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Zeolite synthesis by simulation of their natural formation conditions: from macroscopic to nanosized crystals

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Abstract

A successful route to prepare zeolites with controlled crystal size from the millimeter range down to nanometer scale by simulating the natural formation conditions is presented. Water is used as the solution and reaction medium at high temperatures and pressures ($T = 120$–$400°\mathrm{C}$, $p = 1\,\mathrm{kbar}$); aluminosilicate glasses with identical chemical composition as the zeolite products are used as precursors. The synthesis of heulandite is reported as representative example.

Keywords: Hydrothermal; Heulandite; Nanocrystal; Single crystal

1. Introduction

Zeolites are a class of crystalline aluminosilicates, based on rigid anionic frameworks with well-defined channels and cavities. Conventionally synthesized in large quantities by hydrothermal processing at moderate temperatures and pressures, only an empirical correlation exists between the precursor material and the zeolite product. Macroscopic crystals are only obtained in exceptional cases. Although several industrially important zeolites can be prepared by this way, the conventional low-pressure hydrothermal synthesis process can only be directed to a certain extent by using structure directing agents in order to obtain the zeolite with the desired channel system and structure type [1]. These conditions are, however, not comparable to the natural formation conditions. For example, zeolites such as stilbite or laumontite, which are very common in nature, were not obtained yet by any conventional processing [2,3]. In nature, these materials are formed in geological time scales in the presence of water at elevated pressures; they are among the first crystalline phases in the rock-forming cycle and are also found in altered sediments [4]. Under these natural hydrothermal conditions, zeolites were mostly formed from volcanic rocks containing a certain amount of glassy phase under the influence of pore water in a wide temperature range.

The high-pressure hydrothermal method uses water as the solution and reaction medium in a closed system at a constant temperature. This fluid becomes an excellent solvent at elevated temperatures and pressures for water-free aluminosilicate glasses with the zeolite product composition [5–7]. The high-pressure hydrothermal conditions increase the solubility in the aqueous medium in comparison to autogeneous pressure conditions: below 500 bar the solubility of the precursor glass is too small to form observable quantities of zeolite phases under laboratory conditions, while above 2.5 kbar the process leads to the synthesis of non-zeolitic aluminosilicates with higher framework density. The zone of supersaturation is wider for glasses than for respective crystalline materials and also pressure dependent [8].

The formation of gels is not observed, because bigger molecular units are hydrolyzed at elevated temperatures and pressures [9,10]. The formation of a true solution is therefore assumed, in which the Si and Al tetrahedral units as well as the alkali- and alkaline-earth cations with their respective hydration spheres are transported.

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Type and quantity of cations determine the zeolite channel diameter to be formed, because charge compensating alkali- and alkaline-earth ions with their respective hydration sphere serve in general as inorganic templates for the channel system. The influence of the iron oxide component is not clarified yet [6]: it appears to act as a sort of structure directing catalyst, which is necessary during the constitution of the zeolite cavity system. Even its crystallographic position within the zeolite structure is not exactly known [4].

In the following, the high-pressure synthesis process of zeolites over a wide temperature range is exemplified with the synthesis of Heulandite. Heulandite has a monoclinic structure (*C*2/*m*, zeolite code: HEU [11]) with a quasi-two-dimensional channel system; a Si/Al ratio smaller than 4 is prevailing in the crystal lattice [12]. The two-dimensional channel system causes the commonly observed leafy crystal habits with cleavages parallel to the (010) face. Heulandite is found in different localities all over the world. It was first synthesized by Ames [13] in 1963 using gel mixtures under autogeneous pressures for 2–3 days in a temperature range between 250°C and 300°C. From this time on, several synthesis reports can be found in the literature [14–20]; however, the synthesis process according to the natural conditions without seeds has never been systematically studied.

2. Experimental

We used synthetic glasses of a Heulandite composition $Na_{0.5}K_{0.5}CaMgSrBa[Al_9Si_{27}O_{72}]$ [4] adding 5 mol% Fe_2O_3 as starting materials. These glasses were blend from the respective water-free alkali- and/or alkaline-earth carbonate, iron oxide, α-alumina and silicon dioxide (quartz). The mixtures were repeatedly molten for 5 min at temperatures up to 1800°C in air using a high-frequency furnace and open carbon crucibles (Schunk Kohlenstofftechnik, Germany). The visually homogeneous glasses were amorphous according to powder X-ray-diffraction investigations (XRD).

For the hydrothermal synthesis, the precursor glass (pieces of about 8 mm maximum length) is placed in a container of pure copper with caps on both sides. Three to four containers fixed by a spring are put into a high-temperature–high-pressure autoclave (RMA/112 type, Tem Press) and placed in a temperature-controlled furnace. After reaching the chosen temperature, the fluid pressure is adjusted to the desired value. The synthesis experiments were conducted isothermally between 120°C and 400°C in temperature intervals of 20 K at 1 kbar water pressure and with 60 days of synthesis time. Each experiment was repeated in order to confirm the results.

In addition to the standard methods for phase and morphological characterization, such as scanning electron microscopy (SEM, Philips XL 30 ESEM), EDX and X-ray diffraction (Siemens D5000), the crystal specimen were evaluated by the stereo-comparator method allowing the determination of the mutual position of the crystal face normals, the axis proportions, and, therefore, the crystal system. This characterization method was especially developed for microcrystals [21] if they were idiomorphously formed—which is very often the case in high-pressure hydrothermal experiments; it allows the comparison of crystals synthesized at different temperatures.

3. Results

According to the accuracy of the EDX method, all investigated heulandite crystals show the chemical composition of their natural counterparts given in the literature [4]. At 120°C, leafy HEU single crystals of several millimeter size are obtained (Fig. 1). The single crystals formed at 150°C are larger in the *b*-direction ([010], Fig. 2a). The second crystal generation formed on the primary single crystals (Fig. 2b) indicates that the supersaturation limit was reached at least a second time during the synthesis process, leading to a second nucleation and growth.

The size of the obtained crystals depends drastically on the synthesis temperature: at 185°C the size of the

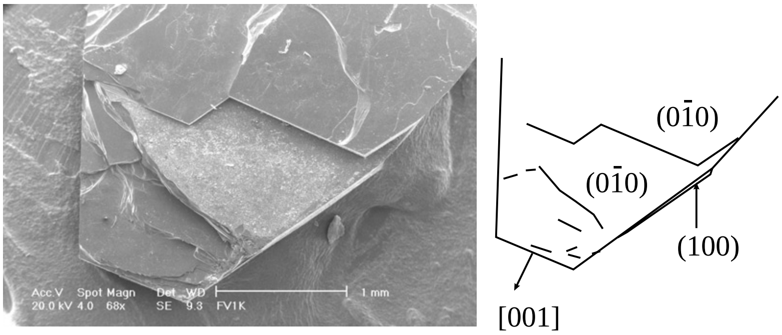

Fig. 1. Leafy heulandite (HEU) single crystals of the first generation obtained at 120°C from glass precursor (crystal indexing aside).

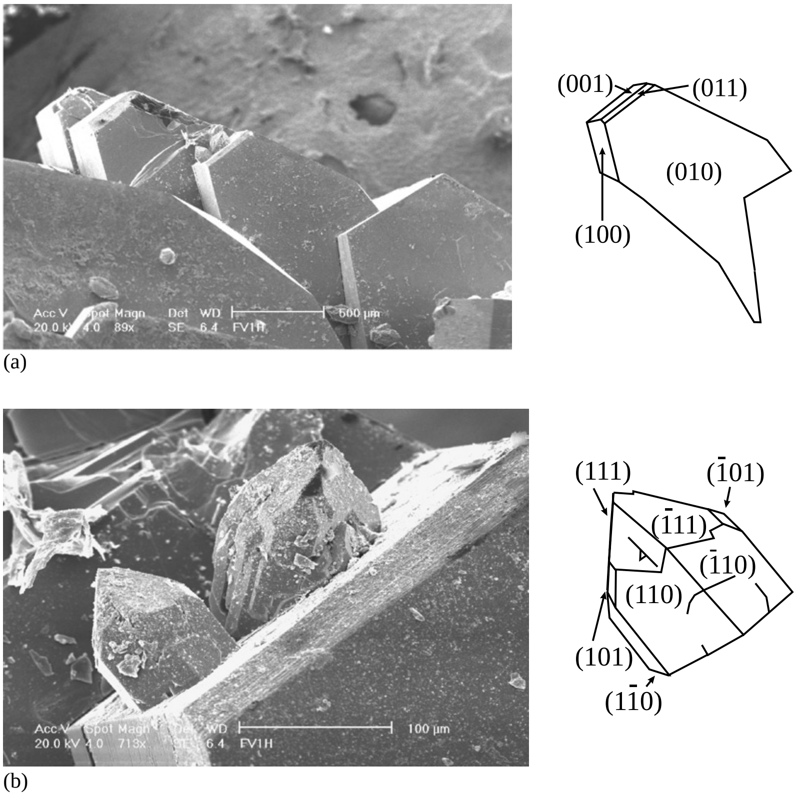

Fig. 2. (a) Leafy heulandite (HEU) single crystals of the first generation obtained at 150°C from glass precursor (crystal indexing aside). One observes twinned second-generation crystals. (b) HEU microcrystals of the second generation at the surface of the first-generation crystals obtained at 150°C. The crystals are twinned due to a relatively higher supersaturation (crystal indexing aside).

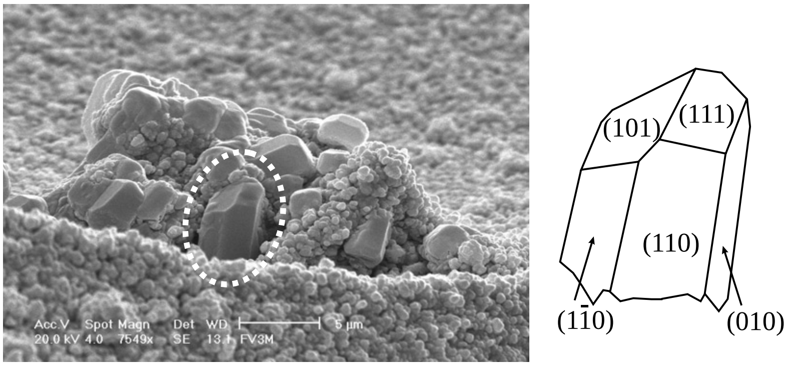

Fig. 3. Heulandite microcrystals obtained at 185°C from glass precursor (crystal indexing aside).

observed crystals is reduced to the micrometer scale (Fig. 3), while at 200°C (Fig. 4), only the crystallization of HEU in the nanoscale is observed. Powder XRD confirmed the presence of the heulandite phase in all cases (JCPDS 25-144) in agreement with the Stereocomparator results. Between 200°C and 350°C no crystals can be resolved by SEM, while above 350°C microcrystals of HEU can be observed with two different morphologies (Fig. 5). At 400°C, Wairakite, a zeolite with a higher framework density, crystallizes as a by-product.

4. Discussion

4.1. *Influence of temperature*

At temperatures between ambient and about 80°C, the synthesis kinetics are too slow to obtain the zeolite phase in quantities sufficient to be detected—even after synthesis times of more than 30 days—unlike in natural processes where the reaction time is nearly unlimited. At too high temperatures, higher than about 400°C, aluminosilicate phases with the same chemical

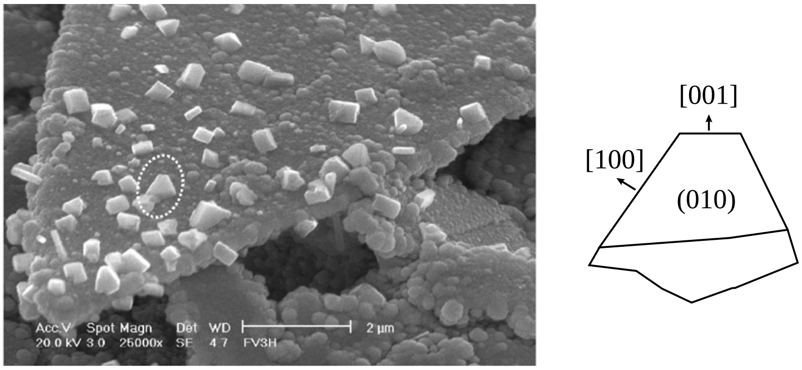

Fig. 4. HEU nanocrystals of about 500 nm maximum size obtained at 200°C (crystal indexing aside).

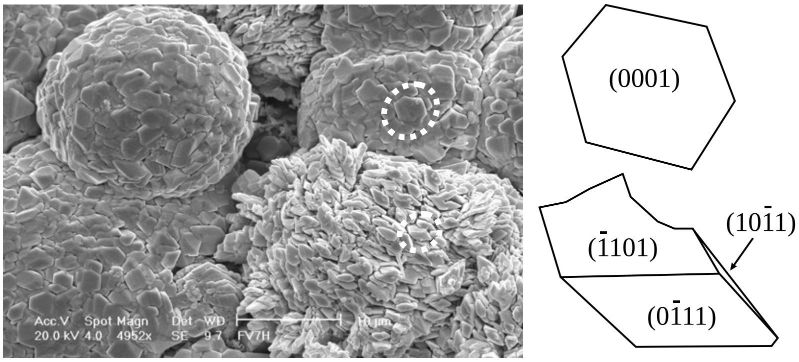

Fig. 5. HEU crystals of rhombohedral (right, below) and hexagonal (right, above) habits obtained at 400°C (crystal indexing aside).

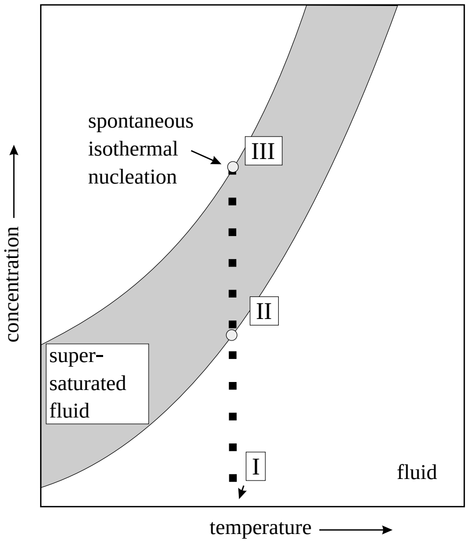

Fig. 6. Schematic representation of the dissolution–crystallization process used for the high-pressure hydrothermal zeolite synthesis from a precursor glass. After the initial nucleation (point III) caused by the continuous glass dissolution (starting at point I), crystal growth takes place in the field of supersaturated solution.

composition but elevated framework densities are formed.

At the starting point of the isothermal experiment (point I in Fig. 6), the system consists only of water with pieces of precursor glass. During the experiment, the hydrothermal fluid gets more and more concentrated. The glass can be dissolved even above the solubility limit of the crystalline zeolite (point II in Fig. 6), because it is a metastable amorphous phase. At a certain level of concentration (point III in Fig. 6), spontaneous crystallization of the zeolite phase occurs, leading to a decrease of the concentration in the hydrothermal fluid. To make a long story short, in the hydrothermal synthesis process the precursor glass is dissolved in the fluid medium and the zeolite crystallizes from the supersaturated solution (see Fig. 6). If the isothermal–isobar conditions are carefully maintained during the long synthesis experiment, neither etching of the zeolite crystals nor formation of a secondary phase is observed.

4.2. Influence on crystal morphology

Fig. 7 illustrates the competition between nucleation and crystal growth: the rates are strongly dependent on supersaturation. However, the crystal growth rate is higher at low supersaturation than the nucleation rate. In order to grow macroscopic single crystals, relatively low supersaturation conditions must be maintained during the whole synthesis process. In the second extreme case, that of a high supersaturation, the rate of nucleation is very high and nanocrystalline zeolites are obtained. Between these two extreme cases, i.e. at intermediate supersaturation levels, secondary crystals

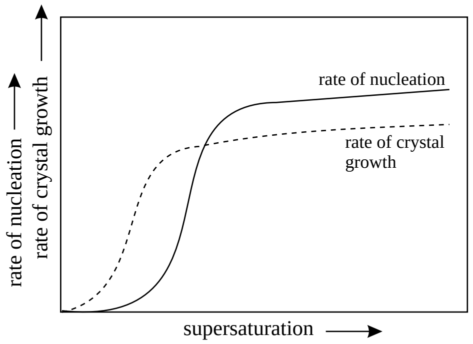

Fig. 7. Dependence of nucleation and growth rates on supersaturation.

can nucleate and grow on the primary crystal generation. This second generation of crystals can be twinned in case of a relatively higher supersaturation during its crystallization.

Finally, while in the temperature range up to 200°C, the glass dissolution is the rate-determining factor, at elevated temperatures above 340°C, the redissolution of already crystallized material in the nanometer scale is predominant. After the growth of low-temperature colloidal beads consisting of crystals in the nanoscale, at high temperatures, microsize crystal beads of heulandite grow (at 400°C with two different habits, see Fig. 5), consuming the nanosized material.

5. Conclusions

In the search for new mesoporous and microporous materials, the ''natural synthesis route'' is explored using high-pressure–high-temperature hydrothermal conditions. A direct correlation exists between glassy precursor materials and the zeolite products; neither acids nor bases have to be present during this zeolite crystallization.

The fine-tuning of the hydrothermal conditions allows the synthesis of crystals from the nanometer scale to the millimeter scale. By simulating the natural formation conditions, all naturally occurring zeolites, but also isomorphous framework-substituted structures are obtainable.

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