Zeolite Synthesis by the High-Pressure Hydrothermal Method: Synthesis of Natural 6-Ring Zeolites with Different Void Systems

Habib Ghobarkar, Oliver Schäf,* and Philippe Knauth*

Their unique properties make zeolites interesting for scientific research as well as for industrial applications—for example they are used as sorbing materials for gaseous and liquid components, as ion exchangers in aqueous systems with a wide variety of applications, and as shape-selective catalysts in the petrochemical industry.

Zeolites are conventionally produced by hydrothermal processing at relatively moderate temperatures.[1] By this method only an empirical correlation exists between the precursor material and the zeolite product. Although several industrially important zeolites can be synthesized by applying such an empirical correlation, the conventional hydrothermal synthesis process is steered in a certain range by using structure-directing agents (templates) to obtain zeolites with the desired channel system and structure type. All known zeolites with 6-ring structural building units have already been synthesized in this way.[2] The empirical character of the zeolite synthesis process remains, however, at least unsatisfactory in the search of new zeolite structure types for advanced specific applications. Furthermore, the removal of the template materials from the zeolite cavity systems may cause problems that have often not been solved satisfactorily: residual template materials in the cavity system reduce the zeolite activity, or these agents are cracked during application processes leading to poisoning. Besides this, some zeolites, such as stilbite or laumontite, that are very common in nature have not yet been obtained by any conventional hydrothermal synthesis process.[3] Consequently, only relatively few zeolite structure types are applied industrially.

Davis and co-workers have developed a synthesis process in which conventional hydrothermal zeolites are modified by ion exchange and the desired zeolite is obtained by using seed material of the zeolite structure type to be produced.[4]

A direct, alternative method for zeolite synthesis is presented here, in which the hydrothermal natural formation conditions of this class of materials are simulated. In this process artificial, water-free glasses of identical composition to those of the respective natural zeolite are used as starting materials, and distilled water is applied as pressure and reaction medium. In general, the pressure range for this kind of synthesis lies between 500 bar and 4 kbar, the temperatures between 30 and 450 °C, and the reaction times between 12 h and 60 days.[5] Neither organic templates nor reactive solutions are necessary to obtain zeolite products of the desired channel size and structure type (Table 1).

Based on the experience of former zeolite syntheses, a water pressure of 1 kbar and a reaction time of 60 days were used in the experiments under isothermal conditions between 170 °C and 270 °C. Earlier experiments have shown that no zeolite products are obtained by using synthesis pressures lower than 500 bar—presumably for kinetic reasons. Up to ¾ of the homogeneous glass pieces with a maximum diameter of 4 mm were hydrothermally converted to crystalline products. All zeolite phases formed show, within the accuracy of the EDX measurements of 10%, the chemical composition of their natural counterparts[3a, 6, 7] (Table 2). Figure 1 presents a scanning electron microscope image of each of the formed crystals of the respective phase and the crystal face orientation obtained from dihedral angle measurements between neighboring crystal planes.[8] The measured values lay within the experimental error of 3% according to the accuracy of the method. Other zeolite phases, namely chabazite and gmelinite, were detected by morphological examinations as by-products of nearly all syntheses, however, the amounts of these other zeolites were too low to be characterized by X-ray diffraction (XRD) investigations. Levyne was the only synthesis product obtainable in a phase-pure form even in the scanning electron micrographs.

The use of precursor glasses of the "idealized" composition of the natural zeolite, as given by single-crystal data, was in several cases not sufficient to obtain the desired zeolite

Table 1. Channel diameters [Å] of synthesized 6-ring alumosilicate zeolites (data from ref. [5]).

Code	Zeolite phase	Channel system in the first crystallographic direction		in the second crystallographic direction
FAU	faujasite	⟨111⟩ **12** 7.4***		
GME	gmelinite	[001] **12** 7.0*	↔	⊥ [001] **8** 3.6 × 3.9**
OFF	offretite	[001] **12** 6.7*	↔	⊥ [001] **8** 3.6 × 4.9**
CHA	chabazite	⊥ [001] **8** 3.8 × 3.8***		
ERI	erionite	⊥ [001] **8** 3.6 × 5.1***		
LEV	levyne	⊥ [001] **8** 3.6 × 4.8**		

[a] The numbers **12** and **8** refer to the number of O, Si, or Al atoms forming the rings that control the access to the zeolite channel system. The dimensionality of the channel system is denoted by the number of stars; interconnected channel systems are denoted by ↔.

Table 2. The JCPDS files applied for phase identification.

Zeolite phase	JCPDS Nr.
faujasite	39-1380
gmelinite	38-435
offretite	25-1186
chabazite	34-137
erionite	39-1379
levyne	26-1381

[*] Dr. O. Schäf, Prof. Dr. P. Knauth
Laboratoire des Matériaux Divisés,
Revêtements, Electrocéramiques (MADIREL)
UMR 6121 Université de Provence, CNRS
Centre St Charles, Case 26, 13331 Marseille Cedex 3 (France)
Fax: (+33) 4-91-10-62-37
E-mail: schaef@newsup.univ-mrs.fr
knauth@up.univ-mrs.fr
Dr. H. Ghobarkar
Institut für Mineralogie
Freie Universität Berlin
Takustrasse 6, 14195 Berlin (Germany)

  1433-7851/01/4020-3831 $ 17.50+.50/0

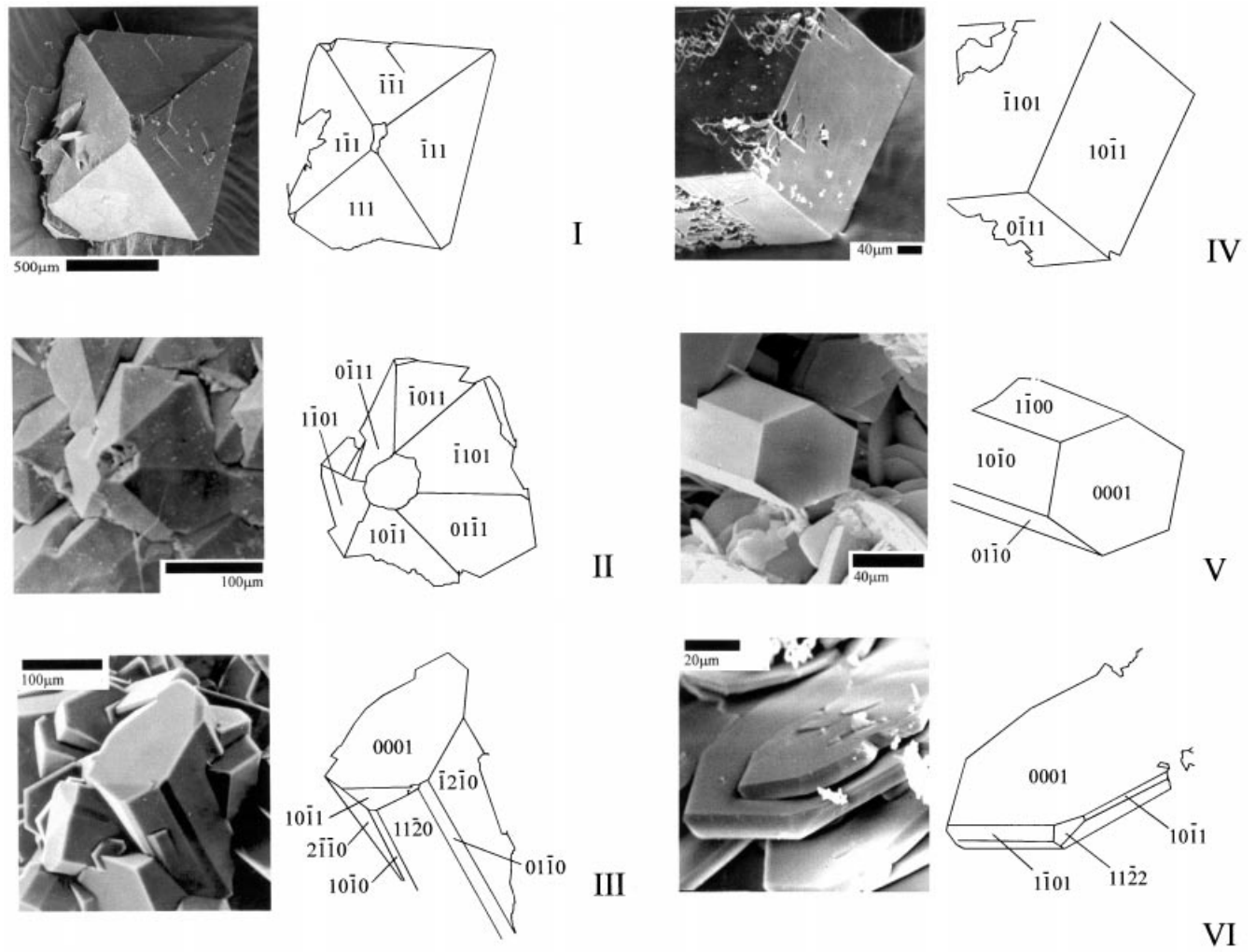

Figure 1. Scanning electron micrographs of single crystals of faujasite (I), gmelinite (II), offretite (III), chabazite (IV), erionite (V), and levyne (VI) synthesized from the precursor glass with the composition of the respective natural zeolite (see Table 3, reaction time 60 days, synthesis pressure 1 kbar, synthesis temperature 220 °C).

structure type:[7] under the chosen high-pressure/high-temperature hydrothermal conditions the 6-ring zeolites faujasite, offretite, and erionite could only be prepared in the presence of iron as "catalyst" (5 mol% Fe_2O_3 added to the precursor glass). The chemical analysis of the surrounding rock matrices of these natural 6-ring zeolites show that they almost always contain iron. Furthermore, faujasite, gmelinite, and chabazite were only obtained if further cations (introduced as the oxide component in the precursor glass in an amout equal to 10 mol% of the total oxide content) were present according to the "actual" average natural zeolite composition as given by Gottardi and Galli.[3a] The necessity of the addition of further channel cations as well as iron to the zeolite precursor glass is evidently due to their special hydration properties, since they act as a sort of ionic template for the formation of the respective channel system. Further investigations are necessary to clarify the mechanism of this behavior.

Based on the experimental results, the isothermal solution–crystallization process can be explained in principle as shown in Figure 2: the synthetic glasses of natural zeolite composition used as starting materials for the synthesis process are dissolved isothermally under the high-pressure

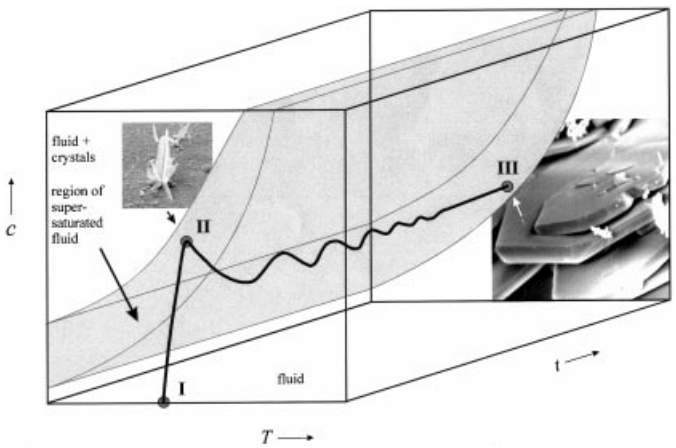

Figure 2. Temperature–concentration–time (T–c–t) diagram for the high-pressure hydrothermal synthesis process (see text for details): I) glass and fluid phase; II) nucleation at the frontier of supersaturated fluid; III) final state of grown microcrystals.

hydrothermal conditions. Therefore, the hydrothermal fluid consisting only of hydrothermal water at the starting point of the experiment (I) becomes more and more concentrated with

  1433-7851/01/4020-3832 $ 17.50+.50/0

time. The glass can still be dissolved even when the solubility limit of the fluid with respect to the crystalline phase is attained (supersaturation). However, at a certain level of concentration (marked as point II in the region of supersaturated fluid) spontaneous crystallization of the zeolite phase occurs, leading to a decrease of the concentration in the hydrothermal fluid. The zeolites are, therefore, synthesized by a process in which the precursor glass is dissolved in the fluid phase and then crystallizes as zeolite.

Crystal growth only occurs in the region of supersaturated fluid. If the isothermal–isobar conditions are carefully maintained during the long duration of the experiment, neither etching of the zeolite crystals nor the formation of a second zeolite phase (by repeated spontaneous crystallization and growth) is observed. From this it can be concluded that the dissolution–crystallization process continues in the range of supersaturated fluid in such a way that the system is self-stabilizing. These are the time-dependent conditions of crystal growth between point II and III (Figure 2). The process will continue as long as there is enough glassy material for the continuous dissolution–crystallization process—if the synthesis process is not interrupted before.

Experimental Section

Glasses of the appropriate zeolite composition (see Table 3) were repeatedly molten for five minutes and quenched and crushed each time in a high-frequency furnace in open carbon crucibles in air (Schunk Kohlenstofftechnik, Germany) at temperatures up to 1800 °C using a blend of the appropriate water-free alkali metal and/or alkaline earth metal carbonate, iron oxide, α-alumina, and silicon dioxide (quartz). Visually homogeneous glasses were amorphous according to powder X-ray-diffraction investigations (XRD, $Cu_{K\alpha}$ radiation, Bragg–Brentano geometry). Then, pieces of the glasses (maximum length 4 mm) were placed in copper capsules (about 1 cm^3 volume), filled up with distilled H_2O as pressure and reaction medium (water:glass ratio approximately 10:1) and tightly closed. Three of these capsules were placed in a high-pressure autoclave (MRA/112R type, TEM-PRESS research division, USA). The whole system was set under pressure by using distilled water as the pressure medium. The hydrothermal experiments were conducted in a temperature range between 170 and 270 °C for 60 days at a synthesis pressure of 1 kbar. Every experiment was repeated twice. These conditions were chosen based on experience with previous zeolite syntheses using this method.[3b,c, 5, 9]

The crystalline phases formed at the surface of the glasses were subsequently investigated by XRD and energy-disperse X-ray analysis for chemical composition (EDX), and the crystal morphology was finally investigated by scanning electron microscopy (SEM). The resulting micrographs were evaluated with the stereo-comparator for crystal indexing and crystallographic analysis.[8]

Table 3. The chemical composition of the glass precursors of the alumosilicate 6-ring zeolites.

Zeolite phase	Precursor glass composition[a]
faujasite[b]	$5\,Na_2O \times 6\,CaO \times 4\,MgO \times 15\,Al_2O_3 \times 66\,SiO_2 \times 9.6\,(Sr,Ba,K_2)O \times 4.8\,Fe_2O_3$
gmelinite	$1\,Na_2O \times 1\,Al_2O_3 \times 4\,SiO_2 \times 0.6\,(Ca,K_2)O$
offretite[b]	$1\,K_2O \times 2\,CaO \times 2\,MgO \times 5\,Al_2O_3 \times 26\,SiO_2 \times 1.8\,Fe_2O_3$
chabazite	$1\,CaO \times 1\,Al_2O_3 \times 4\,SiO_2 \times 0.6\,(Li_2,K_2)O$
erionite[b]	$1\,Na_2O \times 2\,K_2O \times 2\,MgO \times 3\,CaO \times 8\,Al_2O_3 \times 54\,SiO_2 \times 3.5\,Fe_2O_3$
levyne	$1\,Na_2O \times 5\,CaO \times 6\,Al_2O_3 \times 24\,SiO_2$

[a] The cations of the additional mixed oxide components are present in equal proportions. [b] Synthesis only possible in the presence of Fe ions.

Received: May 4, 2001 [Z17048]

[1] R. M. Barrer, *The Hydrothermal Chemistry of Zeolites*, 1st ed., Academic Press, London, **1982**.

[2] a) G. J. Kim, W. S. Ahn, *Zeolites* **1991**, *11*, 745–750; b) M. L. Occelli, H. E. Robson, *Synthesis of Microporous Materials*, *Vol. 2*, Chapman and Hall, London, **1992**; c) *Molecular Sieves, Science and Technology*, *Vol. 1, Synthesis* (Eds.: H. G. Karge, J. Weitkamp), Springer, Berlin, **1998**.

[3] a) G. Gottardi, E. Galli, *Natural Zeolites*, Springer, Heidelberg, **1985**; b) H. Ghobarkar, O. Schäf, *Microporous Mesoporous Mater.* **1998**, *23*, 55–60; c) H. Ghobarkar, O. Schäf, *J. Phys. D: Appl. Phys.* **1998**, *31*, 3172–3176.

[4] O. Chiyoda, M. E. Davis, *Microporous Mesoporous Mater.* **1999**, *32*, 257–264.

[5] H. Ghobarkar, O. Schäf, U. Guth, *Prog. Solid State Chem.* **1999**, *27*, 29–73.

[6] *Atlas of Zeolite Structure Types* (Eds.: W. M. Meier, D. H. Olson, C. Baerlocher), 4th ed., Elsevier, London, **1996**.

[7] a) K. Fischer, *Neues Jahrb. Mineral. Monatsh.* **1966**, 1–13; b) F. Mazzi, E. Galli, *Neues Jahrb. Mineral. Monatsh.* **1983**, 4461–4480; c) S. Merlino, E. Galli, A. Alberti, *TMPM Tschermaks Mineral. Petrogr. Mitt.* **1975**, *22*, 117–129; d) A. Kawahara, H. Curien, *Bull. Soc. Fr. Mineral. Crystallogr.* **1969**, *92*, 250–256; e) J. A. Gard, J. M. Tait, *Acta Crystallogr.* **1972**, *28*, 825–834; f) G. Bergerhoff, W. H. Baur, W. Nowacki, *Neues Jahrb. Mineral. Monatsh.* **1958**, 193–200.

[8] H. Ghobarkar, *Krist. Tech.* **1977**, *12*, K49–51.

[9] a) H. Ghobarkar, O. Schäf, P. Knauth, *Ann. Chim. (Paris)* **1999**, *24*, 209–215; b) H. Ghobarkar, O. Schäf, U. Guth, *High Pressure Res.* **2001**, *20*, 45–54.

Which Structural Elements Are Relevant for the Efficacy of Neocarzinostatin?**

Patrick W. Musch and Bernd Engels*

Neocarzinostatin (NCS) is one representative of the family of natural enediynes that exhibit a high efficacy as antitumor antibiotics.[1] It consists of a 1:1 complex of an apoprotein and a bioactive non-protein chromophore (**1** in Scheme 1).[1, 2] In the first step of the mode of action of NCS[2b, 3] the chromophore **1** is carried to the minor groove of the DNA by the apoprotein which at the same time serves as its stabilizer. After **1** is bound to the DNA the apoprotein is separated off, a stereospecific nucleophilic addition of thiol rearranges **1** to the highly strained enyne-[3]-cumulene **2**.

[*] Prof. Dr. B. Engels, Dipl.-Chem. P. W. Musch
Institut für Organische Chemie
Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4606
E-mail: bernd@chemie.uni-wuerzburg.de

[**] We thank Prof. Dr. M. Schmittel who brought this problem to our attention. P.W.M. thanks the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie for a graduate scholarship.

Supporting information on this contribtion is available on the WWW under http://www.angewandte.com or from the author.