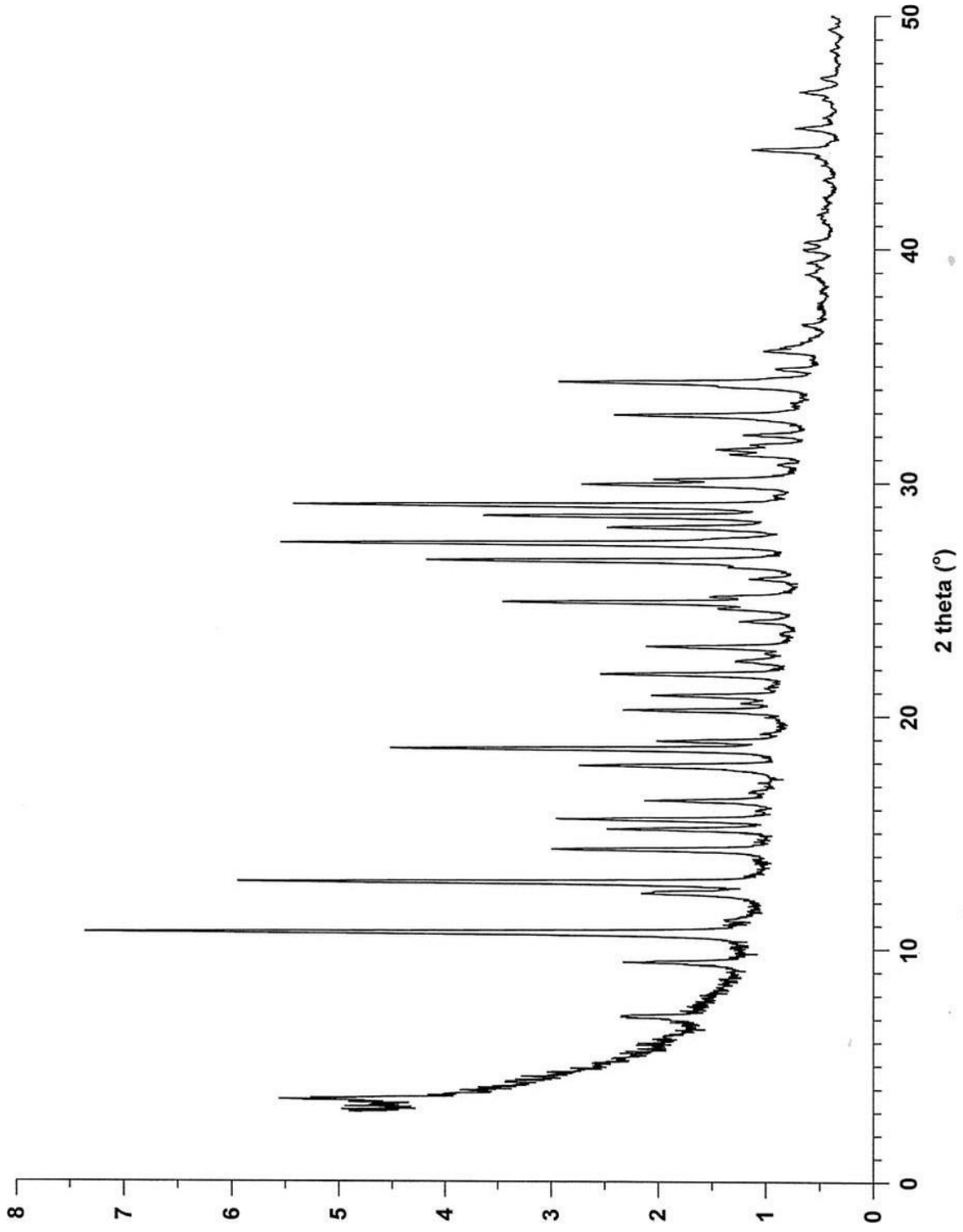
Notes

- a. Both 12 and 16 day samples were excellent PAU.
- b. ¹³C-NMR shows two sites; ²⁹Si-NMR shows three broad peaks.

PAU

ECR-18

Si(76), Al(24)



PAU

Paulingite (Seeded)

Si(76), Al(24)

Contributed by David Vaughan and Karl Strohmaier

Verified by P. Piccione and B. Subotić

Type Material (Na₈₇K₇₂TEA₁₅)[Al₁₆₄Si₅₀₈O₁₃₄₄] : wH₂O (TEA = tetraethylammonium)

Method D. E W. Vaughan, K. C. Strohmaier [1,2]

Batch Composition 0.5 K₂O : 0.7 Na₂O : 1.3 (TEA)₂O : Al₂O₃ : 9 SiO₂ : 0.4 Na₂SO₄ : 135 H₂O

Source Materials

deionized water

sodium hydroxide (J.T. Baker, ~99% NaOH)

alumina (Alcoa C-31, >99% Al₂O₃ · 3 H₂O)

sodium silicate (PQ Corp. N-brand, 8.9% Na₂O, 28.7% SiO₂)

potassium hydroxide (J. T. Baker, >99% KOH. 0.5 H₂O) silica

sol (Dupont HS-40, 40% SiO₂, 0.4% Na₂O)

tetraethylammonium hydroxide (RSA Corp., 40% N(C₂H₅)₄OH)

aluminum sulfate (> 99%Al₂(SO₄)₃ · 17 H₂O)

Batch Preparation (for 17 g dry product)

Preparation of Seed Solution [3,4]

- (1) [30 g water + 16 g NaOH + 3.25 g alumina] reflux until a clear solution forms, then cool to room temperature and add water back to the original weight if necessary
- (2) [54.4 g sodium silicate + 31.3 g water + (1)], add sodium aluminate solution slowly with mixing in a 200 mL Waring blender
- (3) Age for 24 hours at room temperature^a

Preparation of Crystallization Batch

- (4) [6 g water + 2.28 g potassium hydroxide + 2.16 g sodium hydroxide + 4.57 g alumina], stir at 100°C until clear, then cool in an ice bath to below room temperature. Adjust to original weight with water
- (5) [45.9 g silica sol + 4.53 g seed solution + 33.4 g tetraethylammonium hydroxide + (4)], add sequentially with continuous mixing
- (6) [6 g water + 3.2 g aluminum sulfate], mix until dissolved
- (7) [(5) + (6)], add alum solution slowly with continuous mixing
- (8) [(7) + 17 g water], adjust the total weight of gel to 125 g by the addition of water^b

Crystallization

vessel: 125 mL Teflon jar or bottle (Nalgene)

time: 22 days

temperature: 100°C

agitation: none

Product Recovery

- (1) Vacuum filter on a Buechner funnel
- (2) Wash to pH <10
- (3) Dry at 110°C
- (4) Yield: 17 g (~85% on Al₂O₃)

Product Characterization

XRD: excellent PAU

Elemental analyses: 0.44 K₂O : 0.53 Na₂O : 0.09 (TEA)₂O : Al₂O₃ : 6.18 SiO₂

Crystal size and habit: spherical aggregates (2 to 30 μm) of submicron crystals (0.1 to 0.3 μm)^c

References

- [1] D. E. W. Vaughan, K. G. Strohmaier, US Patent 5 013 536 (1991)
- [2] D. E. W. Vaughan, K. G. Strohmaier, Micropor. Mesopor. Mater. 28 (1999) 233
- [3] D. E. W. Vaughan, U S Patent 4 178 352
- [4] D. E. W. Vaughan, Mater. Res. Soc. Symp. Proc. 111 (1988) 89

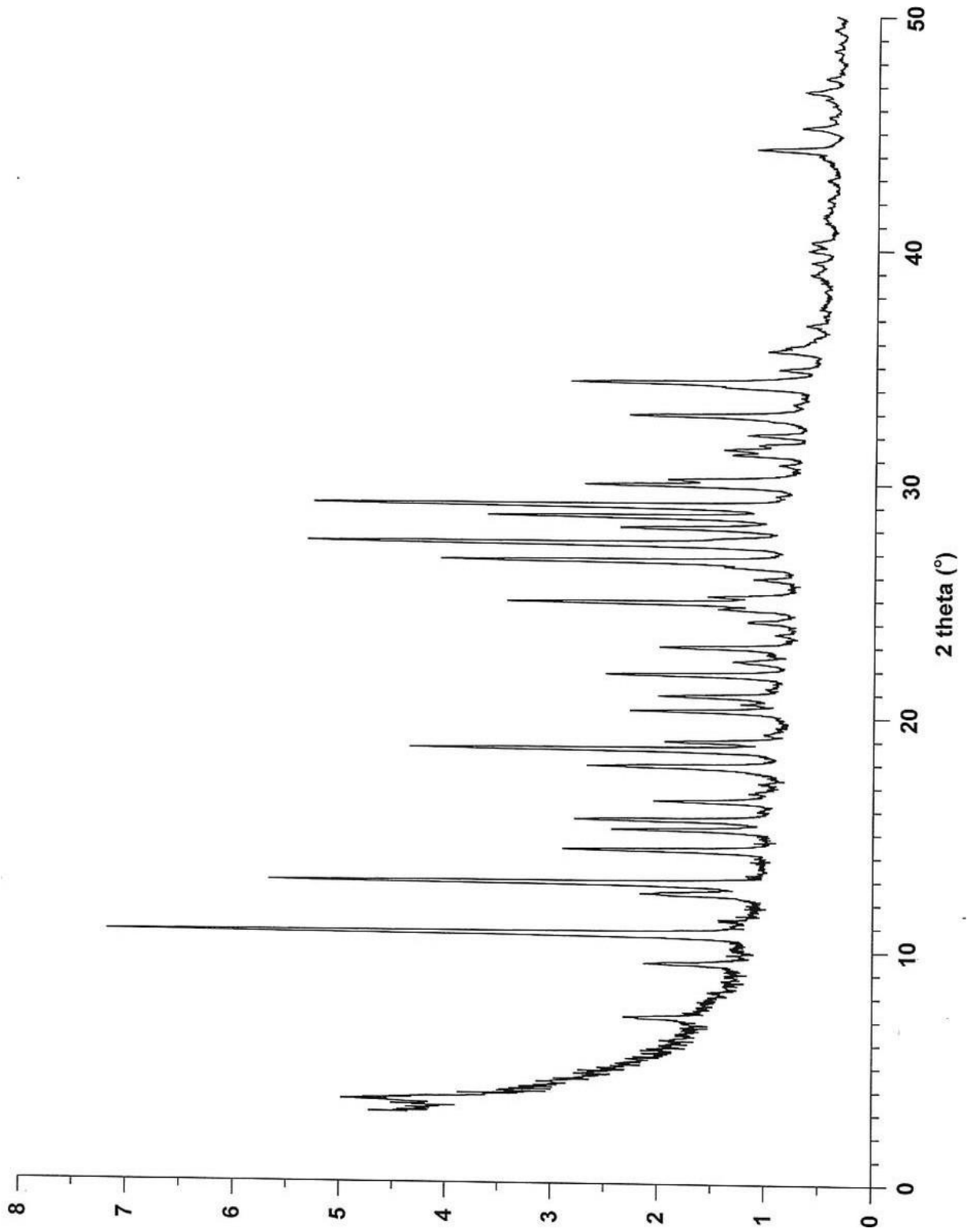
Notes

- a. Stored at room temperature, this seed solution will be stable and usable for several months.
- b. The control of OH⁻/Si ratios can be done either by adding part of the Al as aluminum sulfate, or by using only aluminate and balancing the alkalinity with mineral acid (such as sulfuric acid).
- c. ¹³C-NMR shows two sites; ²⁹Si-NMR shows three broad peaks.

PAU

Paulingite (Seeded)

Si(76), Al(24)



PHI

Phillipsite

Si(72), Al(28)

Contributed by David Hayhurst

Verified by A. Cichocki, A. Rodriguez, E. Falabella Sousa-Aguiar, R. Thompson and A. Giaya

Type Material $K_{3.1}Na_{0.9}[Al_{11}Si_{12}O_{32}] \cdot wH_2O$

Method D. T. Hayhurst, L B. Sand [1]

Batch Composition 6.95 Na₂O : 3.50 K₂O : Al₂O₃ : 18.5 SiO₂ : 325 H₂O

Source Materials

distilled water

potassium hydroxide (Mallinckrodt reagent grade, 87% KOH)

sodium silicate solution (PQCorp., N-brand, 8.9% Na₂O, 28.7% SiO₂)

sodium aluminate (Nalco, 30.5% Na₂O, 45.6% Al₂O₃)

Batch Preparation (for 100 g dry product)

- (1) [636 g water + 91.6 g potassium hydroxide + 826.9 g sodium silicate solution].
Dissolve in a stirred flask at 100°C under reflux
- (2) [(1) + 45.28 g sodium aluminate], continue mixing at 100°C for crystallization

Crystallization

Vessel: 3 L, 3-neck flask under reflux

Temperature: 100°C

Time: 6 to 8 hours

Agitation: mechanically stirred

Product Recovery

- (1) Filter to recover solids
- (2) Wash to pH<10
- (3) Dry at 120°C
- (4) Yield: 100% on Al₂O₃

Product Characterization

XRD: PHI (only crystalline product); Competing phases; MOR,^a ERI,^a LTL,^b GIS,^b ANA^c

Elemental Analysis: 0.8 K₂O . 0.2 Na₂O . Al₂O₃ : 5.24 SiO₂

Crystal Size and Habit: multi-crystalline aggregates, ~5 μm dia.

Reference

- [1] D. T. Hayhurst, L B. Sand, in ACS Symposium Series 40, 1. R Katzer (ed.), Am. Chem. Soc., Washington, D. C., 1977, p. 219

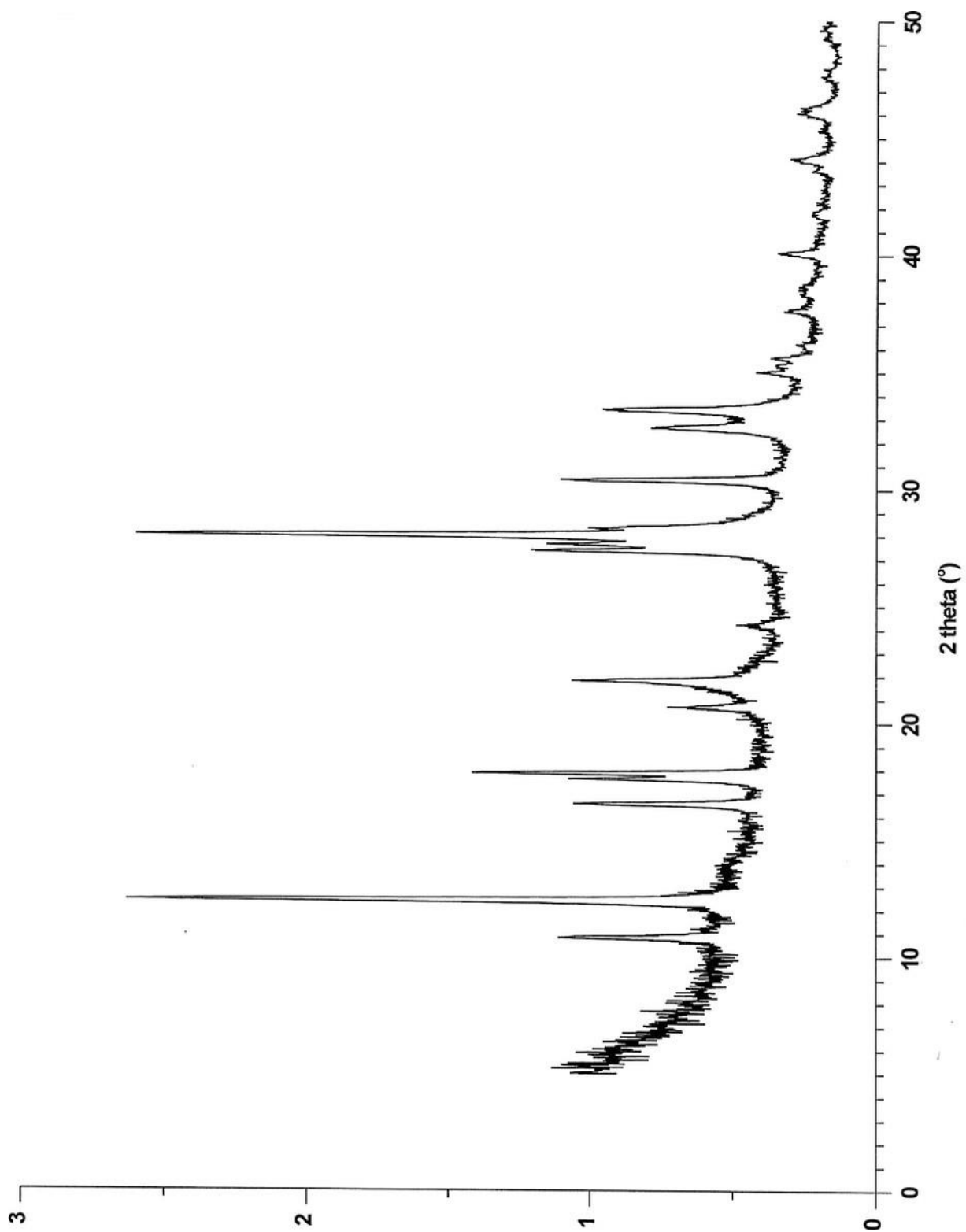
Notes

- a. Higher silica batch composition
- b. $K^+/(Na^+ + K^+) > 0.4$
- c. $K^+/(Na^+ + K^+) < 0.1$

PHI

Phillipsite

Si(72), Al(28)



PHI

High-alumina Philipsite

Si(67), Al(33)

Contributed by Andrzej Cichocki

Verified by J. Bronic and G. Kuhl

Type Material $\text{Na}_{6.3}\text{K}_{4.2}[\text{Al}_{10.5}\text{Si}_{21.5}\text{O}_{64}]. 23 \text{H}_2\text{O}^{\text{a}}$

Method A. Cichocki [1,2]

Batch Composition 1.53 Na_2O : 0.44 K_2O : Al_2O_3 : 5.0 SiO_2 : 82.7 H_2O

Source Materials

distilled water

sodium hydroxide (reagent grade, 97% NaOH)

potassium hydroxide (reagent grade, 86% KOH)

silica sol (Rudnild Chemical Works, 29.5% SiO_2 , 0.22% Na_2O)

sodium aluminate solution (26.6% Al_2O_3 , 19.6% Na_2O)^b

Batch Preparation (for 26 g product)

- (1) [36.0 g water + 1.53 g sodium hydroxide + 3.78 g potassium hydroxide], dissolve and cool to room temperature
- (2) [67.0 g silica sol + (1), mix in a porcelain mortar and stir for 2 minutes
- (3) [(2) + 25.22 g sodium aluminate solution], add sodium aluminate drop by drop to the stirred silicate over a 10 minutes period and continue stirring for 20 minutes

Crystallization

Vessel: stainless steel autoclave, 120 cm³ capacity

Aging: 24 hours at room temperature

Temperature: 100°C

Time: 7 days

Agitation: none

Product Recovery

- (1) Cool to room temperature; transfer the reaction mixture to a porcelain mortar and grind
- (2) Filter and wash in a Buechner funnel until pH of the filtrate is ~10
- (3) Dry at 110°C
- (4) Equilibrate in laboratory air for a few days
- (5) Yield: 25.8 g (near 100% on Al_2O_3)^c

Product Characterization

XRD: Pure phillipsite (ZK-19 [3] in ASTM Powder Diffraction File) competing phases: ANA, CHA, ERI, LTL
Elemental Analysis: 0.60 Na₂O : 0.41 K₂O : Al₂O₃ : 4.07 SiO₂ : 4.30 H₂O^d
Crystal Size and Habit: ~0.5 to 3 μm diameter, round twinned polycrystals

References

- [1] A. Cichocki, Zeolites 11(1991) 758
- [2] A. Cichocki, PL Patent 161 557 (1993)
- [3] G. H. Kuehl, Am. Mineral. 54 (1969) 1607
- [4] A. Cichocki, PL Patent 100 912 (1979)
- [5] A. Cichocki, J. Grochowski, L. Lebioda, Kristall. Technik 14 (1979) 9
- [6] A. Cichocki, PL Patent 162 653 (1993)

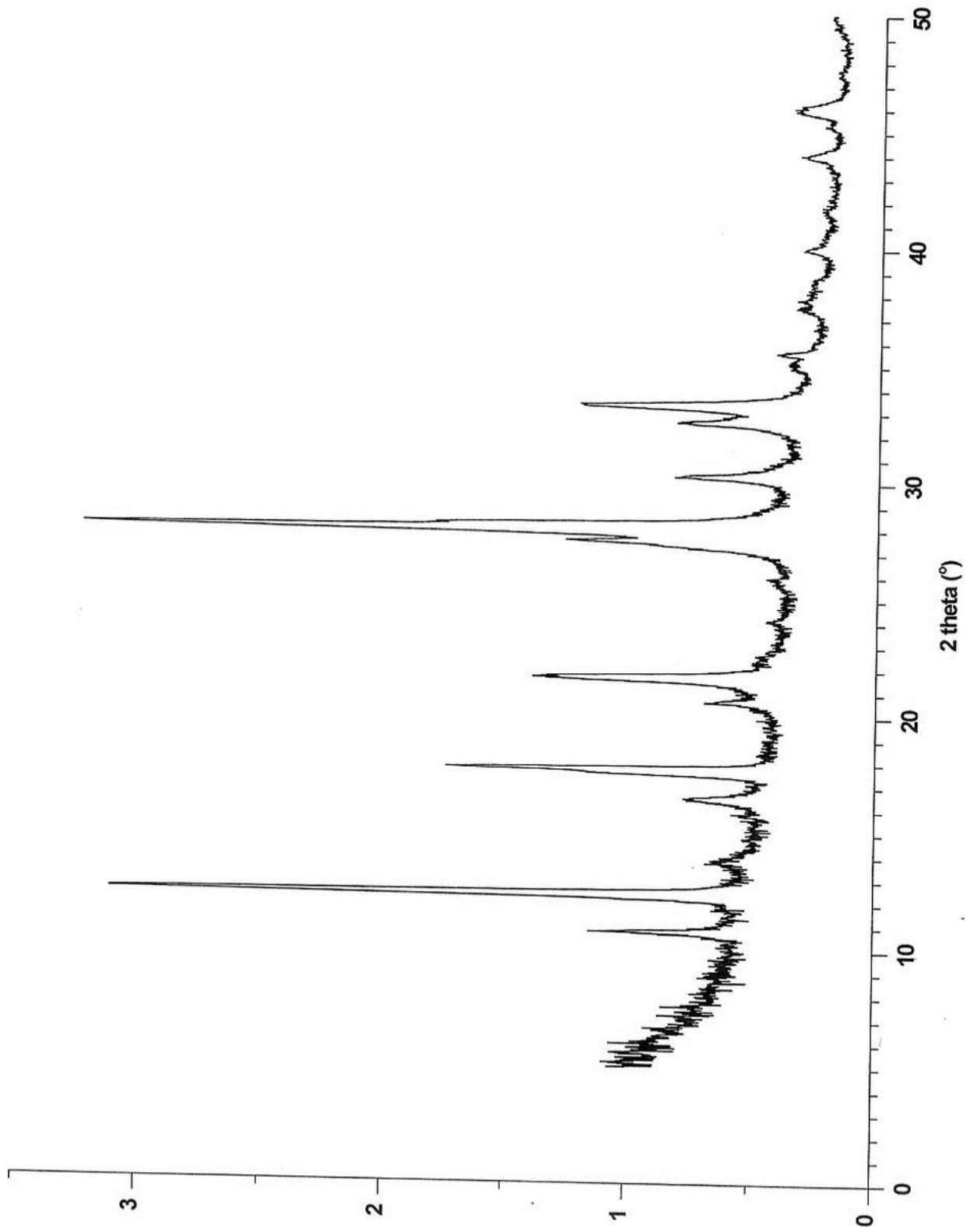
Notes

- a. Al content of the unit cell varies from 9.5 to 12.8. More siliceous synthetic-type phillipsite forms when (1) higher silica batch composition is used or (2) borosilicate glass corrodes in the alkaline reaction mixture. Phillipsite with SiO₂/Al₂O₃ = 6.27 crystallized in a stainless steel autoclave from a reaction mixture of composition 7.16 Na₂O : 2.81 K₂O : Al₂O₃ : 26.5 SiO₂ : 442 H₂O. [4,5] Phillipsite with SiO₂/Al₂O₃ = 4.34 forms from a reaction mixture of composition 1.29 Na₂O : 0.37 K₂O : Al₂O₃ : 4.20 SiO₂ : 69.5 H₂O when crystallization is carried out in a borosilicate glass vessel. These compositions differ slightly from those given in reference [4] and [6] where NaOH and KOH were assumed 100%.
- b. Prepared by the reaction of aluminum shavings with concentrated sodium hydroxide solution (~30 wt% NaOH).
- c. Dry product contains 72.0% of the sum of Na₂O, K₂O, Al₂O₃ and SiO₂ masses introduced into the reaction mixture.
- d. Sorptive Capacity (g/g at p/p₀ = 0.2): 0.185 for H₂O at 298 K, 0.002 for Ar at 77 K.

PHI

High-alumina Philipsite

Si(67), Al(33)



Contributed by Alain Matijasic and Joël Patarin

Verified by S. Schwarz, T. Cholley, G. Gbery and K. Balkus

Type Material $\text{Na}_{6.8}\text{Cs}_{3.0}[\text{Al}_{98}\text{Si}_{38.2}\text{O}_{96}] \cdot (18\text{-C-6}) \cdot w\text{H}_2\text{O}$ ($w \approx 29$)

Method T. Chatelain, J. Patarin, E. Fousson, M. Soulard, J. L Guth, P. Schulz [1]

Batch Composition $1.8\text{Na}_2\text{O} : 0.3\text{Cs}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 0.5(18\text{-C-6}) : 100\text{H}_2\text{O}$

Source Materials

distilled water

18-C-6 (Lancaster, > 98% cycl. $(\text{C}_2\text{H}_4\text{O})_6$)

cesium hydroxide (Aldrich, 50% CsOH in water)

sodium hydroxide (SDS, > 98% NaOH)

sodium aluminate (Carlo Erba, 56% Al_2O_3 , 37% Na_2O , 7% H_2O)

silica sol (Dupont Ludox AS-40, 40% SiO_2)

Batch Preparation (for ~6 g product)^a

- (1) [7.84 g water + 1.35 g 18-C-6 + 1.80 g cesium hydroxide solution + 0.59 g sodium hydroxide], stir until dissolved^b
- (2) [(1) + 1.82 g sodium aluminate], stir until homogenized
- (3) [(2) + 15.00 g silica sol], stir until homogenized (formation of a gel) Continue stirring with magnetic stirrer for 24 h., then transfer to a PTFE-lined stainless-steel autoclave. Gel pH = 14

Crystallization

Vessel: 120 mL PTFE-lined stainless steel autoclave

Time: 192 hours

Temperature: 110°C in a preheated oven

Agitation: none. Final pH approximately 12

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) Filter and wash until pH 10
- (3) Dry at 60°C overnight
- (4) Yield: 6g as-synthesized RHO-type sample (product containing about one molecule 1 8-C-6 as organic template per unit cell)^b

Product Characterization

XRD: Strong RHO pattern showing cubic symmetry. ($a_0=15.031(1)\text{\AA}$);^c no visible impurities

Elemental Analyses: Si/Al is close to 3.9^b

Crystal size and habit: The crystals display a sphere-like shape with an average size of 1 μm

Reference

- [1] T. Chatelain, J. Patarin, E. Fousson, M. Soulard, J. L Guth, P. Schulz, *Micropor. Mat.* 4 (1995) 231

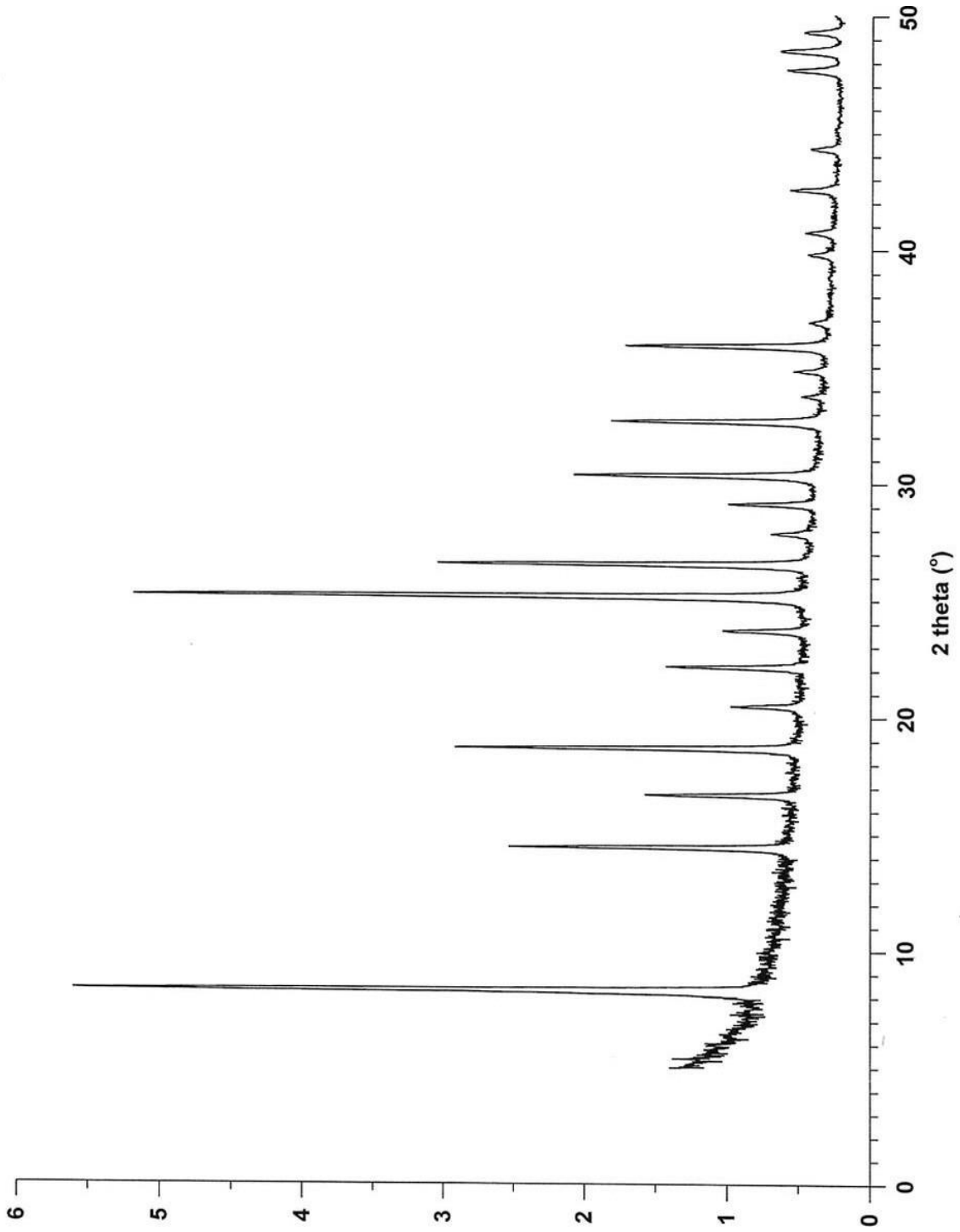
Notes

- a. This recipe has been successfully scaled up by a factor of six.
- b. The starting mixture is prepared in a polyethylene vessel.
- c. According to Ref. [1].

RHO

High Silica Rho

Si(80), Al(20)



RSN

RUB-17

Si(78), Zn(22)

Contributed by Ana Palčić

Verified by A. Ristic, J. Grand

Type Material: $K_4Na_{12}[Si_{28}Zn_8O_{72}] \cdot 18H_2O$

Method: C. Röhrig and H. Gies [1]

Batch Composition: TEOS : 0.1 ZnO : 0.5 NaOH : 0.5 KOH : 0.08 TEAOH : 44 H₂O

Source Materials

deionized water (DI)
zinc oxide (99%, Prolabo)
sodium hydroxide (97%, Sigma Aldrich) potassium
hydroxide (97%, Sigma Aldrich) tetraethylammonium
hydroxide (35% water solution, Aldrich) tetraethoxysilane
(98%, Sigma Aldrich)

Batch Preparation (for 2.9 g dry product)

- (1) [53.434 g water + 2.078 g TEAOH + 1.44 g NaOH + 2.302 g KOH] stir in a polypropylene bottle until clear solution is formed
- (2) [(1) + 0,574 g zinc oxide] stir for 30 min
- (3) [(2) + 15 g tetraethoxysilane] hydrolyze for 8 h^a

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 180° C
Time: 10 days
Agitation: none

Product Recovery

- (1) Dilute reaction mixture with water^b
- (2) Filter and wash with water
- (3) Dry at 80° C
- (4) Yield: 2.9 g

Product Characterization

XRD: RSN; competing phase: no
Crystal size and habit: intergrown crystals forming large aggregates, size 100-1500 nm.

Reference

- [1] C. Röhrig, H. Gies, Angew. Chem. Int. Ed. 34 (1995) 63

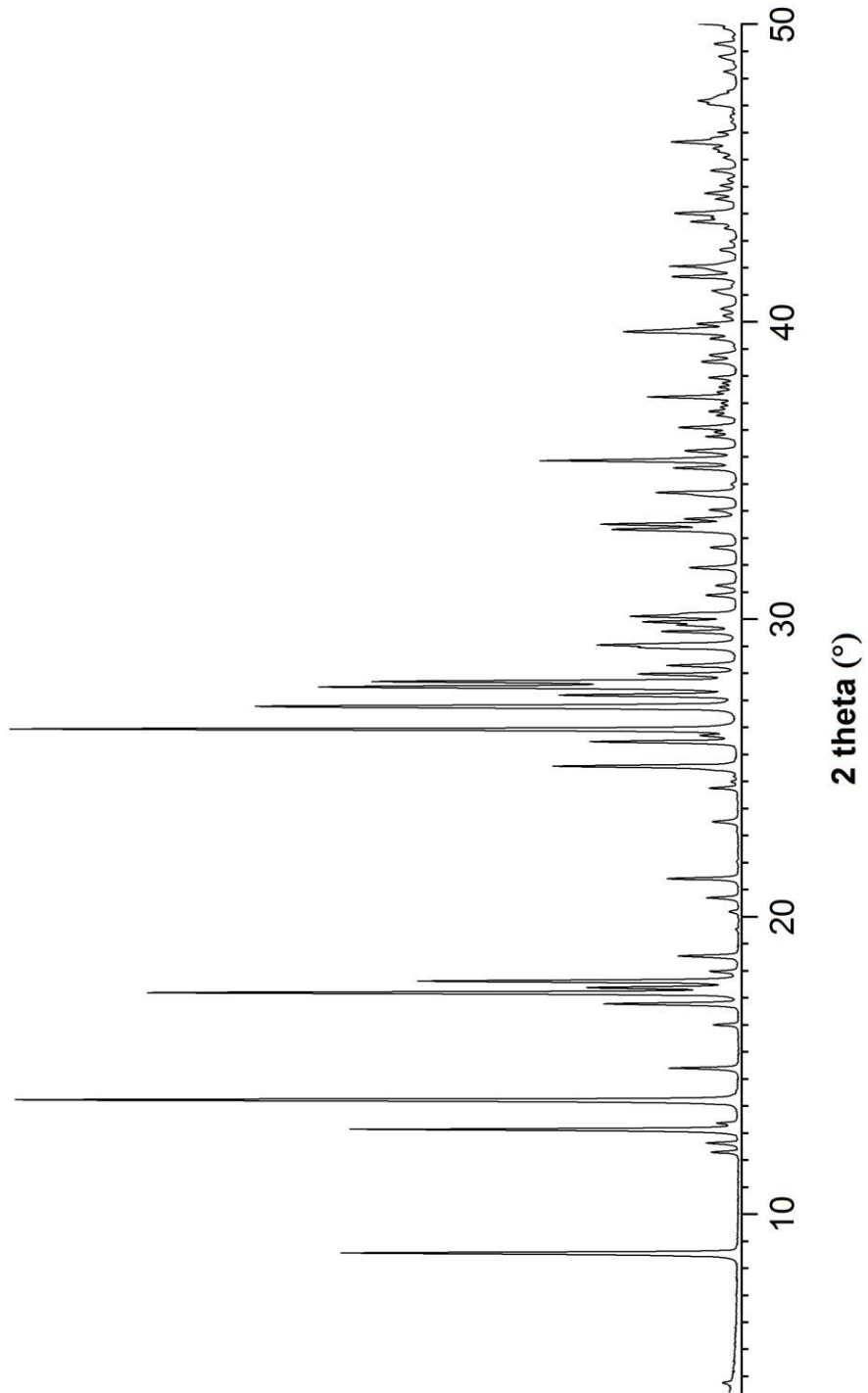
Notes

- a. ZnO is dispersed in the silicate solution.
- b. The product precipitates at the bottom of the autoclave. It is very hard to crush.

RSN

RUB-17

Si(78), Zn(22)



SEW

SSZ-82

Si(98), B(2)

Contributed by Christopher M. Lew and Tracy M. Davis

Verified by J. Cejka, F. Rey, A. Khartchenko

Type Material: $(\text{H}_2\text{O})_{15.7}[\text{Si}_{61.3}\text{B}_{4.7}\text{O}_{132}]^{\text{a}}$
(SDA = 1,6-bis(N-cyclohexylpyrrolidinium)hexane dihydroxide)

Method: A. W. Burton, Jr. [1]

Batch Composition: 1 SiO_2 : 0.02 B_2O_3 : 51 H_2O : 0.1 (SDA²⁺)O : 0.05 Na_2O

Source Materials deionized
water (DI) fumed silica
(Cabosil M-5)
sodium tetraborate (Sigma-Aldrich)
sodium hydroxide (Fisher, 1N)
1,6-bis(N-cyclohexylpyrrolidinium)hexane dihydroxide (made in-house; 13.46 wt%; purity confirmed by NMR and CHN)

Batch Preparation (for 0.8 g dry product)

- (1) Combine 7.28 g DI water, 4.07 g SDA, and 1.06 g sodium hydroxide in a 23 mL Teflon liner; stir for 10 minutes.
- (2) Add 0.05 g sodium tetraborate; stir for 10 minutes.
- (3) Add 0.80 g fumed silica; mix with a spatula for 10 minutes to homogenize.^b

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 160° C
Time: 21 days^c
Agitation: 43 rpm (tumbling oven)

Product Recovery

- (1) Remove reactor from oven and quench
- (2) Filter (with glass-frit funnel) to recover solids
- (3) Wash product with ~300 mL DI water
- (4) Air dry overnight while pulling vacuum on frit
- (5) Dry at ambient temperature or at 80°C
- (6) Yield: 0.51 g

Product Characterization

XRD: SEW
Elemental analysis: 59.8 SiO_2 : 1 B_2O_3 ^d
Crystal size and habit: clusters of thin platelet-like crystals
Micropore volume of the sodium-form is 0.16 cc/g by nitrogen adsorption

Reference

- [1] A. W. Burton Jr., U.S. Patent 7,820,141 B2 (2010)
- [2] D. Xie, L. B. McCusker, and C. Baerlocher, *J. Amer. Chem. Soc.* 133 (2011) 20604

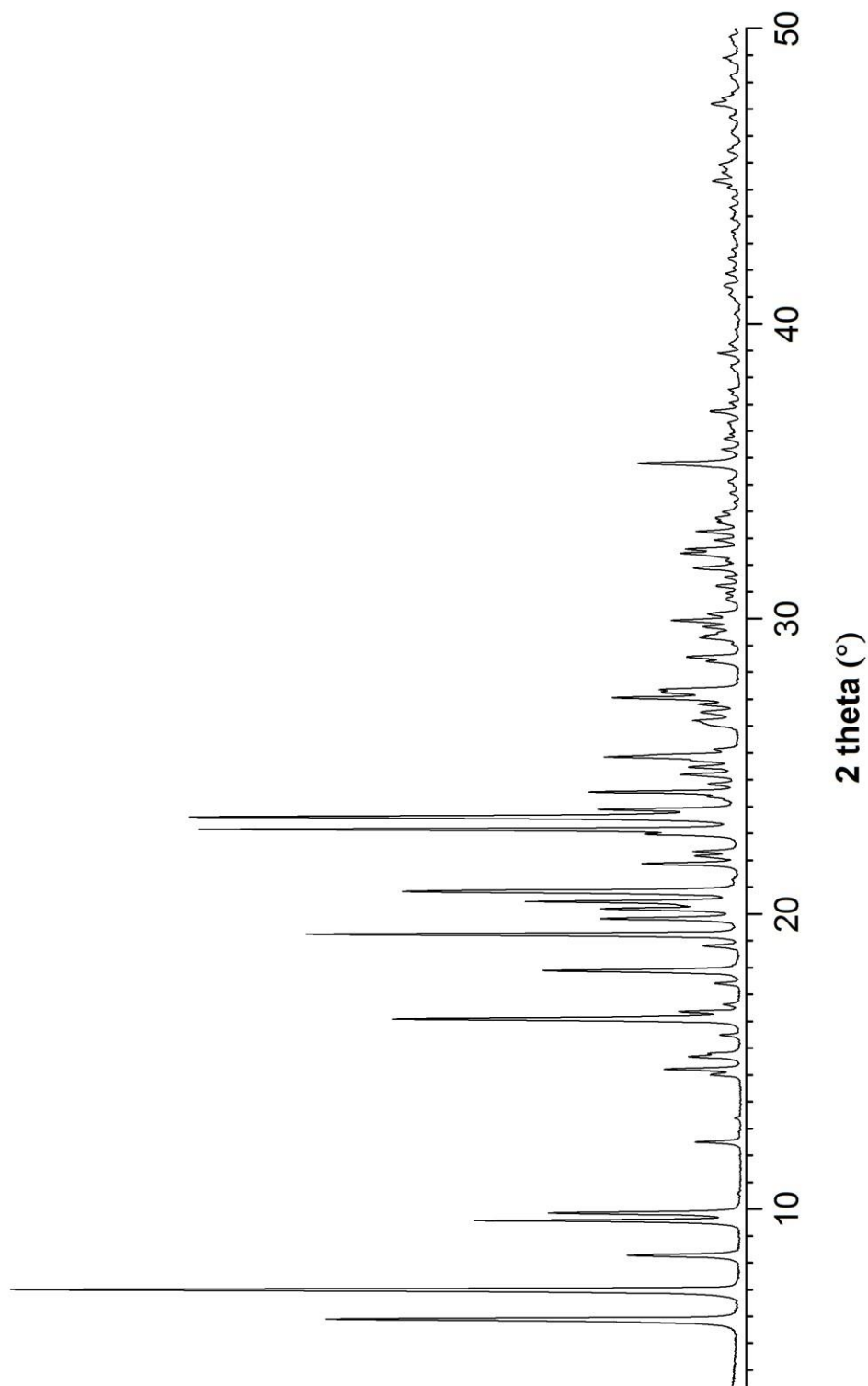
Notes

- a. calcined form; from ref. 2
- b. pH of the final gel is 13.16
- c. adding 5 wt% (to SiO₂) seeds of as-made SEW and increasing the synthesis temperature to 170 °C will reduce the synthesis time to six days
- d. as-synthesized; organic content not specified

SEW

SSZ-82

Si(98), B(2)



SOD

NaBr-Sodalite

Si(50), Al(50)

Contributed by Andreas Stein

Verified by B. Schoeman and S. Kowalak

Type Material $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2 \text{NaBr}$ ^{a,b}

Method A. Stem, G. Ozin, G. Stucky [1, 2]^c

Batch Composition $\text{Al}(\text{OH})_3$ SiO_2 : 12.5 NaOH : 7.5 NaBr: 144 H_2O

Source Materials

deionized water

sodium hydroxide (Mallinckrodt, 98.7%)

sodium bromide (Mallinckroft, 99.0%)

silica sol (DuPont Ludox HS-40, 40% SiO_2) aluminum hydroxide (Fisher, 99.8%)

Batch Preparation (for 34 g dry product)

- (1) [300 mL water + 60.0 g sodium hydroxide + 154.3 g sodium bromide], stir until dissolved
- (2) [(1) + 30.0 g silica soil, stir rapidly, heat to 95°C
- (3) [200 mL water + 40.0 g sodium hydroxide + 15.6 g aluminum hydroxide], stir, heat at 95°C until dissolved
- (4) [Add hot (3) with hot (2)], shake gel vigorously for 5 minutes

Crystallization

Vessel: 1000 mL capped Teflon bottle

Time: 24 hours

Temperature: 95°C

Agitation: none

Product Recovery

- (1) Cool to ambient temperature
- (2) Filterd
- (3) Wash with deionized water until filtrate is bromide-free and pH ~7
- (4) Dry at 110°C
- (5) Yield; close to 100% on silica and alumina

Product Characterization

XRD: SOD, no other crystalline or amorphous material detected

Elemental Analysis: $\text{Na}_{7.5}\text{Br}_{18}(\text{AlSiO}_4)_6$ ^e

Crystal Size and Habit: 50-500 nm^f dodecahedra, some malformed dodecahedra and penetration twins

References

- [1] A. Stem, G. A. Ozin, G. Stucky, J. Am. Chem Soc. 114 (1992) 5171

- [2] A. Stem, G. Ozin, in *Advances in the Synthesis and Reactivity of Solids*, Vol. 2, JAI Press, Greenwich, CT, 1994, p. 93
- [3] D. J. Schipper, C. Z. van Doorn, P. T. Bolwijn, *J. Am. Ceram. Soc.* 55 (1972) 256
- [4] R. R. Neurgaonkar, F. A. Hummel, *Mater. Res. Bull.* 11(1976) 61
- [5] I. F. Chang, *J. Electrochem. Soc.* 121 (1974) 815
- [6] S. C. Zilio, V. S. Bagnato, *J. Phys. Chem.* 88 (1984) 1373

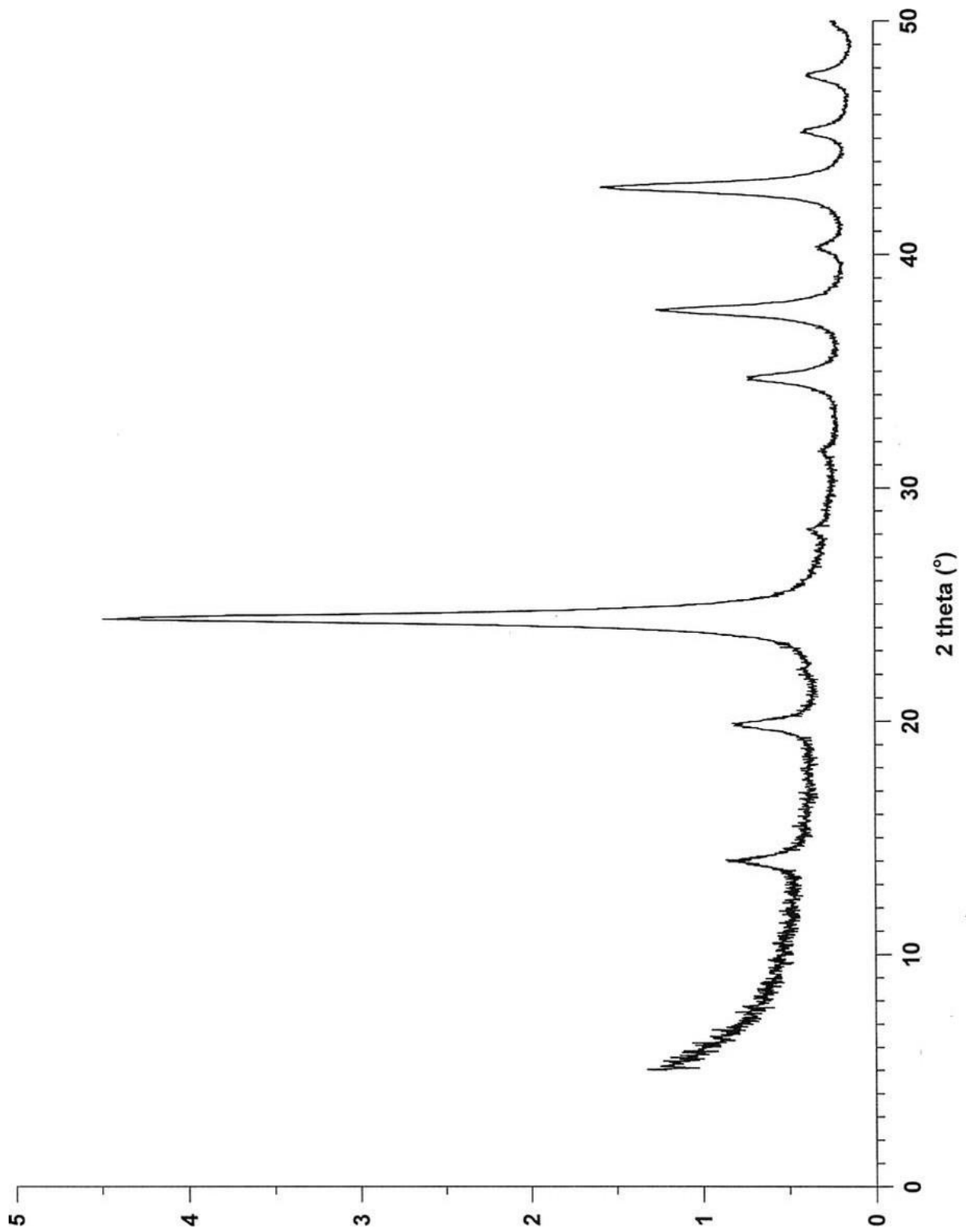
Notes

- a. Other anions that can be introduced by various methods include OH^- , Cl^- , Br^- , I^- , CN^- , SCN^- , ClO_3^- , ClO_4^- , BrO_3^- , NO_2^- , N_3^- , $\text{B}(\text{OH})_4^-$, $\text{Al}(\text{OH})_4^-$, HCO_2^- , CH_3CO_2^- , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , S_2^{2-} , SO_3^{2-} , SO_4^{2-} , MnO_4^- , SeO_4^{2-} , MoO_4^{2-} , TeO_4^{2-} , WO_4^{2-} , PO_4^{3-} , e^- .
- b. Synthesis of NaOH-SOD: $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2 \text{NaOH} \cdot 8 \text{H}_2\text{O}$: batch $\text{Al}(\text{OH})_3$ SiO_2 : 5 NaOH : 41 H_2O . [1] Extensive washing, especially with hot water, results in extraction of hydroxide and sodium ions.
- c. Other methods for sodalite synthesis include sintering [3, 4] and structure conversion. [5]
- d. Alternately: centrifuge for 20 minutes, decant mother liquor, add fresh water and disperse the solid phase by shaking, followed by centrifuging. Repeat six times.
- e. Low cation and anion content is due to formation of some OH^- containing cages (or anion-free cages in washing). These can be removed by heating the sodalite with NaBr. [6]
- f. The larger crystallites are obtained in more dilute solutions.

SOD

NaBr-Sodalite

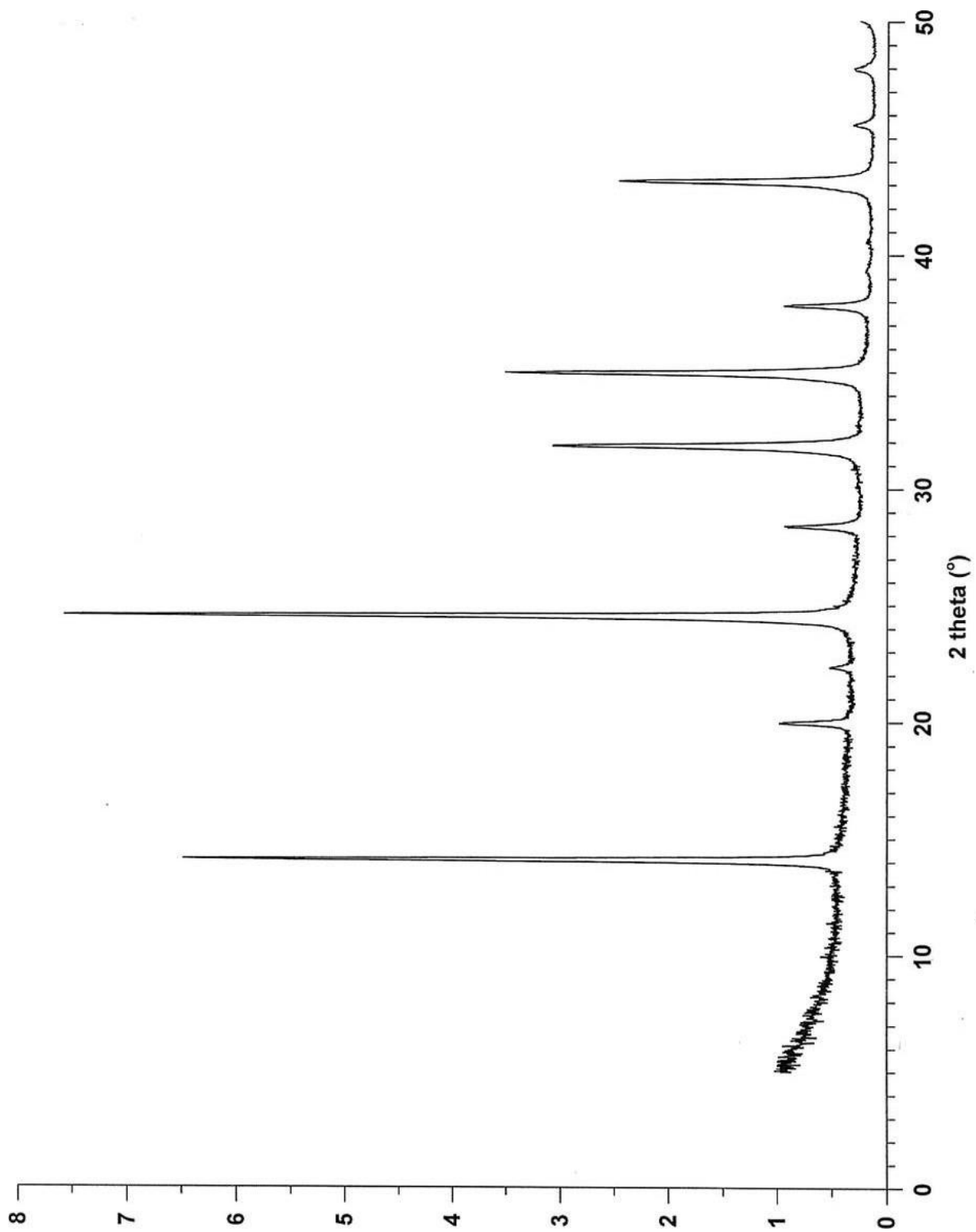
Si(50), Al(50)



SOD

Hydroxy-Sodalite

Si(50), Al(50)



Contributed by Suk Bong Hong

Verified by J. Rimer, M. Hartmann, T. Okubo, S. H. Cha

Type Material: $\text{Na}_{4.0}(\text{SDA})_{3.3}[\text{Al}_{8.9}\text{Si}_{63.1}\text{O}_{144}] : w \text{ H}_2\text{O}$ ($w \sim 8$)
(SDA = 1,4-bis[*N*-methylpyrrolidinium]butane (1,4-MPB))

Method: S. B. Hong, E. G. Lear, P. A. Wright, W. Zhou, P. A. Cox, C. -H. Shin, J. -H. Park, I. -S. Nam [1]

Batch Composition: 4.5 (1,4-MPB) : 15.0 Na_2O : 1.0 Al_2O_3 : 30 SiO_2 : 1200 H_2O

Source Materials

deionized water
1,4-MPB dibromide^a
sodium hydroxide (Aldrich, 50% NaOH solution)
aluminium nitrate nonahydrate (Junsei, 98%, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
silicon dioxide (Degussa Aerosil 200 or Cabot Cab-O-Sil M5)

Batch Preparation (for 2 g dry product)

- (1) [66.57 g water + 1.15 g aluminium nitrate nonahydrate + 8.00 g sodium hydroxide (50% solution)], stir until dissolved
- (2) [(1) + 6.00 g silica] mix thoroughly and stir for 30 minutes
- (3) [(2) + 5.46 g 1,4-MPB dibromide], stir for 24 hours^b

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 160 °C
Time: 7 days
Agitation: 100 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 90 °C
- (4) Yield: 1.97 g

Product Characterization

XRD: STI; competing phase: ANA (when $\text{NaOH}/\text{SiO}_2 > 1.13$)
Elemental analysis: Si/Al = 6.5 ~ 7.5 [1]
Crystal size and habit: agglomerates and intergrown rectangular plates of about $0.5 \times 1.0 \times 0.1 \mu\text{m}^3$

Reference

- [1] S. B. Hong, E. G. Lear, P. A. Wright, W. Zhou, P. A. Cox, C. -H. Shin, J. -H. Park, I. -S. Nam, *J. Am. Chem. Soc.* 126 (2004) 5817

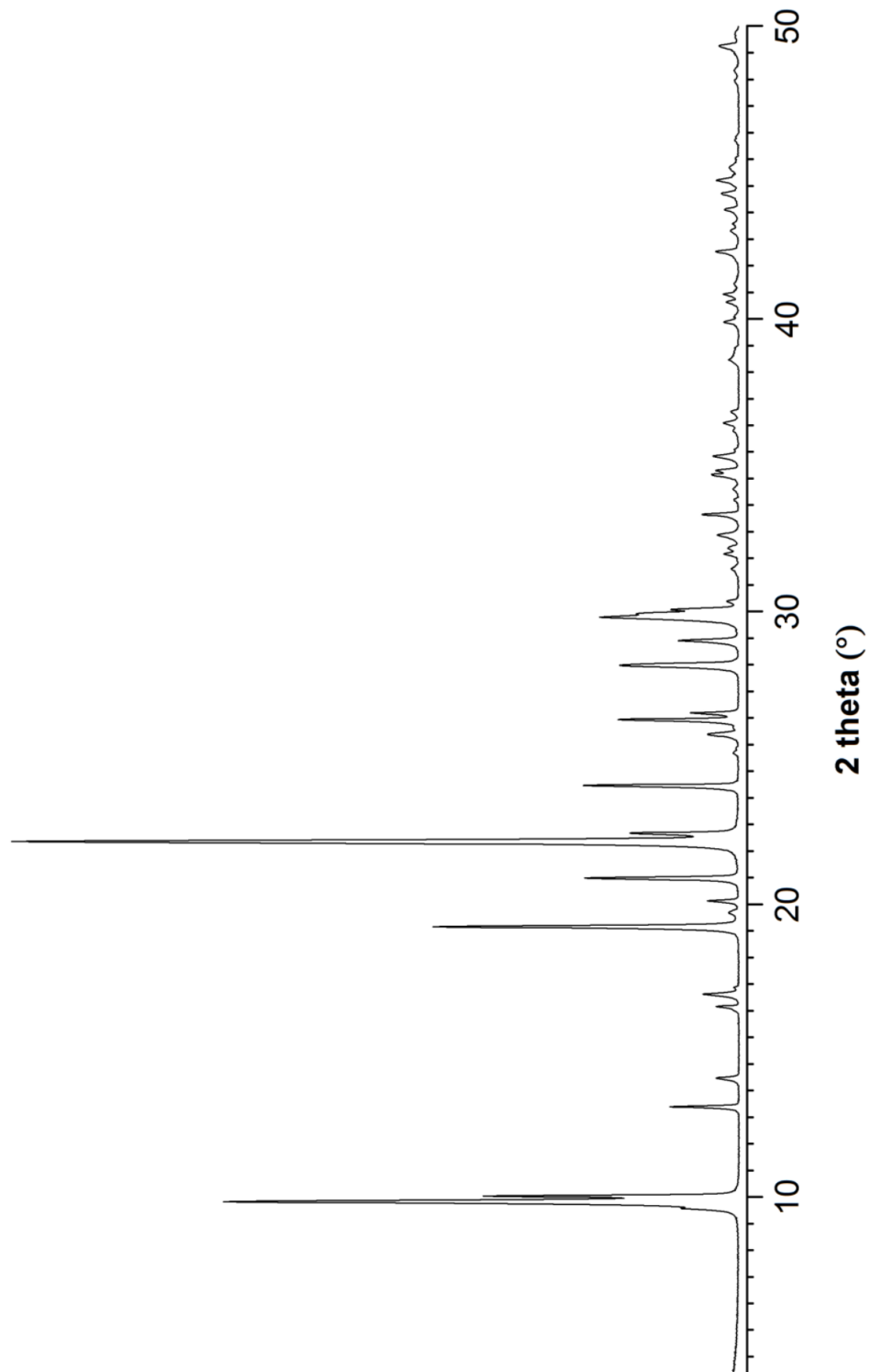
Notes

- a. The description of template preparation is given in [1]
- b. pH of the final gel is 11.8.

STI

TNU-10

Si(88), Al (12)



Contributed by M. A. Cambor and M. J. Díaz-Cabañas

Verified by S. Zones, Y. Kubota and R Bandyopadhyay

Type Material [Si₆₄O₁₂₈]

Method M. A. Cambor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R E. Morris [1]

Gel Composition SiO₂ : 0.51 TMAOH : 0.51 HF:10 H₂O^a
(TMAOH = N,N,N-trimethyl-1-adamantammonium hydroxide)

Source Materials

tetraethylorthosilicate (TEOS), Merck, (>98%)
N,N,N-trimethyl-1-adamantammonium hydroxide (0.435 mol/1000 g)^b
hydrofluoric acid (Aldrich, 48% HF)

Gel Preparation (for 5 g product)

- (1) [15.60 g TEOS + 86.10 g TMAOH (aq. 0.435 mol/1000 g)], stir until ethanol evaporation is completed and until the water is reduced as required to give H₂O/SiO₂ = 10 after addition of HF^c
- (2) [(1) + 1.56 g hydrofluoric acid], stir manually^d

Crystallization

Vessel: 60 mL stainless steel autoclave with Teflon liner
Time: 11 days
Temperature: 150 ± 2°C
Agitation: autoclaves rotated at 60 rpm

Product Recovery

- (1) Quench autoclaves in cold water; final pH ~ 8
- (2) Filter contents; wash the solid with deionized water and dry overnight at 100°C
- (3) Yield: 20 g of solid/100 g gel (98% based on SiO₂)

Product Characterization

XRD: STT (no other crystalline phases); competing phases: CHA, SSZ-31^a
Elemental Analysis (wt%): 1.20 N, 13.50 C, 2.16 H, 1.32 F^{e,f}
Crystal size and habit: large plate-like twinned crystals; broad crystal-size distribution with crystals up to 30 x 20 x 2 μm

References

- [1] M. A. Cambor, M. J. Díaz-Cabañas, P. A. Cox, I. J. Shannon, P. Lightfoot, P. A. Wright, R E. Morris, submitted to Chem. Mater.
- [2] S. I Zones, Eur. Patent 231 018 (1987)
- [3] S. I. Zones, R A. van Nordstrand, D. S. Santilli, D. M. Wilson, L Yuen, L D. Samparia, Stud. Surf. Sci. Catal. 49 (1989) 299

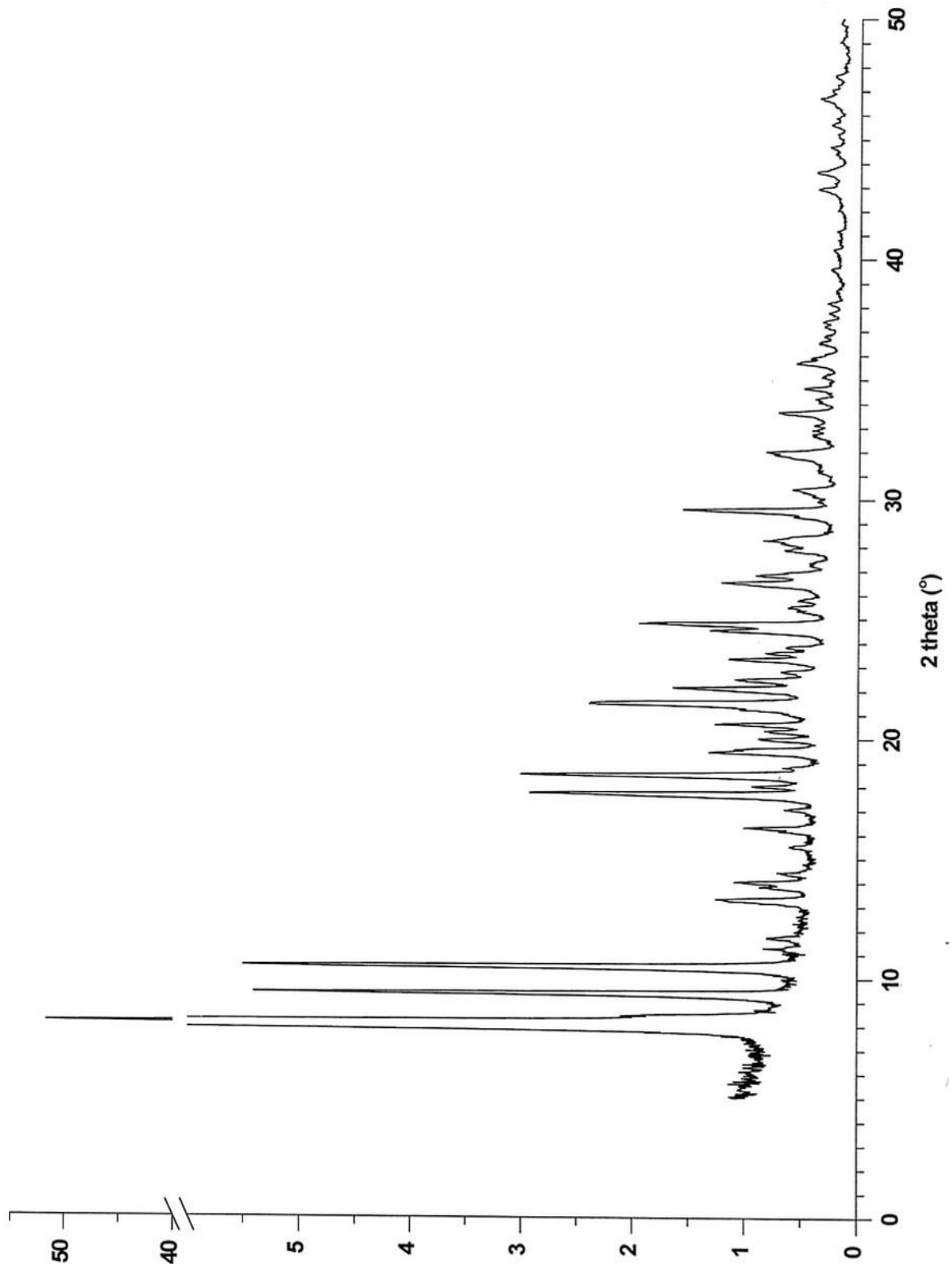
Notes

- a. Final gel composition: In the calculation of the final water to silica ratio two things should be taken into account:
- (1) Two water molecules per SiO₂ are consumed during the hydrolysis of TEOS and are eliminated from the reaction mixture according to $\text{Si}(\text{OEt})_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{EtOH}$
 - (2) Evaporation of water must be accounted for (see gel preparation). The water to silica ratio has a large effect on the phase selectivity of the crystallization: at low (<6) and high ratios (>15) pure silica CHA and SSZ-31, respectively, crystallize after short heating, although SSZ-23 is the crystallization product after prolonged heating (in the H₂O/SiO₂ range between 3 and 20). At the reported H₂O/SiO₂ ratio of 10, SSZ-23 is the only phase observed between 11 and 45 days of crystallization.
- b. Concentration of OH⁻: TMAda OH may be prepared by anion exchange of the iodide, which can be obtained by reaction of 1-adamantamine with an excess of methyl iodide at room temperature. In a typical synthesis 1-adamantamine (4.667 g) was dissolved in 50 g of chloroform. Then, 11.350 g of K₂CO₃·1.5H₂O was added and the mixture was cooled in an ice bath. 13.14 g of CH₃I was then added followed the next day by a second portion of CH₃I (6.5 g). After 7 days, the mixture was filtered and the solid washed with CHCl₃. The iodide was converted to the hydroxide by anion exchange with Dowex 1 resin. The yield in the anion exchange of TMAda-I to TMAdaOH is typically >90-95%.
- c. Evaporation of ethanol plus water can be monitored by the change in weight. In this example a total weight loss of 76.61 g was necessary. The time needed for this process depends on many factors (total batch weight, size of the vessel, temperature, etc.) and is typically several hours. Complete evaporation of ethanol may be checked by ¹H NMR of the reaction mixture.
- d. A white fluid slurry is obtained after addition of HF.
- e. Corresponding to [(TMAda⁺)_{4.1}F⁻_{3.3}(OH⁻)_{0.8}(H₂O)_{1.6}][SiO]₆₄ per unit cell (OH⁻ is included for electroneutrality and relates to a small concentration of connectivity defects in the as-made material).
- f. Al may be introduced into SSZ-23 either in hydroxide medium (as in Ref. [2] and [3] and, apparently more favorably, in fluoride medium (unpublished results).

STT

SSZ-23

Si(100)



TON

ZSM-22

Si(95), Al(05)

Contributed by Gunter Kühn

Verified by M. Derewinski and Y. Oumi

Type Material $K_{0.1}Al_{0.6}Si_{23.4}O_{48}(DAO)_{0.86}^a$ (DAO = 1,8-diamino-octane)

Method E. W. Valyocsik [1]

Batch Composition 8.9 K₂O : Al₂O₃ : 90 SiO₂ : 3 K₂SO₄: 27.3 DAO : 3588 H₂O

Source Materials

deionized water

aluminum sulfate (99+% Al₂(SO₄)₃ · 18 H₂O)

potassium hydroxide (87.9% KOH)

1,8-diamino-octane (99+%)

silica sol (Dupont AS-30, ammonia stabilized, 30% SiO₂)

Batch Preparation (for 7.5 g dry product)

- (1) [18.2 g water + 1.76 g aluminum sulfate], stir until dissolved
- (2) [18.2 g water + 4.0 g potassium hydroxide], stir until dissolved
- (3) [72.8 g water + 10.4 g 1,8-diamino-octane], stir until dissolved
- (4) [26.95 g water + 47.65 g silica sol], mix well
- (5) [(1) + (2)], mix well
- (6) [(3) + (5)], add (3) to (5); blend
- (7) [(4) + (6)], add (4) to (6), stir for 30 minutes^b

Crystallization

Vessel: stirred autoclave with stainless steel liner

Incubation: 24 hours at room temperature^c

Temperature: 160 °C

Time: 2-3 days

Agitation: vigorous stirring^d

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 110 °C
- (4) Yield: 7.5 g (near 100% on Al₂O₃)

Product Characterization

XRD: TON; competing phase: MEL (trace)^d

Elemental Analysis: 0.2 K₂O : Al₂O₃ : 39 SiO₂ : 1.44 DAO

Crystal size and habit: needles^e

Reference

- [1] E. W. Valyocsik, US Patent 4 902 406

Notes

- a. Missing cations assumed to be protonated DAO.
- b. Reaction mixture becomes cloudy but does not gel.
- c. It is not certain that aging (or seeding) is beneficial.
- d. Ref. [1] recommends a stirring rate of 400 rpm; static preparations or slow stirring produce MEL or mixtures of MEL + TON.
- e. The size of the crystallites decreases with increasing stirring rate.

TUN

TNU-9

Si(95), Al(5)

Contributed by Suk Bong Hong

Verified by J. Rimer, M. Hartmann, T. Okubo, W. Chaikittisilp

Type Material: $\text{Na}_{1.5}(\text{SDA})_{7.1}[\text{Al}_{9.3}\text{Si}_{182.7}\text{O}_{384}] \cdot w \text{H}_2\text{O}^a$ ($w \sim 28$)

(SDA = 1,4-bis[*N*-methylpyrrolidinium]butane (1,4-MPB))

Method: S. B. Hong, H. -K. Min, C. -H. Shin, P. A. Cox, S. J. Warrender, P. A. Wright [1]

Batch Composition: 4.5 (1,4-MPB) : 11.0 Na_2O : 1.0 Al_2O_3 : 30 SiO_2 : 1200 H_2O

Source Materials

deionized water

1,4-MPB dibromide^b

sodium hydroxide (Aldrich, 50% NaOH solution)

aluminum nitrate nonahydrate (Junsei, 98%, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)

silicon dioxide (Degussa Aerosil 200 or Cabot Cab-O-Sil M5)

Batch Preparation (for 3 g dry product)

(1) [62.62 g water + 1.18 g aluminum nitrate nonahydrate + 5.42 g sodium hydroxide (50% solution)], stir until dissolved

(2) [(1) + 5.54 g silica], mix thoroughly and stir for 30 minutes

(3) [(2) + 5.46 g 1,4-MPB dibromide], stir for 24 hours^c

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 160 °C

Time: 14 days^d

Agitation: 100 rpm

Product Recovery

(1) Dilute reaction mixture with water

(2) Filter and wash with water

(3) Dry at ambient temperature or at 90 °C

(4) Yield: 3.2 g

Product Characterization

XRD: TUN; competing phase: MOR (when $\text{SiO}_2/\text{Al}_2\text{O}_3 < 30$)

Elemental analysis: 1,4-MPB is approximately 12 wt.% and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 39$ [1]

Crystal size and habit: rod-like crystals with ca. 1.0 μm in length and 0.3 μm in diameter

Reference

[1] S. B. Hong, H. -K. Min, C. -H. Shin, P. A. Cox, S. J. Warrender, P. A. Wright, J. Am. Chem. Soc. 129 (2007) 10870

- [2] S. B. Hong, E. G. Lear, P. A. Wright, W. Zhou, P. A. Cox, C. -H. Shin, J. -H. Park, I. -S. Nam, *J. Am. Chem. Soc.* 126 (2004) 5817

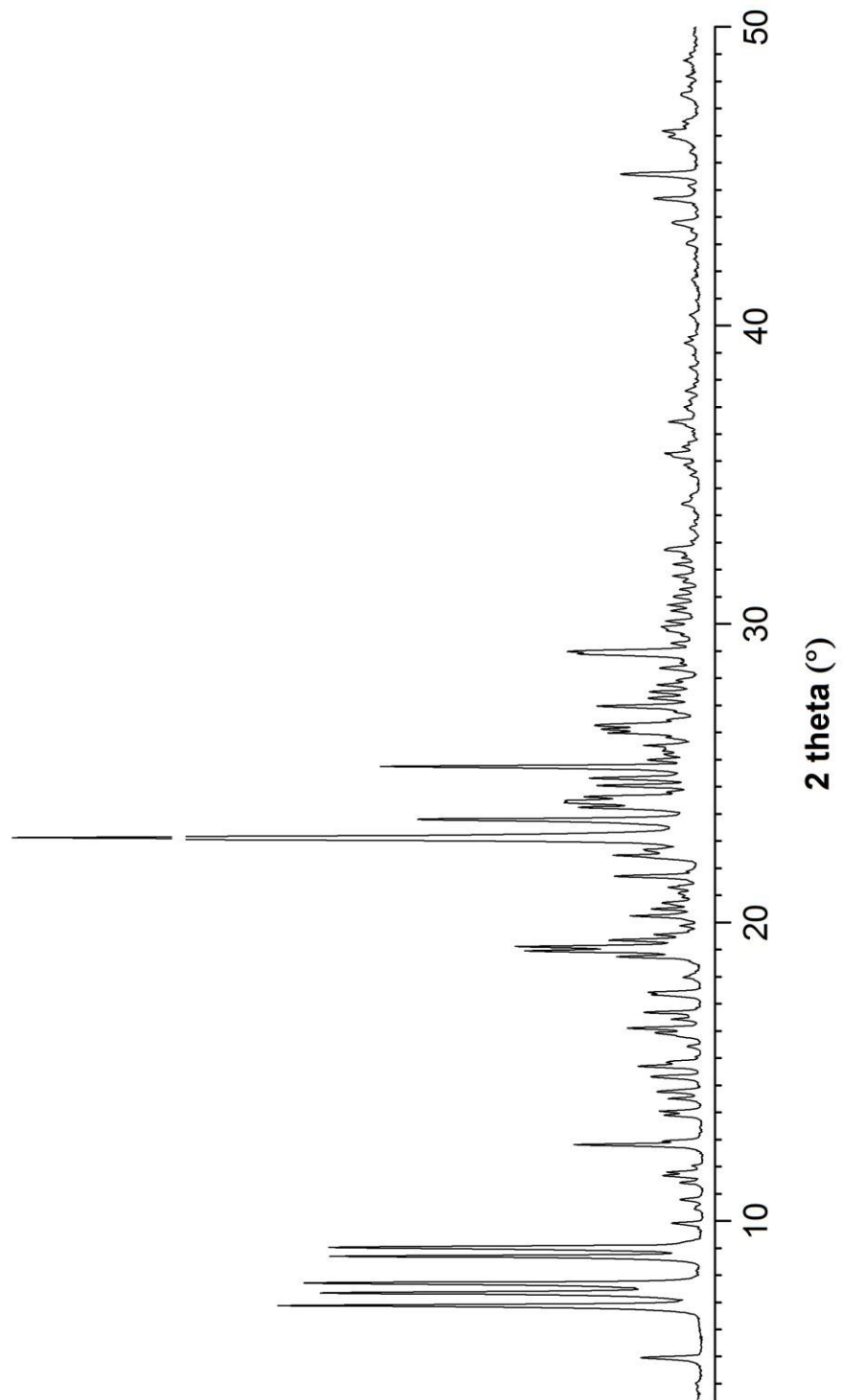
Notes

- a. The imbalance between the amount of Al and the sum of organic and alkali cations indicates that a fraction of the *N*-methylpyrrolidinium ions occluded within TNU-9 serves as spacefilling species rather than as charge-compensating cations.
- b. The description of template preparation is given in [2].
- c. pH of the final gel is 11.5.
- d. After about 7 days of heating, MCM- 22(P) is first crystallized. Continuing the crystallization for more than 14 days produces fully crystalline TUN.

TUN

TNU-9

Si(95), Al(5)



UOS

IM-16

Si(57.8), Ge(42).2

Contributed by Jean-Louis Paillaud

Verified by Y. Kubota, C. Kirschhock, W. Schmidt

Type Material: $[(C_6N_2H_{11})_{6.88}] [Si_{55.5}Ge_{40.5}O_{192}F_{6.88}]$
(SDA = 1-ethyl-3-methyl-imidazol-3-ium)

Method: Y. Lorgouilloux, M. Dodin, J.-L. Paillaud, P. Caullet, L. Michelin, L. Josien, O. Ersen, N. Bats [1]

Batch Composition: 0.5 SiO₂ : 0.5 GeO₂ : 1 SDAOH/Br : 1 HF : 20 H₂O

Source Materials

deionized water

1-ethyl-3-methyl-imidazol-3-ium bromide (98%, Solvionic)

resin Dowex[®] SBR LC NG, OH Form (Supelco)

hydrofluoric acid (HF, 40% in water, Carlo Erba),

amorphous germanium oxide GeO₂ (>99.99%, Aldrich)

silica SiO₂ (Degussa Aerosil 200)

Batch Preparation (for 0.38 g dry product)

(1) [10 g 1-ethyl-3-methyl-imidazol-3-ium bromide + water + 52 g Dowex[®]] in a polypropylene flask,^a stir overnight, remove Dowex[®] by filtration, gently rotoevaporate the water to concentrate the solution to more than 2 mol/L^b

(2) [5.08 mL solution (1)^c + 0.58 g germanium oxide] in a polypropylene beaker, stir until dissolved^d

(3) [(2) + 0.333 g Aerosil], stir

(4) [(3) + slowly 487 μL HF], stir^{e,f}

Crystallization

Vessel: 20 mL Teflon-lined stainless steel autoclave

Temperature: 170° C

Time: 14 days

Agitation: no

Product Recovery

(1) Dilute reaction mixture with water

(2) Filter and wash with water

(3) Dry at ambient temperature or at 90°C

(4) Yield: 0.78 g

Product Characterization

XRD: **UOS**; competing phase^e: MFI (when Si / Ge > 1.5)

Elemental analysis: 1.37 SiO₂ : GeO₂

Crystal size and habit: thin plate-like crystals displaying prismatic shape (reminding the one of MFI) with dimensions between 1 and 20 μm

Reference

- [1] Y. Lorgouilloux, M. Dodin, J.-L. Paillaud, P. Caullet, L. Michelin, L. Josien, O. Ersen, N. Bats, *Journal of Solid State Chemistry* 182 (2009) 622

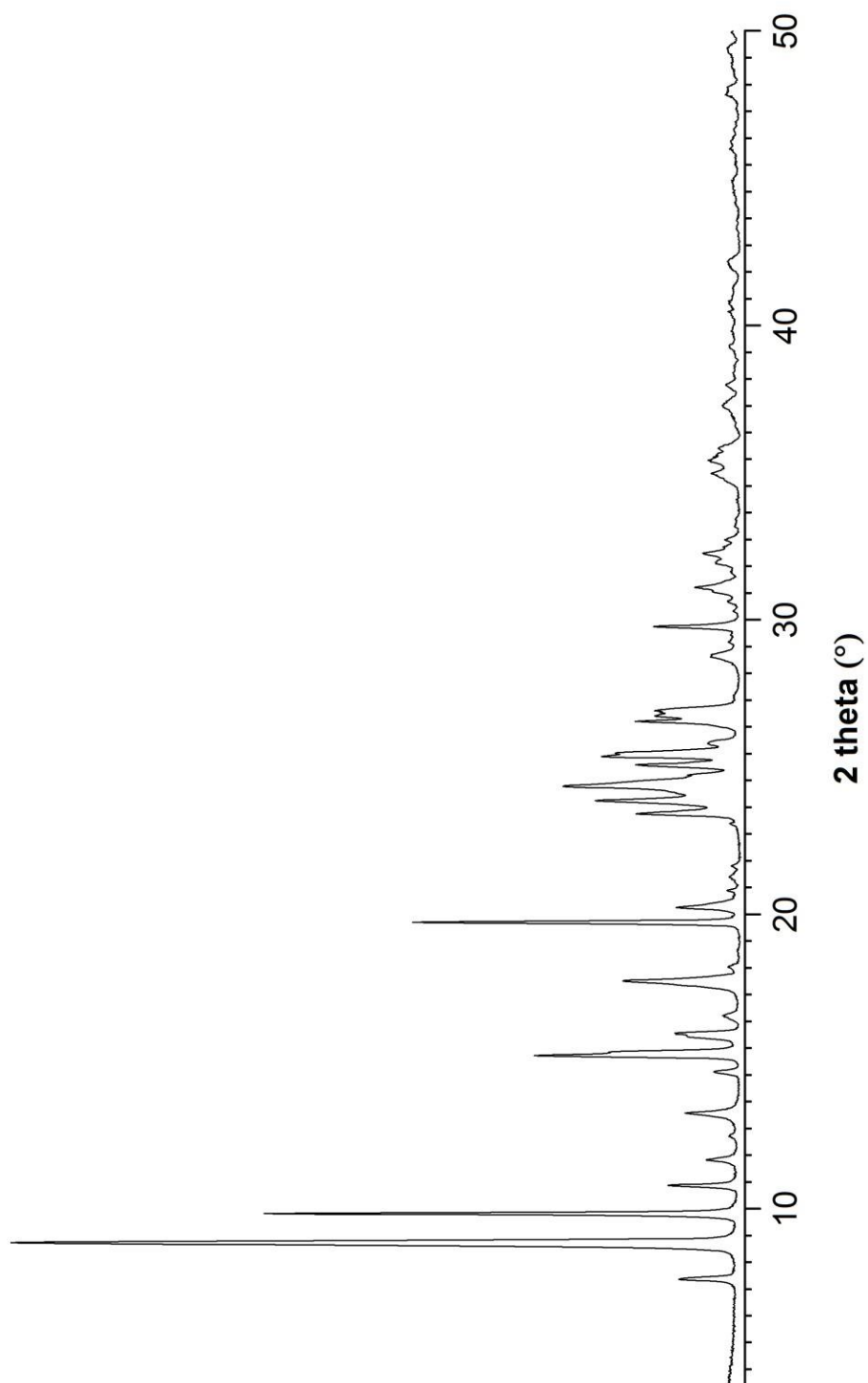
Notes

- a. The water volume is such that the height of the solution is twice the resin layer in the flask.
- b. The exchange rate ($\text{Br}^- \rightarrow \text{OH}^-$) is about 95 %, which is determined by acid-base titration and liquid proton NMR. If necessary, a second exchange may be achieved if the first exchange rate is too low.
- c. Here the concentration of the SDA solution is 2.2 mol/L.
- d. Clear solution is obtained
- e. Translucent gel, low viscosity, adjust the water content (keep to evaporate at room temperature under stirring or add water) to obtain the right stoichiometry.
- f. pH of final mixture gel is 9.5.

UOS

IM-16

Si(57.8), Ge(42).2



Contributed by Jean-Louis Paillaud

Verified by Y. Kubota, W. Schmidt

Type Material: $[(C_{16}H_{38}N_2)_{5.5} (OH^-)_{11} (H_2O)_2][Si_{125.7}Ge_{50.3}O_{352}]$
(SDA = decamethonium)

Method: Y. Lorgouilloux, M. Dodin, E. Mugnaioli, C. Marichal, P. Caullet, N. Bats, U. Kolb, J.-L. Paillaud [1]

Batch Composition: 0.6 SiO₂ : 0.4 GeO₂ : 0.25 SDA(OH/Br)₂ : 10 H₂O

Source Materials

deionized water

decamethonium bromide (98%, Fluka)

resin Dowex[®] SBR LC NG, OH Form (Supelco)

amorphous germanium oxide GeO₂ (>99.99%, Aldrich)

silica (SiO₂, Degussa Aerosil 200)

Batch Preparation (for 1.08 g dry product)

(1) [10 g decamethonium bromide + water + 48 g Dowex[®]] in a polypropylene flask,^a stir overnight, remove Dowex[®] by filtration, gently rotoevaporate the water to concentrate the solution to about 0.5 mol/L^b

(2) [0.753 g Aerosil + 11.03 g solution (1)^c + 0.836 g germanium oxide] in a polypropylene beaker, evaporate under stirring until it reaches a total weight of 3.65 g

(3) [(2) + slowly 288 μL HF], stir manually with a non metallic spatula (ideally with a Teflon stirrer)^{d,e}

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 170° C

Time: 14 days

Agitation: no

Product Recovery

(1) Dilute reaction mixture with water

(2) Filter and wash with water

(3) Dry at ambient temperature or at 70°C

(4) Yield: 1.08 g

Product Characterization

XRD: UOV; competing phase: MFI when Si/Ge < 1

Elemental analysis: 2.5 SiO₂ : GeO₂^f

Crystal size and habit: rhombus shaped plate-like crystals with dimension 1 μm.

Reference

- [1] Y. Lorgouilloux, M. Dodin, E. Mugnaioli, C. Marichal, P. Caullet, N. Bats, U. Kolb, J.-L. Paillaud, RSC Advances 4 (2014) 19440

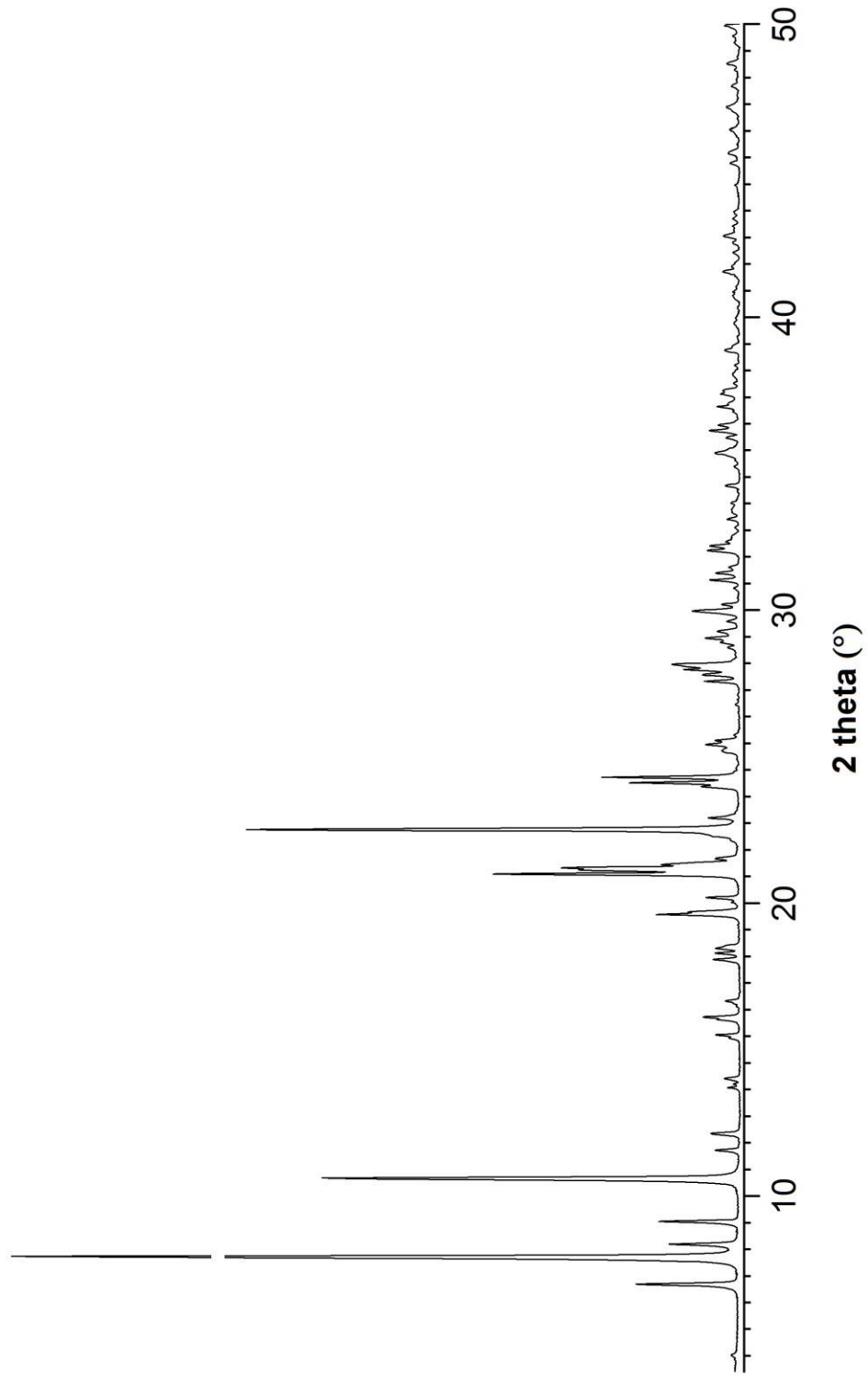
Notes

- a. The water volume is such that the height of the solution is twice the resin layer in the flask.
- b. The exchange rate ($\text{Br}^- \rightarrow \text{OH}^-$) is about 95 %, which is determined by acid-base titration and liquid proton NMR. If necessary, a second exchange may be achieved if the first exchange rate is too low.
- c. Here the concentration of the SDA solution is 0.453 mol/L.
- d. Thick dough.
- e. pH of the final mixture is 14.
- f. A higher Si/Ge molar ratio is also possible with TEOS in the same procedure but the yield is low.

UOV

IM-17

Si(71.4), Ge(28.6)



UOZ

IM-10

Ge(100)

Contributed by Jean-Louis Paillaud

Verified by Y. Kubota, W. Schmidt

Type Material: $[\text{C}_{12}\text{N}_2\text{H}_{30}]_2[\text{F}_4\text{Ge}_{40}\text{O}_{80}]$
(SDA = hexamethonium)

Method: Y. Mathieu, J.-L. Paillaud, P. Caullet, N. Bats [1]

Batch Composition: 1 GeO_2 : 0.25 $\text{SDA}(\text{OH}/\text{Br})_2$: 0.5 HF : 5 H_2O

Source Materials

deionized water

hexamethonium bromide (98%, Aldrich)

resin Dowex[®] SBR LC NG, OH Form (Supelco)

hydrofluoric acid (HF, 40% in water, Carlo Erba),

amorphous germanium oxide GeO_2 (>99.99%, Aldrich)

Batch Preparation (for 0.375 g dry product)

(1) [10 g hexamethonium bromide + water + 55 g Dowex[®]] in a polypropylene flask,^a stir overnight, remove Dowex[®] by filtration, gently rotoevaporate the water to concentrate the solution to about 1 mol/L^b

(2) [6.34 g solution (1)^c + 1.74 g germanium oxide] in a polypropylene beaker, evaporate under stirring until it reaches a total weight of 2.214 g

(3) [(2) + slowly 365.7 μL HF], stir manually with a non metallic spatula (ideally with a Teflon stirrer)^{d,e}

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 170° C

Time: 7 days

Agitation: 60 rpm

Product Recovery

(1) Dilute reaction mixture with water

(2) Filter and wash with water

(3) Dry at ambient temperature or at 70°C

(4) Yield: 0.375 g

Product Characterization

XRD: UOZ; competing phase: no

Elemental analysis: GeO_2

Crystal size and habit: truncated square bipyramidal morphology, with dimension 1 μm .

Reference

- [1] Y. Mathieu, J.-L. Paillaud, P. Caullet, N. Bats, *Micropor. Mesopor. Mater.* 75 (2004) 13

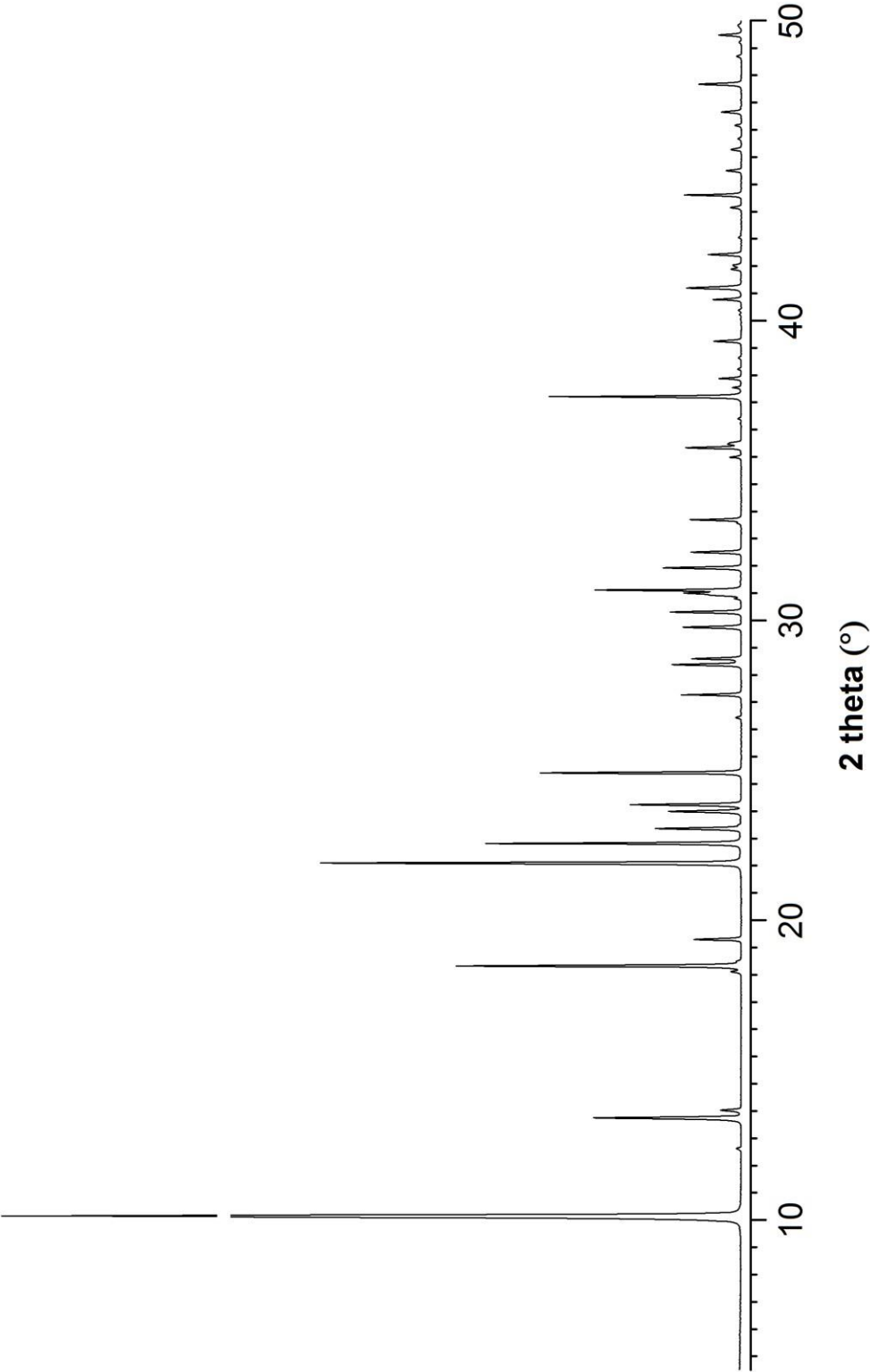
Notes

- a. The water volume is such that the height of the solution is twice the resin layer in the flask.
- b. The exchange rate ($\text{Br}^- \rightarrow \text{OH}^-$) is about 98 %, which is determined by acid-base titration and liquid proton NMR. If necessary, a second exchange may be achieved if the first exchange rate is too low.
- c. Here the concentration of the SDA solution is 0.65 mol/L.
- d. Thick dough.
- e. pH of final mixture is 6.5-7.

UOZ

IM-10

Ge(100)



Contributed by Jiri Čejka

Verified by R. Ryoo, A. Puškarić

Type Material: (SDA)₄[Si₆₄Ge₁₁Al₁O₁₅₂] : w H₂O
(SDA = 7-Ethyl-6-azoniaspiro[5.5]undecane hydroxide)

Method: M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko, P. S. Yaremov, L. G. Sarkisyan, P. Chlubná, A. Zukał, V. R. Marthala, M. Hartmann, J. Čejka [1]

Batch Composition: 0.788 SiO₂ : 0.4 GeO₂ : 0.006 Al₂O₃ : 0.45 SDAOH/Br : 30 H₂O

Source Materials

deionized water
sodium hydroxide (98%, NaOH)
1,5-dibromopentane (97 %)
2-ethylpiperidine (98%)
chloroform (99%)
sodium sulfate anhydrous (99 %, Na₂SO₄)
diethyl ether (99%)
Dowex[®] SBR LCNG, hydroxide form (Supelco)
aluminum hydroxide (r.g., Al(OH)₃)
germanium oxide (99.99 % GeO₂)
silica (Degussa Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 3.5 g dry product)

- (1) [33.1 g water + 1.34 g sodium hydroxide + 7.67 g 1,5-dibromopentane], stir in a flask
- (2) [(1) + 3.80 g 2-ethylpiperidine], add 2-ethylpiperidine to (1) drop by drop over a period of 30 min under reflux; reflux for 12 h under vigorous stirring^a; cool with an ice bath
- (3) [8.3 g water + 8.3 g sodium hydroxide], stir until dissolved, cool with ice bath
- (4) [(2) + (3)], stir, recover solid by filtration
- (5) [solid (4) + 150 ml chloroform], stir until dissolved
- (6) [(5) + 25 g sodium sulfate anhydrous], stir, left for 30 min, remove solid by filtration, evaporate about 80 ml of chloroform using rotovap
- (7) [(5) + 250 ml diethyl ether], mix, recover solid by filtration, wash with diethyl ether, dry at ambient temperature for 12 h
- (8) [solid (6)^b + 36 g water + 30 g Dowex[®]], stir for 2 h, remove Dowex[®] by filtration
- (9) [solution (7) + 0.062 g aluminum hydroxide], stir until dissolved^c
- (10) [solution (8) + 2.79 g germanium oxide], stir until dissolved^c
- (11) [(9) + 3.15 g Cabosil], stir for 30 minutes^d

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 170° C
Time: 20 days

Agitation: 60 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 90°C
- (4) Yield: 3.5 g

Product Characterization

XRD: UTL; competing phase: STF (when $Al / (Si + Ge + Al) > 0.015$ or the pH > 12.0 in initial gel)

Elemental analysis: 84 SiO₂ : 15 GeO₂ : 0.5 Al₂O₃^e

Crystal size and habit: thin platelet-like crystals

Reference

- [1] M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko, P. S. Yaremov, L. G. Sarkisyan, P. Chlubná, A. Zukal, V. R. Marthala, M. Hartmann, J. Čejka, J. Chem. Mater. 22 (2012) 15793
- [2] M. Shamzhy, O. V. Shvets, M. V. Opanasenko, D. Procházková, P. Nachtigall, J. Čejka, Adv. Porous Mater. 1 (2013) 103

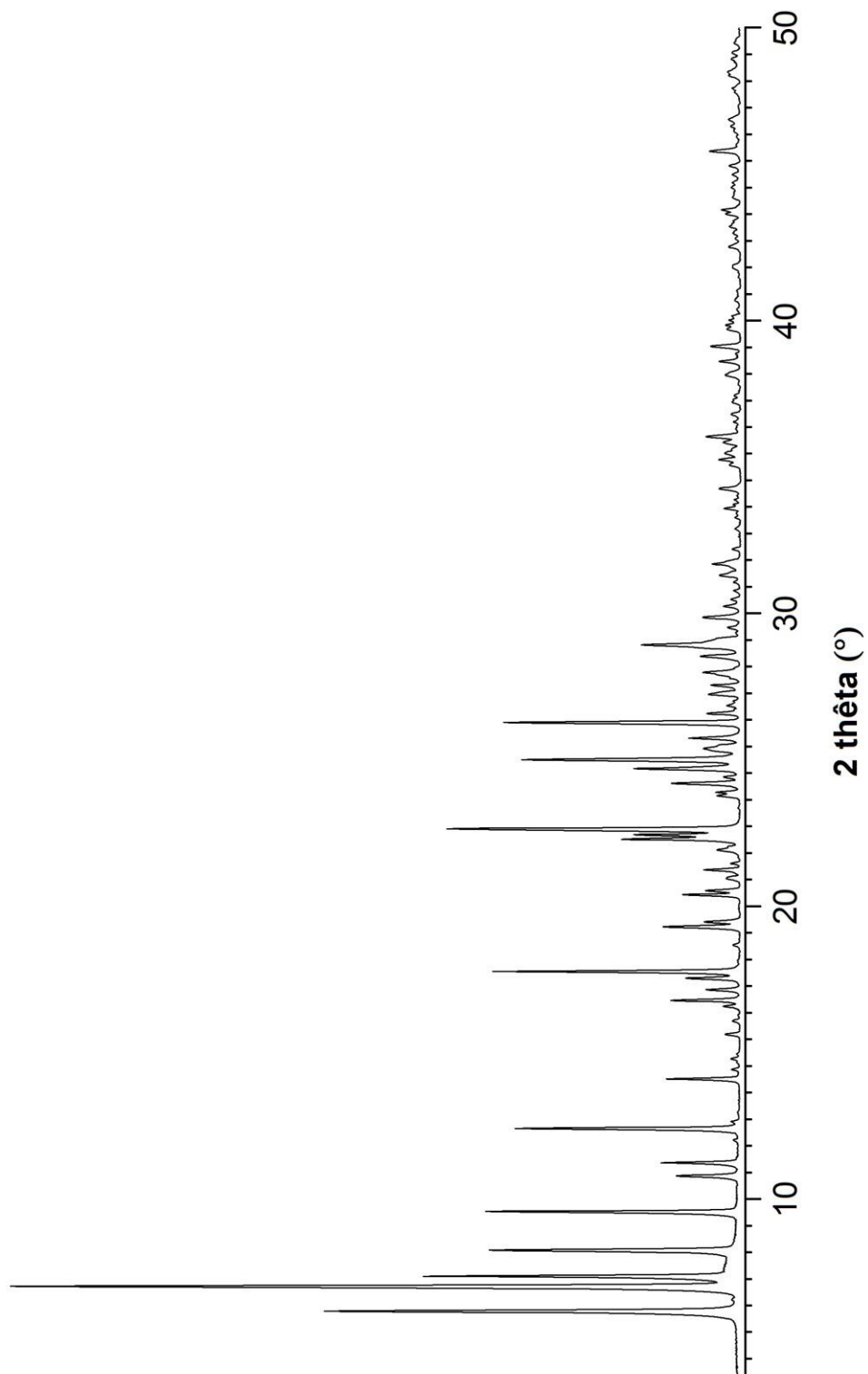
Notes

- a. The satisfactory mixing of two phases at > 1000 rpm.
- b. 90 % yield of SDA
- c. Clear solution
- d. pH of final gel is 12.0. The required amount of 1M SDAOH solution or 5 M HCl was added to the above mixture under stirring to adjust the pH of the gel.
- e. According to Ref. [1] and [2] the chemical composition of the product depends on the pH of the final gel.

UTL

Al-IM-12

Si(84), Ge(15), Al(1)



Contributed by Jiri Čejka

Verified by R. Ryoo, A. Puškarić

Type Material: (SDA)₄[Si₆₃Ge₁₂B₁O₁₅₂] : w H₂O
(SDA = 7-Ethyl-6-azoniaspiro[5.5]undecane hydroxide)

Method: O. V. Shvets, M. V. Shamzhy, P. S. Yaremov, Z. Musilová, D. Procházková, J. Čejka [1]

Batch Composition: 0.74 SiO₂ : 0.4 GeO₂ : 0.03 B₂O₃ : 0.3 SDAOH/Br : 30 H₂O

Source Materials

deionized water
sodium hydroxide (98 %, NaOH)
1,5-dibromopentane (97 %)
2-ethylpiperidine (98%)
chloroform (99%)
sodium sulfate anhydrous (99 %, Na₂SO₄)
diethyl ether (99%)
Dowex[®] SBR LCNG (Supelco)
boric acid (99.99%, H₃BO₃)
germanium oxide (99.99 % GeO₂)
silica (Degussa Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 3.2 g dry product)

- (1) [22.0 g water + 0.89 g sodium hydroxide + 5.11 g 1,5-dibromopentane], stir in a flask
- (2) [(1) + 2.53 g 2-ethylpiperidine], add 2-ethylpiperidine to (1) drop by drop over a period of 30 min under reflux; reflux for 12 h under vigorous stirring^a; cool with an ice bath
- (3) [5.5 g water + 5.5 g sodium hydroxide], stir until dissolved, cool with ice bath
- (4) [(2) + (3)], stir, recover solid by filtration
- (5) [solid (4) + 100 ml chloroform], stir until dissolved
- (6) [(5) + 15 g sodium sulfate anhydrous], stir, left for 30 min, remove solid by filtration, evaporate about 50 ml of chloroform using rotovap
- (7) [(5) + 150 ml diethyl ether], mix, recover solid by filtration, wash with diethyl ether, dry at ambient temperature for 12 h
- (8) [solid (7)^b + 35.9 g water + 30 g Dowex[®]], stir for 2 h, remove Dowex[®] by filtration
- (9) [solution (7) + 0.248 g boric acid], stir until dissolved^c
- (10) [solution (8) + 2.789 g germanium oxide], stir until dissolved^c
- (11) [(9) + 2.96 g Cabosil], stir for 30 minutes^d

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 170° C
Time: 11 days

Agitation: 60 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 90°C
- (4) Yield: 3.2 g

Product Characterization

XRD: UTL; competing phase: STF (when $B / (Si + Ge + B) > 0.11$ in initial gel)

Elemental analysis: 83 SiO₂ : 16 GeO₂ : 0.5 B₂O₃^e

Crystal size and habit: thin platelet-like crystals

Reference

- [1] O. V. Shvets, M. V. Shamzhy, P. S. Yaremov, Z. Musilová, D. Procházková, J. Čejka, Chem. Mater. 23 (2011) 2573

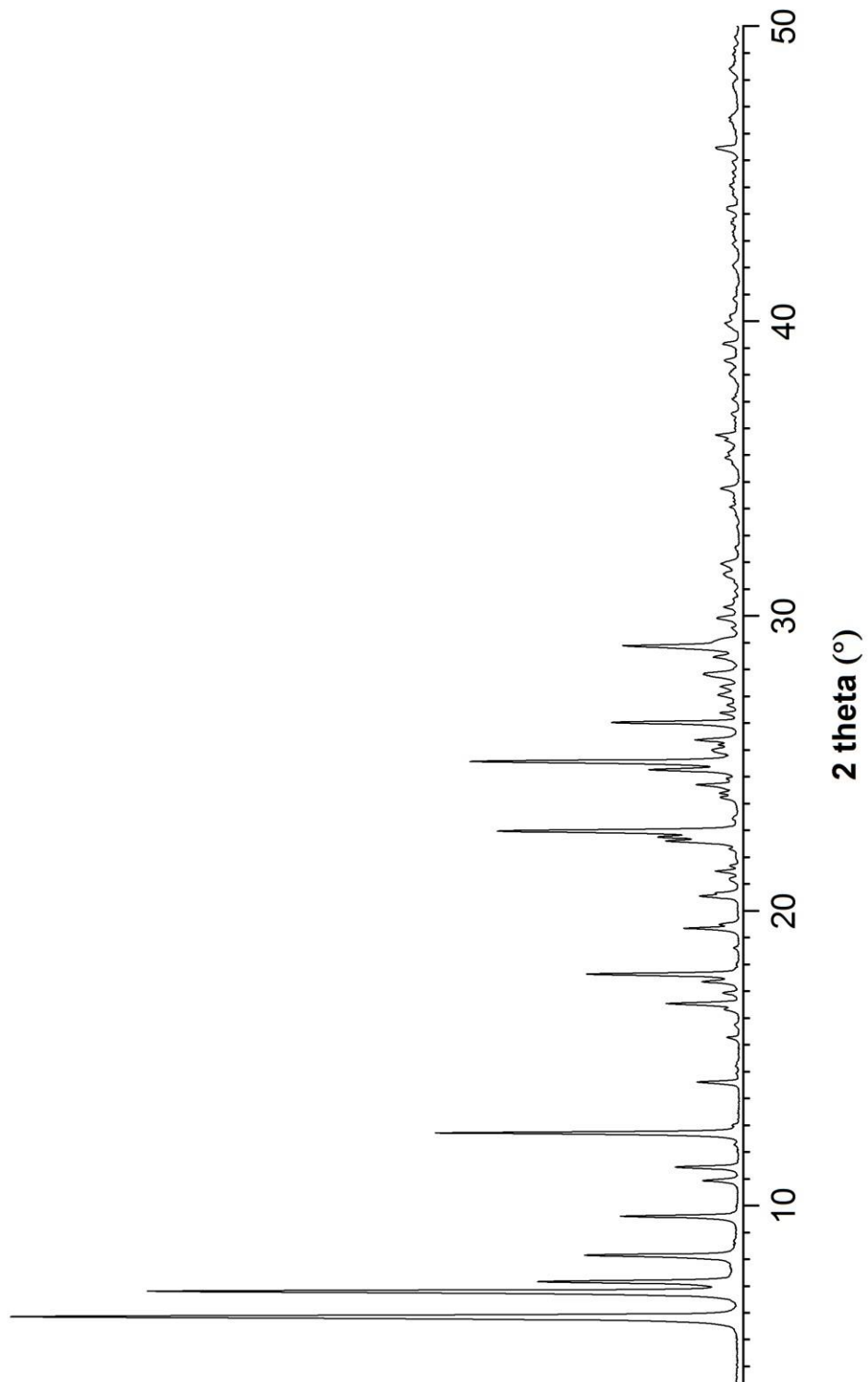
Notes

- a. The satisfactory mixing of two phases at > 1000 rpm.
- b. 90 % yield of SDA
- c. Clear solution
- d. pH of final gel is 10.096. The required amount of 1M SDAOH solution or 5 M HCl was added to the above mixture under stirring to adjust the pH of the gel.
- e. According to Ref. [1] the chemical composition of the product depends on the pH of the final gel.
- f. An additional aqueous solution of sodium hydroxide could be added into the mixture until SDA was precipitated.

UTL

B-IM-12

Si(83), Ge(16), B (1)



Contributed by Jiri Čejka

Verified by R. Ryoo, A. Puškarić, J. Bronic, M. Derewinski

Type Material: (SDA)_{4.6}[Si₆₅Ge₁₁O₁₅₂] : w H₂O

(SDA = 6,10-dimethyl-5-azoniaspiro [4,5]decane hydroxide)

Method: J.-L. Paillaud, B. Harbuzaru, J. Patarin, N. Bats [1]

Batch Composition: 0.8 SiO₂ : 0.4 GeO₂ : 0.5 SDAOH/Br : 30 H₂O

Source Materials

deionized water

sodium hydroxide (98 %, NaOH)

1,4-dibromobutane (99 %)

2,6-dimethylpiperidine (98 %)

chloroform (99 %)

sodium sulfate anhydrous (99 %, Na₂SO₄)

diethyl ether (99 %)

Dowex[®] SBR LCNG, hydroxide form (Supelco)

germanium oxide (99.99 % GeO₂)

silica (Degussa Aerosil 200, or Cab-O-Sil M5)

Batch Preparation (for 4 g dry product)

(1) [43.5 g water + 1.76 g sodium hydroxide + 9.47 g 1,4-dibromobutane], stir in a flask

(2) [(1) + 5.0 g 2,6-dimethylpiperidine], add 2,6-dimethylpiperidine to (1) drop by drop over a period of 30 min under reflux; reflux for 12 h under vigorous stirring,^a cool in ice bath

(3) [10.9 g water + 10.9 g sodium hydroxide], stir until dissolved, cool in ice bath

(4) [(2) + (3)], stir, recover solid by filtration

(5) [solid (4) + 200 ml chloroform], stir until dissolved

(6) [(5) + 30 g sodium sulfate anhydrous], stir, left for 30 min, remove solid by filtration, evaporate about 100 ml of chloroform using rotavap

(7) [(5) + 300 ml diethyl ether], mix, recover solid by filtration, wash with diethyl ether, dry at ambient temperature for 12 h

(8) [solid (6)^b + 45 g water + 12 g Dowex[®]], stir for 2 h, remove Dowex[®] by filtration

(9) [solution (7) + 3.49 g germanium oxide], stir until dissolved^c

(10) [(8) + 4.00 g Cabosil], stir for 30 minutes^d

Crystallization

Vessel: Teflon-lined stainless steel autoclave

Temperature: 170 °C

Time: 6 days

Agitation: 60 rpm

Product Recovery

(1) Dilute reaction mixture with water

- (2) Filter and wash with water
- (3) Dry at ambient temperature or at 90°C
- (4) Yield: 3.5 g

Product Characterization

XRD: UTL; competing phase: STF (when Si / Ge > 5)
Elemental analysis: 6.5 SiO₂ : GeO₂^e
Crystal size and habit: thin platelet-like crystals

Reference

- [1] J.-L. Paillaud, B. Harbuzaru, J. Patarin, N. Bats, *Science* 304 (2004) 990
- [2] O. V. Shvets, A. Zukal, N. Kasian, N. Žilkova, J. Čejka, *Chem. Eur. J.* 14 (2008) 10134
- [3] M. V. Shamzhy, O. V. Shvets, M. V. Opanasenko, P. S. Yaremov, L. G. Sarkisyan, P. Chlubná, A. Zukal, V. R. Marthala, M. Hartmann, J. Čejka, *J. Chem. Mater.* 22 (2012) 15793

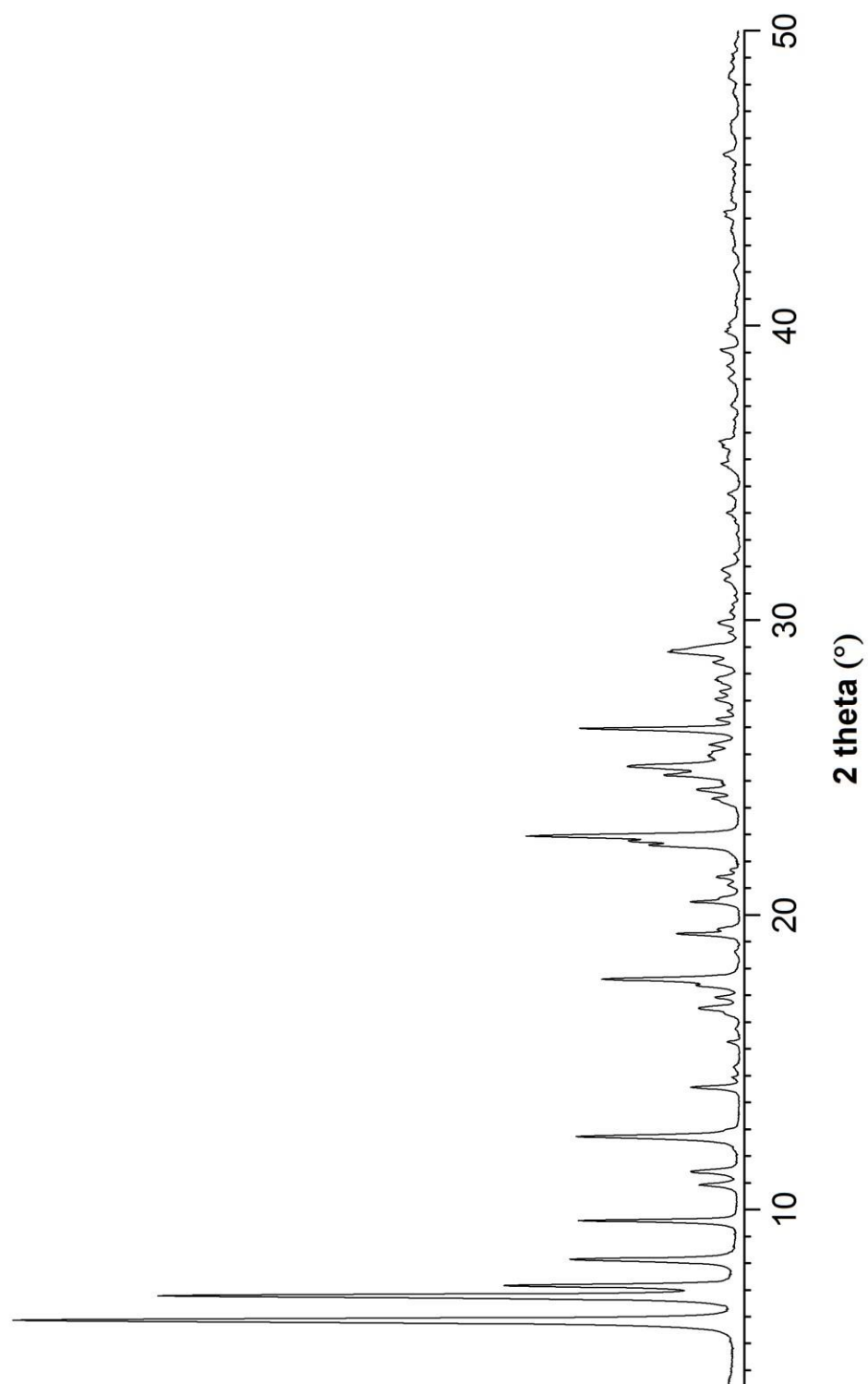
Notes

- a. The satisfactory mixing of two phases at > 1000 rpm.
- b. 95 % yield of SDA
- c. Clear solution
- d. pH of final gel is 8.0
- e. According to Ref. [2]

UTL

IM-12

Si(86), Ge(13)



VFI

VPI-5 (DPA method)

Si(95), Al(05)

Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and W. Schmidt

Type Material: $[\text{Al}_{19}\text{P}_{17}\text{O}_{72}]$: 0.4 DPA: 42 H_2O (DPA = di-n-propylamine)

Method: H. He, J. KHnowski [1]

Batch Composition: 1.00 Al_2O_3 : 1.00 P_2O_5 : 40 H_2O : 1.00 DPA^a

Source materials

distilled water

pseudoboehmite (Catapal B, 68.01 wt% Al_2O_3)

phosphoric acid (Aldrich, 88.30 wt% H_3PO_4)

di-n-propylamine (DPA) (Aldrich, > 98% pure)

Batch Preparation (for -18 g dry product)

- (1) [64.60 g water + 15.00 g pseudoboehmite], disperse alumina in water
- (2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
- (3) [(2) + 10.11 g di-n-propylamine], stir for 2 hours^b

Crystallization

Vessel: Teflon-lined autoclave

Time: 4 hours

Temperature: 142°C

Agitation: none

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
- (3) Filter and wash the crystals with distilled water
- (4) Dry in an air oven below 50°C

Product Characterization

XRD: VFI ($a_0 = 18.9752 \text{ \AA}$, $C_0 = 8.1044 \text{ \AA}$, space group P63); competing phase: $\text{AlPO}_4\text{-11}^c$

Elemental Analysis: 0.04 DPA: Al_2O_3 : 0.9 P_2O_5

Crystal Size and Habit: Crystals are spherical and aggregated, - 100 μm dia.

Reference

[1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192

Notes

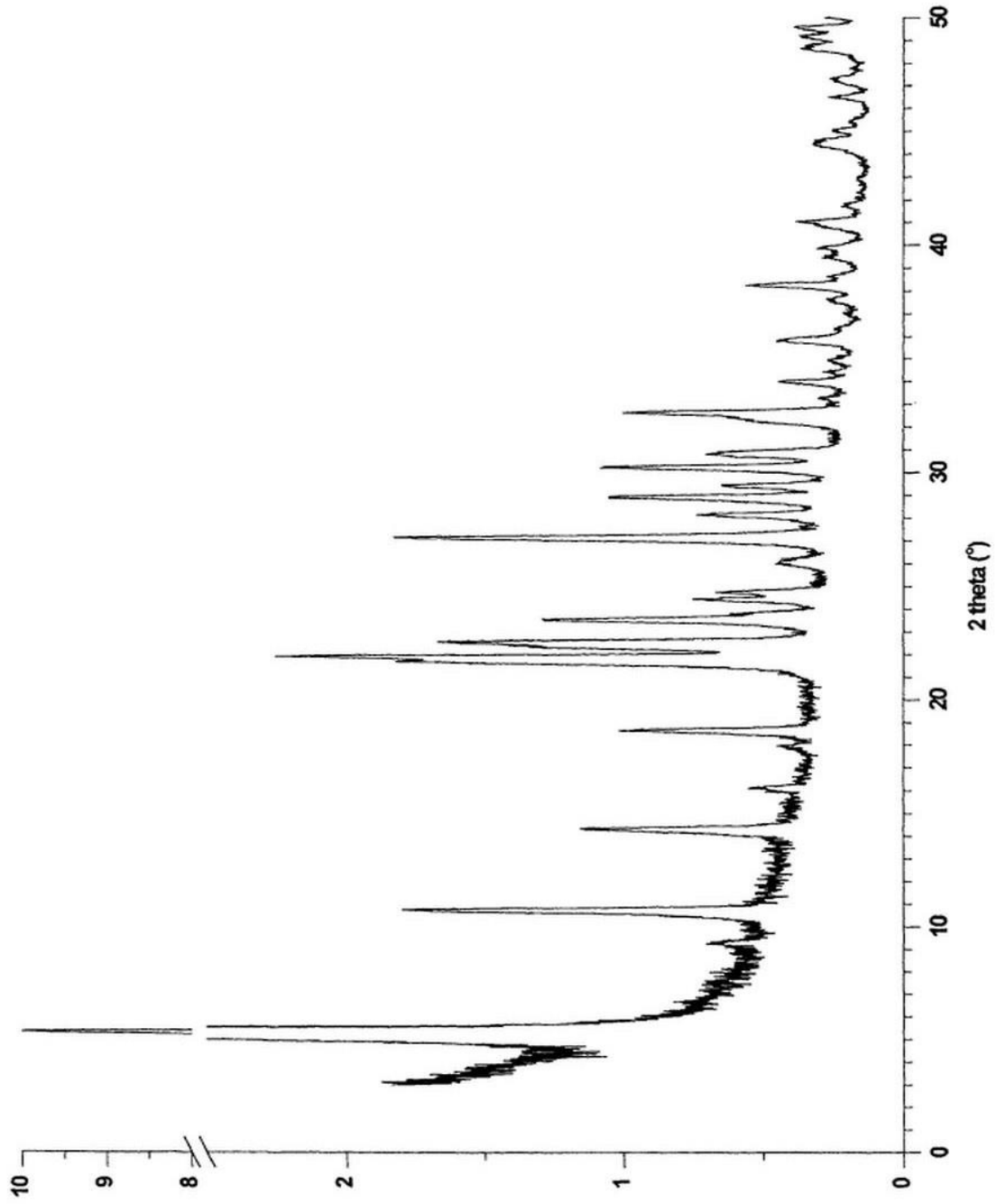
- a. The amount of water quoted includes water in pseudoboehmite (100% - wt% Al_2O_3), phosphoric acid (100% - wt% P_2O_5).

- b. After adding DPA, the gel is very viscous. Homogeneous stirring is therefore essential.
- c. $\text{AlPO}_4\text{-11}$ is found when stirring during Batch Preparation (3) is not vigorous enough.

VFI

VPI-5 (DPA method)

Si(95), Al(05)



VFI

VPI-5 (TBA method)

Al(50), P(50)

Contributed by Heyong He and Jacek Klinowski

Verified by A. Karlsson and W. Schmidt

Type Material: [Al₁₈P₁₈O₇₂]: 42 H₂O

Method: H. He, J. Klinowski [1]

Batch Composition: 1.00 Al₂O₃: 1.00 P₂O₅: 50 H₂O: 1.12 TBA-OH_a
(TBA-OH = tetrabutylammonium hydroxide)

Source materials

distilled water

pseudoboehmite (Catapal B, 68.01 wt% Al₂O₃)

phosphoric acid (Aldrich, 88.30 wt% H₃PO₄)

tetrabutylammonium hydroxide (Fluka, 58.08 wt% TBA-OH)

Batch Preparation

- (1) [61.63 g water + 15.00 g pseudoboehmite], disperse alumina in water
- (2) [(1) + 22.20 g phosphoric acid], stir until homogeneous (for several minutes) and age for 2 hours without stirring
- (3) [(2) + 50.04 g tetrabutylammonium hydroxide], stir for 2 hours

Crystallization

Vessel: Teflon-lined autoclave

Time: 20 hours

Temperature: 150°C

Agitation: none

Product Recovery

- (1) Dilute the reaction mixture with distilled water
- (2) After the crystals precipitate, decant the upper layer of liquid and discard. Repeat the operation three times
- (3) Filter and wash the crystals with distilled water
- (4) Dry in an air oven below 50°C

Product Characterization

XRD: VFI ($a_0 = 18.9752$ Å, $C_0 = 8.1044$ Å, space group P6₃); competing phases: AlPO₄-H₂ and H₃ [2]

Elemental Analysis: 0.006 TBA+: Al₂O₃: P₂O₅

Crystal Size and Habit: needle-like and aggregated into bundles, - 10 μm. dia.

References

- [1] H. He, J. Klinowski, J. Phys. Chem. 98 (1994) 1192
- [2] F. d'Yvoire, Bull. Soc. Chim. 372 (1961) 1762

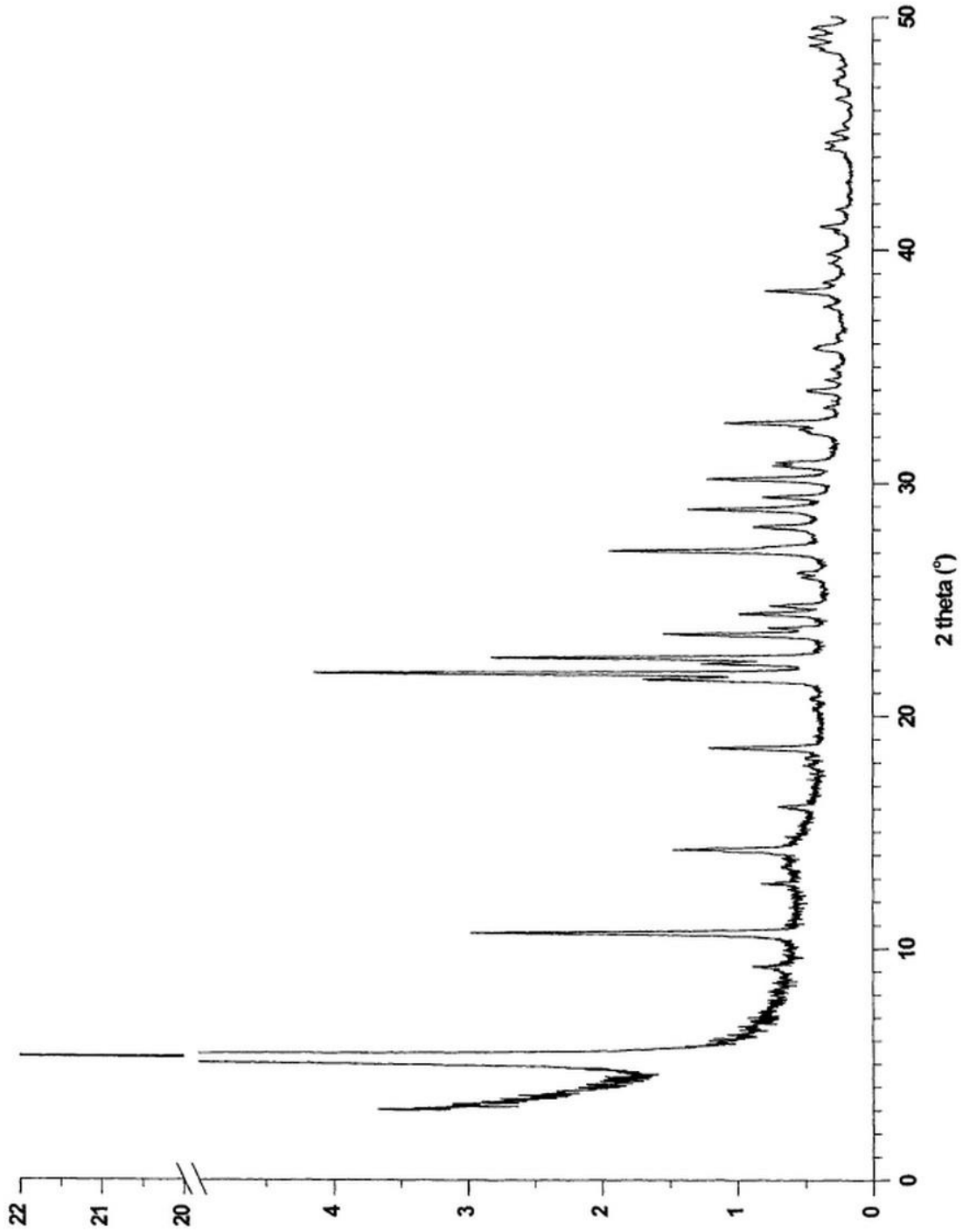
Note

- a. The amount of water quoted includes water in pseudoboehmite (100% - wt% Al_2O_3), phosphoric acid (100% - wt% P_2C_5), and tetrabutylammonium hydroxide (100% - wt% TBA-OH).

VFI

VPI-5 (TBA method)

Al(50), P(50)



VSV

VPI-7

Si(78), Zn(22)

Contributed by Ana Palčić

Verified by A. Ristic and J. Grand

Type Material: $|\text{Na}^+_{26} \text{H}^+_6 (\text{H}_2\text{O})_{44}|[\text{Si}_{56}\text{Zn}_{16}\text{O}_{144}]$

Method: Y. Suzuki, T. Wakihara, S. Kohara, K. Itabashi, M. Ogura, T. Okubo [1]

Batch Composition: $\text{SiO}_2 : 0.13 \text{ ZnO} : 0.42 \text{ Na}_2\text{O} : 44 \text{ H}_2\text{O}$

Source Materials

deionized water
zinc oxide (99%, Prolabo)
sodium hydroxide (97%, Sigma Aldrich)
fumed silica Cab-O-Sil (Cabot Corp.)

Batch Preparation

[1.468 g NaOH + 0.44 g ZnO + 2.5 g SiO_2 + 33 g H_2O] mix in Teflon liner of a stainless steel autoclave

Crystallization

Vessel: Teflon-lined stainless steel autoclave
Temperature: 175° C
Time: 5 days
Agitation: 20 rpm

Product Recovery

- (1) Dilute reaction mixture with water
- (2) Filter and wash with water
- (3) Dry at 80°C

Product Characterization

XRD: VSV
Competing phase: no
Crystal size and habit: truncated square bipyramidal morphology with dimension 1 μm

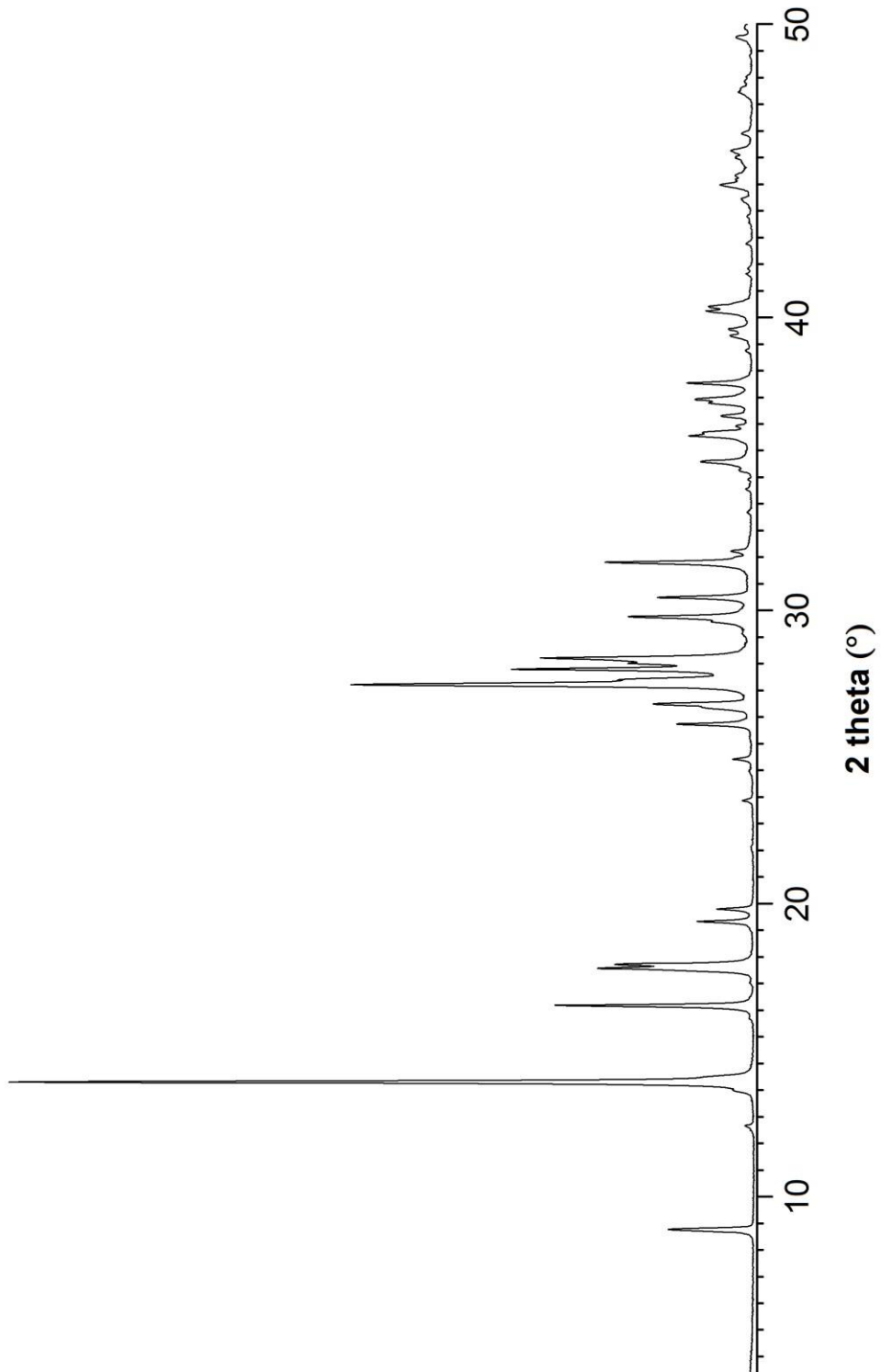
Reference

- [1] T. Wakihara, S. Kohara, K. Itabashi, M. Ogura, T. Okubo, J. Phys. Chem. C 115 (2011) 443

VSV

VPI-7

Si(78), Zn(22)



SUZ-4

Si(86), Al(14)

Contributed by Geoffrey L Price

Verified by M. Cambor, P. Piccione and E. Creighton

Type Material: $K_x(\text{TEA})_{5-x}[\text{Al}_5\text{Si}_{31}\text{O}_{72}] \cdot \text{W}\text{H}_2\text{O}$ (TEA = tetraethylammonium)

Method: G. L Price

Batch Composition 7.35 K_2O : Al_2O_3 :33.3 SiO_2 : 3.10 $(\text{TEA})_2\text{O}$: 681 H_2O

Source Material

distilled, deionized water

potassium hydroxide (Fisher A.C.S. pellets, 86% KOH)

aluminum pellets (Aldrich, 99.99+% Al)

tetraethylammonium hydroxide (Aldrich aqueous solution, 35% TEA-OH)

silica sol (Dupont Ludox AS-40, ammonium stabilized, 40% SiO_2)

Batch Preparation (for 13 g dry product)^a

- (1) [33.98 g water + 6.709 g potassium hydroxide], stir until dissolved
- (2) [(1) + 0.3776 aluminum pellets], stir overnight or until Al pellets dissolve completely in a loosely capped plastic bottle (hydrogen gas evolved)
- (3) [18.226 g tetraethylammonium hydroxide + 35.00 g silica sol + 29.04 g water]. Stir together
- (4) [(2) + (3)], mix well

Crystallization

Vessel: 200 mL stainless steel autoclave

Temperature: 150°C

Time: 4 days

Agitation: rotated autoclave^a

Product Recovery

- (1) Cool to ambient temperature; decant and discard liquid
- (2) Wash with water to pH < 10
- (3) Dry at 100°C
- (4) Yield: near 100% on Al_2O_3

Product Characterization

XRD: strong SUZ-4 [1, 2]; competing phases MOR^b plus an unidentified phase^c

Elemental analysis: wt% Si36, Al5.5, K1.5

Crystal size and habit: rods, 0.1 μm dia. x 1 μm long

References

- [1] S. L Lawton, J. M. Bennett, J. L Schlenker, M. J. Rubin, J. Chem. Soc., Chem. Commun.(1993) 894

- [2] D. B. Lukyanov, V. L. Zholobenko, J. Dwyer, S. A. I. Barri, W. J. Smith, J. Phys. Chem B 103 (1999) 197

Notes

- a. This preparation has been successfully scaled up to a one-liter stirred autoclave.
- b. Na⁺ level too high.
- c. Produced by inadequate agitation during crystallization. XRD lines observed at 14.0°(2θ) m, 22.8° ms, 28.3 s, 29.8° ms, 30.6 m and 40.9 mw.
22.8° ms, 28.3 s, 29.8° ms, 30 m and 40.9 mw.

SUZ-4

Si(86), Al(14)

