

# Synthesis of nanocrystalline nitrate enclathrated zeolite with intermediate framework structure between sodalite (SOD) and cancrinite (CAN)

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## ABSTRACT

Nanocrystalline  $\text{NaNO}_3$  enclathrated microporous material with intermediate structure (INT) between the well known zeolites sodalite (SOD) and cancrinite (CAN) can be prepared from aluminosilicate gels under addition of high amounts of NaOH and  $\text{NaNO}_3$  using low temperature conditions (333 K) within reaction periods of 1 - 96 h. The nanocrystalline products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and simultaneous thermal analysis (STA). Crystal sizes around 50 nm were found within the products. The nanocrystallites were compared with microcrystalline nitrate cancrinite synthesized under the well known conditions of hydrothermal transformation of kaolinite in NaOH at 473 K for 48 h.

In further experiments triethanolamine (TEA) was added to the starting batch to study the influence on nanocrystalline phase formation in superalkaline salt bearing gels under the low temperature conditions at 333 K. A strong effect of TEA was found persisting in a remarkable influence on the morphology of the nanoparticles. In the TEA system INT always crystallized as big spheres each one consisting of countless nanocrystalline rods of about 40 nm diameter and about 250 nm in length.

**Keywords:** nanocrystalline solids, nitrate cancrinite, nitrate storage, synthesis, TEA effect, morphology of nanocrystals

## 1 INTRODUCTION

Zeolites of the cancrinite family offer suitable conditions for the enclathration of nitrate anions into their one dimensional channel system, as already known since the outstanding work of R. M. Barrer [1]. Each channel, running parallel c-direction, exhibits a  $5.9 \times 5.9 \text{ \AA}$  wide 12-ring window and bigger ion groups can only enter this intra-crystalline space during the crystallization period. Thus material properties of CAN are ranging from zeolite-like to clathrate-like behaviour revealing that cancrinites

are interesting materials for applications as reservoir mineral in techniques and environmental protection. Effective future utilizations of nitrate enclathrated zeolites require economic low temperatures of synthesis and nitrate uptake combined with tailoring of nitrate release properties. In the present work we investigate low temperature synthesis of nanocrystallites at only 333 K and point out these conditions as a suitable way to obtain a nanocrystalline nitrate zeolite with special properties, related to its intermediate aluminosilicate framework structure (INT) between cancrinite (CAN) and sodalite (SOD). Whereas the CAN structure can be described by the AB stacking of hexagonal sheets formed by 6-rings of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra along c-axis, the INT structure is characterized by random AB or ABC stacking disorder of the same aluminosilicate sheets in c-direction, giving rise to formation of cages of various size by blocking channels by sheets shifted in C sequence [2].

The effect of the additive triethanolamine (TEA) was investigated in further series of syntheses to study the influence on formation of  $\text{NaNO}_3$  enclathrated zeolite phases, because deceleration of nucleation rate is well known in the zeolite A and X system due to the complexing effect of TEA on the reactive aluminium-species in the solution [3].

## 2 EXPERIMENTAL

The system  $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O-NaNO}_3\text{-(TEA)}$  was investigated within reaction periods of 1 - 96 h under superalkaline low temperature conditions at 333 K. Strong alkaline gels and low temperatures were first used in [4] for zeolite A and hydrosodalite formation without addition of a further guest salt. In the present study we use mixtures of aluminosilicate gels, NaOH and  $\text{NaNO}_3$  as educts.

Syntheses were performed in Teflon-coated steel autoclaves. Therefore a solution, prepared from 1,25 g  $\text{NaAlO}_2$  (Riedel-de Haen 13404), 2 g  $\text{NaNO}_3$  (Fluka 71758) and 10 ml 8 molar NaOH (Merck 1.06467) was mixed with a second solution, prepared from 1,25 g  $\text{Na}_2\text{SiO}_3$  (Aldrich 30.781-5), 2 g  $\text{NaNO}_3$  (Fluka 71758) and 10 ml 8 molar NaOH (Merck 1.06467). The gel formed this way was filled into a Teflon lined 50 ml steel autoclave. The autoclave was

heated at 333K for reaction times between 1h – 96 h. The products were washed with 200 ml water and dried at 353 K for 24 hours. To compare the products with microcrystalline CAN material the latter was hydrothermally grown at 473K for 48 hours heating time by alkaline transformation of zeolite A (Fluka 69836) in 20 ml 8-molar NaOH (Merck 1.06467) using the same autoclaves and washing procedure as for low temperature syntheses.

For the experiments under addition of triethanolamine 3,3 g TEA (Merck 822341) was added to the gels, prepared as described above. The same conditions (temperature 333K and reaction times between 1h – 96 h) were used for these experiments.

The products were characterized by X-ray powder diffraction on a Philips PW-1800 powder diffractometer (CuK $\alpha$  radiation, 2 Theta range from 5° to 85°, step width of 0,03° and measuring time of 1sec per step). The WinXpow software (STOE) and the TOPAS software (Bruker) were used for data evaluation.

Selected nanocrystalline samples were further examined on a JEOL JSM-6390A scanning electron microscope.

All samples were analysed by FTIR spectroscopy using a Bruker Vertex 80 FTIR spectrometer and KBr pellets (2 mg of sample and 198 mg KBr).

In addition thermogravimetric measurements were carried out for the nanocrystalline sample of the 3 h experiment without TEA and the microcrystalline CAN for comparison. A Setaram Setsys evolution 1750 thermoanalyzer up to 1673 K at a heating rate of 2 K/minute under flowing He atmosphere (20ml/minute) was therefore used. For additional informations on the thermal stability both samples were heated at 4K/min up to at 873 K under open conditions in a furnace, before quenched to room temperature and characterised by XRD.

### 3. RESULTS

#### 2.1 Synthesis

Nanocrystalline NaNO $_3$  enclathrated material was already successfully synthesized after a reaction time of 3 h in both series i.e. with and without TEA. The X-ray powder patterns of these 3h products are shown in Figure 1 together with the pattern of the microcrystalline CAN obtained at 473 K. Both patterns of the low temperature 3 h products are identical, but compared with microcrystalline CAN remarkable differences were observed. Besides the signals of the patterns of Fig. 1a, b are not only much broader due to the nanocrystalline character and amorphous parts within each batch it is noticeable that important reflections of the CAN pattern are absent in the XRD diagrams of both nanocrystalline products. Pattern analysis clearly indicates that the nanocrystalline samples show only the reflections, that cancrinite has in common with sodalite. As known from carbonate enclathrated aluminosilicates described in [2] this is a clear sign that the structure of both low temperature products is characterized by random disorder

of aluminosilicate sheets between AB stacking along [001] of CAN and ABC stacking found along [111] in SOD [2].

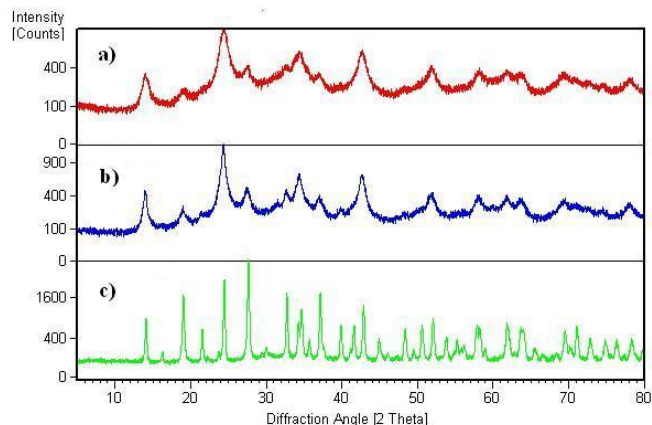


Figure 1: XRD pattern of the nanocrystalline products, obtained at 333 K after 3h: gel synthesis (a) gel synthesis under addition of TEA (b) and the microcrystalline sample of NaNO $_3$ - cancrinite grown at 473 K (c).

The refinement of the pattern of the samples as a disordered CAN is possible giving typical for hexagonal cell parameters  $a = 1269.27(9)$  pm and  $c = 519.84(3)$  pm as example for pattern of Fig. 1b. As demonstrated in [2] also a smaller cell of  $a \approx 730$  pm and half of the c-lattice constant of CAN ( $c \approx 259$  pm) can be used for average structure description of an aluminosilicate intermediate phase (INT) between SOD and CAN.

An estimation of the crystal size according to the Scherrer equation was performed using six strong lines of the X-ray powder diagram. Average values of 1  $\mu$ m for CAN micro and 63 nm for INT nano were calculated.

The IR spectra obtained in the mid-infrared regions of the nanocrystalline samples and the spectrum of the microcrystalline CAN are given in Figure 2. The microcrystalline CAN sample shows very sharp modes. In the range of the asymmetric T-O-T stretching vibrations (T= Si, Al) of the aluminosilicate framework the strong absorption bands in the 1100 cm $^{-1}$  – 950 cm $^{-1}$  region can be clearly distinguished. The somewhat weaker symmetric stretching modes  $\nu_s$  of the framework between 760 cm $^{-1}$ -560 cm $^{-1}$  and the bending modes (500 cm $^{-1}$ - 400 cm $^{-1}$ ) are all very well resolved (Fig. 2c) typical for NaNO $_3$  CAN [5]. The spectra of the nanocrystalline samples (Fig. 2 a, b) in principal exhibit the same bands, but with much lower resolution and somewhat weaker, caused by the small particle size and lower degree of crystallinity compared to the microcrystalline CAN. Especially the resolution and intensity of the  $\nu_s$  modes seems to be strongly influenced by the degree of disorder of the INT structure of the nanocrystalline samples (Fig. 2 a, b) compared to the microcrystalline ordered CAN (Fig. 2 c).

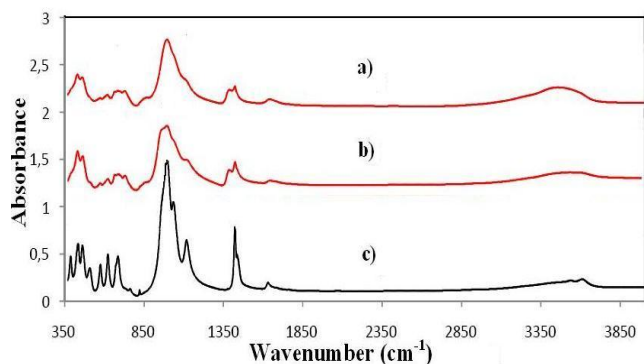


Figure 2: FTIR spectra of the nanocrystalline  $\text{NaNO}_3$ -zeolite INT synthesis without TEA (a), under addition of TEA (b) and the microcrystalline sample of  $\text{NaNO}_3$ -cancrinite (c).

The enclathrated  $\text{NO}_3^-$  anions can be clearly detected in all samples by the absorption peaks of nitrate in the  $1380\text{ cm}^{-1}$  -  $1440\text{ cm}^{-1}$  range [5]. Beside nitrate anions water can be seen in the spectra (especially high amounts in the nanocrystalline INT phases) by the vibration modes of water molecules at  $1650\text{ cm}^{-1}$  and a broad band in the  $3100\text{ cm}^{-1}$  -  $3600\text{ cm}^{-1}$  range [5].

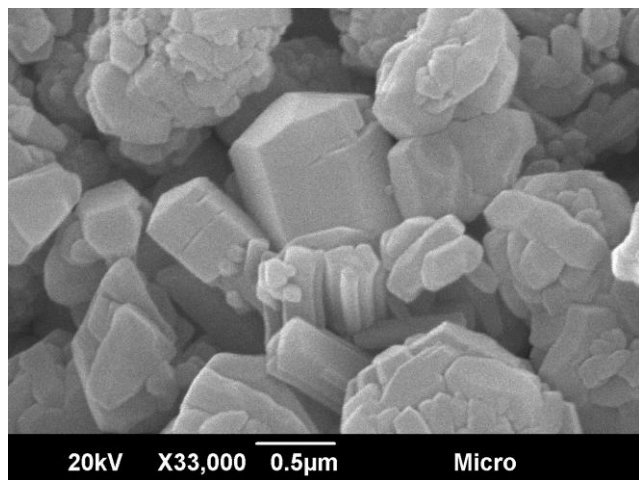


Figure 3: SEM image of the microcrystalline CAN.

Figures 3-7 show SEM-images of the samples. Compared to the big crystals of the microcrystalline CAN (Fig. 3) very fine grained material was found for the nanocrystalline product, obtained at 333 K after 3h from gel synthesis without addition of TEA. Here more or less nanocrystals are agglomerated to spherical grains up to 200 nm size (see Fig. 4).

In the TEA system INT always crystallized as big spheres each one consisting of countless nanocrystalline rods of about 40 nm diameter and about 250 nm in length as can be derived from the SEM images of Figs. 5-7. The mechanism of formation of this unusual morphology of micro-spheres from nanorods is unclear up to now.

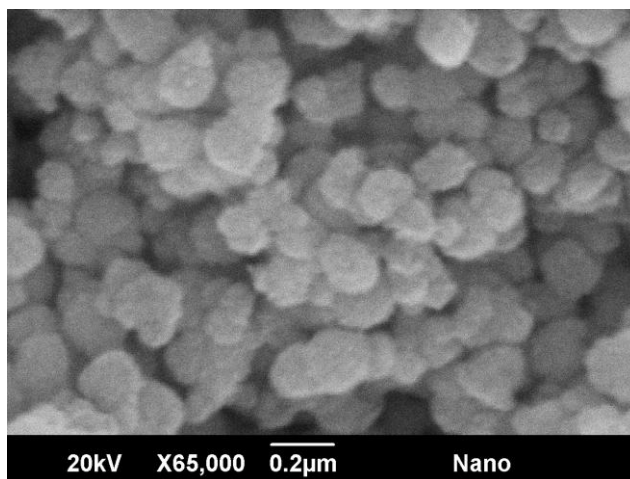


Figure 4: SEM image of the nanocrystalline INT sample of synthesis without TEA additive.

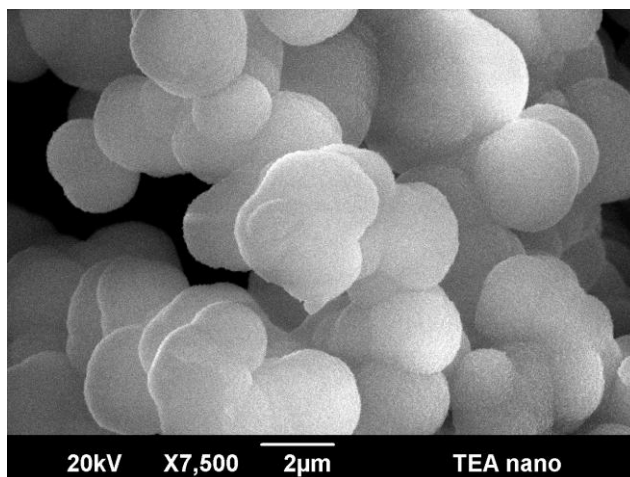


Figure 5: SEM image of the nanocrystalline INT sample of synthesis with TEA additive.

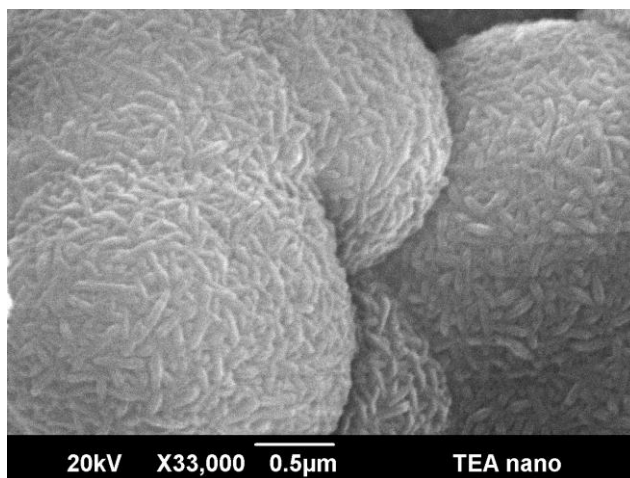


Figure 6: SEM image of the nanocrystalline INT sample of synthesis with TEA additive at higher magnification.



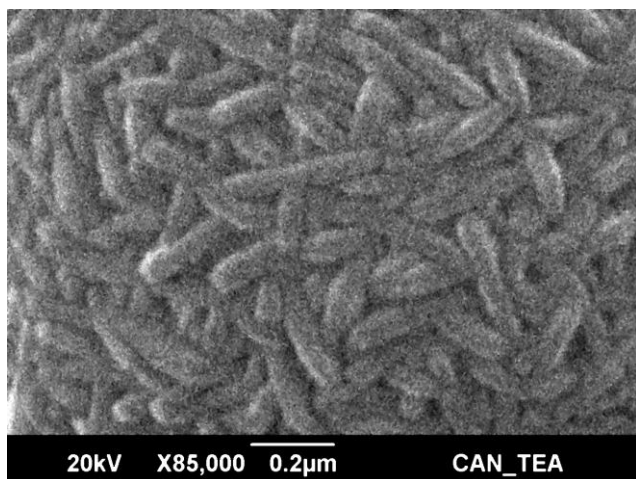


Figure7: SEM image of the nanocrystalline INT sample of synthesis with TEA additive at very high magnification.

A composition  $\text{Na}_{7.5}[\text{AlSiO}_4]_6(\text{NO}_3)_{1.5} \cdot 3.8\text{H}_2\text{O}$  could be derived from TG shown in Fig. 8 for the nanocrystalline sample without TEA and  $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_3) \cdot 2.4\text{H}_2\text{O}$  for microcrystalline CAN (Fig. 9).

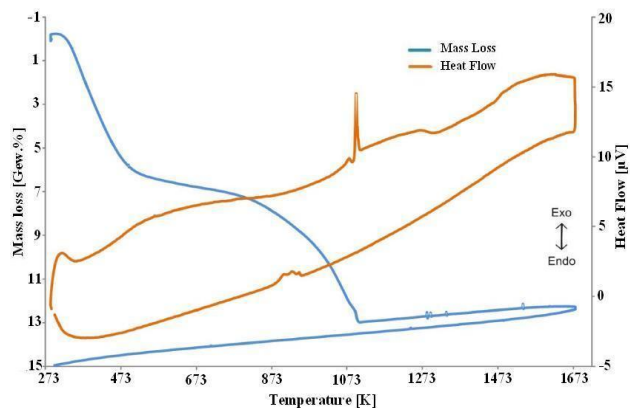


Figure 8: Thermogram of the nanocrystalline INT of synthesis without TEA (total weight loss: 14.9 wt %).

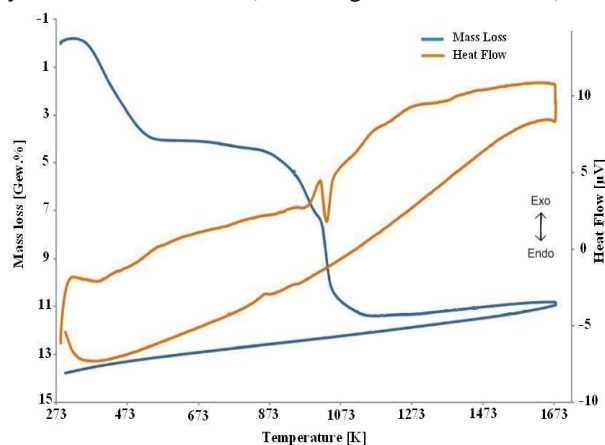


Figure 9: Thermogram of the microcrystalline  $\text{NaNO}_3$ -CAN (total weight loss: 13.8 wt %).

Further heating experiments showed thermal stability of CAN and INT during heating up to 873 K under open conditions, but formation of nepheline as thermal decomposition product (Fig. 10).

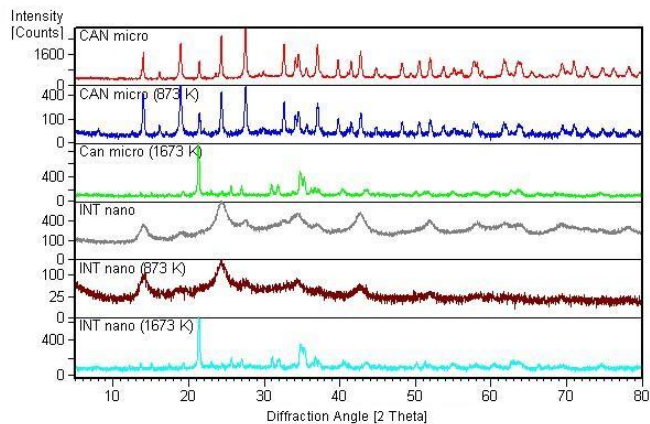


Figure 10: XRD pattern of the samples CAN micro and INT nano after heating in air at 873 K and the residues of thermal analysis (heated up to 1673 K in He-atmosphere).

#### 4. CONCLUSIONS

High alkaline nitrate bearing aluminosilicate gels are suitable educts to synthesize nanocrystalline  $\text{NaNO}_3$ -enclathrated zeolites at low temperature and short time.

This new nanocrystalline material of composition  $\text{Na}_{7.5}[\text{AlSiO}_4]_6(\text{NO}_3)_{1.5} \cdot 3.8\text{H}_2\text{O}$  exhibits a three dimensional framework with structural features of CAN and SOD.

TEA addition was found to have an important effect on the morphology of these nanoparticles. The formation of micro spheres by the growth together of nanocrystalline rods of the new material was caused by this additive.

$\text{NaNO}_3$  “nano INT” can be of interest for future applications as nitrate reservoir mineral in techniques and environmental protection.

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