



Enhanced methods of crystallization: The crossover synthesis from gel to melt flow - A case study on sodalites



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ABSTRACT

A new crystallization pathway composed of a combination of gel synthesis and crystallization in a melt flow is demonstrated using the sodalite system as a case study. The specific characteristics of this enhanced method of crystallization persists in a controlled heating of a pressed pellet of a mixture of selected solids, containing a “water donator” as well as a “fluxing agent”. The reaction of zeolite 13 X (“water donator and Si–Al-source”) NaOH granulate (“fluxing agent”) and a template salt like NaCl (or others) is shown to yield suitable products already after a few hours of heating the mix-pellet under open conditions.

In a first synthesis series experiments were performed to investigate the details of the reaction mechanism. Beside a study of the role of the hydrate water, the NaOH granulate and certain template salts, even the total decomposition of the zeolite 13 X framework structure could be demonstrated under the conditions of the crossover from gel to flux growth. According to the results it could be clarified that the mechanism consists of alkaline aluminosilicate gel formation and crystallization in the early period but shifts into crystal growth in NaOH melt at elevated temperature.

In a second series examples of tailored sodalites and the characterization of these products will show the effectiveness of the new method. From SEM investigations could be further derived that the crystal size and morphology depends on T_{\max} , the holding period at T_{\max} , and nano- or micro-crystalline sodalites can be observed.

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1. Introduction

Today hydrothermal synthesis is widely used in materials science. Especially in zeolite chemistry this method is often inserted [1–5] but modifications of well known syntheses procedures are more and more important to obtain new materials with tailored properties. Problems of common hydrothermal synthesis like decomposition of hydrolysis sensitive templates [6–8] or preparation of large crystals at elevated temperatures accompanied with difficulties of handling high pressures, often arise [9,10] beside other restrictions. The expansive technical input is the main reason that synthesis experiments on tailor-made zeolites were only rarely done at temperatures higher than 200 °C.

Beside those problems during direct synthesis even special modifications of “as synthesized materials” require the development of enhanced preparation methods. Here often expansive multistep procedures are required like subsequent thermal

treatment steps to modify enclosed guest species in the cavities of as-synthesized zeolites. The diffusion controlled intra-cage reactions of water and hydrogen in hydroxoborate and tetrahydroborate sodalites can be mentioned here as typical examples. Multistep thermal reactions are necessary to obtain these materials with intermediate guests to study their behavior for hydrogen storage [11–13]. In a related context even a transition of $\text{NaB}(\text{OH})_4$ sodalite into pure phase $\text{NaBO}(\text{OH})_2$ sodalite by heat treatment was already proved to be problematically [14,15]. Here it would be advantageous, if a tailored material could be simply prepared by an optimized one step process without further cycles of modification.

These are only some points which refer to the significance of development of enhanced methods of crystallization. Without future work on synthesis improvement the preparation of new and tailor-made materials would be distinctly limited.

On these reasons the present paper deals with the introduction of a modified synthesis procedure by controlled heating of suitable educts under open conditions. A simple tailored heating process at optimized heating rate and holding period at maximum

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temperature (T_{\max}) is therefore inserted. The aim is a combination of synthesis from an aqueous gel at low temperature followed by growth in a melt at elevated temperature as a one pot process. The preparation techniques is demonstrated using the sodalite system as a case study. Fully hydrated zeolite 13 X is therefore inserted as Si and Al source and as water donator for the early step of the process. During heating up the process starts as a crystallization from gel-like solution in the hydrate water of zeolite 13X until the water is evaporated. Afterwards the mechanism changed into a crystal growth from melt in the NaOH flux by holding the samples at elevated temperature (T_{\max}) for optimized time.

The study starts with a series of test experiments to clarify essential details of the mechanism of the whole reaction, like the role of the hydrate water of the educt zeolite 13 X and the significance of addition of NaOH as mineralizer and fluxing agent. The clarification of the degree of decomposition of the 13 X zeolite aluminosilicate framework as Si–Al source for the new phases is included in this experimental series.

In a second synthesis series selected examples of tailor-made sodalites will demonstrate the effectiveness of the method. Firstly the formation of NaNO_2 sodalite is of interest because the material is a model for the uptake of CO_2 [16–18].

Furthermore NaCl-sodalite was prepared because pure samples, known since decades as minerals from nature [19]) are problematically to grow under usual hydrothermal conditions. Due to the excess of aqueous NaOH–NaCl solutions in conventional synthesis remarkable amounts of water and base were enclathrated in several of the sodalite cages. Beside synthesis of pure NaCl sodalite according to the new method of the present paper NaCl sodalite formation is also used here as a case study of the influence of heating and holding temperature. Therefore the synthesis at $T_{\max} = 700\text{ }^\circ\text{C}$ is performed in this second series for comparison with the product of the $400\text{ }^\circ\text{C}$ process, observed in the first experimental row. In addition a further synthesis at $T_{\max} = 400\text{ }^\circ\text{C}$ is performed without a holding period. Changes of crystal size and morphology will thus be discovered in dependence of T_{\max} and the holding period at T_{\max} .

Furthermore the preparation of two species of borate sodalites is presented in this series of tailored sodalites, starting with the template salt $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ but using different holding temperatures (T_{\max}). This investigation of borate templates in sodalites was selected to study if temperature dependant formation of intermediates like $\text{NaBO}(\text{OH})_2$ or NaBO_2 is possible by the new procedure. In common hydrothermal process always $\text{NaB}(\text{OH})_4$ sodalite is the “as-synthesized” product [20,21]. A subsequent multistep heating procedure of such a hydrothermal product is necessary to obtain tailored borates as guests, but chemical zoning of the samples often results [22].

2. Experimental

Zeolite 13-X (Fluka 69856) $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}](\text{H}_2\text{O})_{264}$ was selected as a suitable reactant for the controlled thermal reaction. Beside the role as Al–Si-source this compound simultaneously also acts as “water provider” (264 H_2O per formula unit) for alkaline gel formation in the early period of heating up process. The following preparation procedure was revealed: a powder mixture of zeolite 13X, solid NaOH granulate (Merck 1.06467) and a certain amount of a template salt (NaCl Merck 1.06464, $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ Aldrich S0251, NaNO_2 Sigma-Aldrich 237213, NaNO_3 Fluka 71758) were pressed into a pellet using a hydraulic press at 50 kN for 5 min before a controlled heating process was performed under open conditions. The nitrate salt was selected for the test of the structure decomposition of zeolite 13 X according to a possible formation of

cancrinite, a zeolite with ϵ -cages instead β -cages as in zeolite 13X and sodalite (for more details see below).

The first synthesis series was performed to clarify the details of the reaction mechanism. Beside a study of the role of the hydrate water, the NaOH granulate and the template salts NaCl and NaNO_3 a heating program from room temperature (RT): $\text{RT} \rightarrow T_{\max} \rightarrow \text{RT}$ was revealed with $T_{\max} = 400\text{ }^\circ\text{C}$ under attention of the melting point of NaOH (318 $^\circ\text{C}$ [23]). A constant time of heating up of 90 min and a holding time of 60 min was inserted in this series.

In the second experimental series of syntheses of tailored sodalites the following temperatures were used: $T_{\max} = 300\text{ }^\circ\text{C}$ for nitrite sodalite (melting point of NaNO_2 : 271 $^\circ\text{C}$; decomposition at 320 $^\circ\text{C}$ [23]), 400 $^\circ\text{C}$ for borate sodalite 1, 500 $^\circ\text{C}$ for borate sodalite 2 and 400 $^\circ\text{C}$ as well as 700 $^\circ\text{C}$ for NaCl sodalite. The low T_{\max} value for synthesis in the nitrite system was revealed to prevent nitrite decomposition into NO_x and O_2 , indeed the temperature (300 $^\circ\text{C}$) is slightly beneath the NaOH melting point but some degradation of melting temperature is expected in the multicomponent reaction system.

Heating up times were 90 min for the 300 $^\circ\text{C}$ and 400 $^\circ\text{C}$ experiments as well as 120 min for the 700 $^\circ\text{C}$ experiment. In order to synthesize sodalites with tailored crystal size NaCl sodalite was further investigated without a holding time (only heating up).

The experimental scheme is given in Fig. 1 and all experimental data are summarized in Table 1.

After synthesis the product pellets were grinded. The products of the experiments of the series on the reaction mechanism No. 1–3, Table 1 were characterized in its unwashed form by XRD to prevent any effect of water. After XRD analysis these samples as well as all other products were washed with 150 ml water and dried on air over night, before they were prepared for further analyses.

All products were analyzed by X-ray powder diffraction (XRD). The products were further characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

X-ray powder diffraction was performed using a Philips PW-1800 diffractometer (Bragg-Brentano geometry, CuK_α radiation, 2 Theta range 5° – 80° , step width 0.02° , measuring time of 5 s per step). The WinXPow software (STOE) was used for data evaluation.

MIR-FTIR measurements were performed with a Vertex 80v spectrometer (Bruker AXS) in the range of 400–4000 cm^{-1} with KBr pellets. Therefore 1–2 mg sample and 200 mg KBr were inserted.

SEM investigations were performed for selected products on a JEOL JSM-6390A at an acceleration voltage of 20 kV and 30 kV respectively. The SEM was equipped with a Bruker Quantax-200 EDX system.

3. Results

The first series with samples No. 1–5 (Table 1) was performed to clarify the following essential questions on the mechanism and the course of the whole reaction process:

- (1) Is the hydrate water of zeolite 13 X absolutely essential for the first phase of the process?
- (2) Is the NaOH really significant for starting the crystallization process?
- (3) Does an insertion of a template salts (here NaCl) result in sodalite formation?
- (4) Is the crystallization process of sodalite even possible without NaCl?
- (5) Is the 13 X zeolite totally dissolved into its primary building units or do we only observe a rearrangement of (stable)

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