

Nanocrystalline NaBH₄-enclathrated zeolite SOD: a model for the improvement of safeness and reactivity of boron hydride based hydrogen storage systems

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ABSTRACT

Incorporation of boron hydride anions into a protective microporous zeolite matrix is a suitable way to prevent NaBH₄ decomposition under open conditions. Therefore synthesis and properties of nanocrystalline NaBH₄-sodalite-type structure is investigated and compared with microcrystalline material.

We show that the nanocrystalline sodalite host framework exhibits hydrogen release during heating already significantly above about 373 K. i.e. about 100K lower compared to the microcrystalline material. A 100% conversion rate was found for the BH₄⁻ anions in the nanocrystalline sample instead of only 40% under the same experimental conditions for the microcrystals. We conclude that the small particle size and the amount of water, available from poorly crystalline hydrosodalite parts of the nanocrystalline sample control the hydrogen release.

Keywords: nanocrystalline solids, boron hydride sodalite, hydrogen storage, synthesis, thermal behaviour

1 INTRODUCTION

Boron hydride is an interesting material for hydrogen storage in view of a high gravimetric storage density of 10.6 wt. % hydrogen but to become widely accepted in technical applications, several problems have to be solved in future. Predominantly the high reactivity of NaBH₄ salt under atmospheric conditions belongs to this point. Here the possibility of self ignition under influence of air moisture offers a general safety problem. Incorporation of the salt into a protective microporous matrix is a suitable way to overcome this difficulty. The pores of such a host structure must be blocked for the entrance of water molecules. R. M. Barrer was the first who suggested an impregnation of zeolite cavities with light metal hydride salts [1]. But it has been taken more than two decades of research until the first boron hydride enclathrated zeolite material was successfully synthesized [2, 3]. From the more than 130 zeolite structure types only the sodalite structure (SOD) proved to be a suitable host for a secure long-time stable encapsulation of BH₄⁻ units. Additionally the NaBH₄-sodalite exhibits a remarkable hydrothermal stability [4].

Whereas the microcrystalline BH₄⁻ sodalite was an important first step of material design we investigate the

synthesis and properties of nanocrystalline sodium boron hydride sodalite in the present work. Instead of the alkaline transformation of kaolinite at elevated temperatures used for microcrystalline material preparation the nanoparticles were successfully synthesized by low temperature gel crystallization under high alkaline conditions and addition of NaBH₄ salt. Preparation of basic hydrosodalite by this very simple method was described by Fischer et al. and Hadan and Fischer nearly 20 years ago during their experiments on zeolite LTA crystallization at very low temperatures under superalkaline conditions [5, 6]. In the present study we show that crystallization of those gels is a very suitable way for preparation of NaBH₄-sodalite nanoparticles by fine tuning of the system parameters temperature, reaction time and NaOH concentration. A further aim of this study is the investigation of thermal decomposition behaviour of the BH₄ connected with hydrogen release in heating experiments of the nanocrystalline and the microcrystalline sample.

2 EXPERIMENTAL

Syntheses were performed in Teflon-coated steel autoclaves. A gel composition of 13 Na₂O : 2 SiO₂ : 1,5 Al₂O₃ : 5 NaBH₄ : 220 H₂O proved to be very suitable for pure phase sodalite formation. In-situ gel formation within the autoclaves was used to prevent an early decomposition of the NaBH₄ salt during external gel-preparation before the onset of sodalite host formation. Therefore 1,6 g NaBH₄ salt (Merck 8.06373) was filled into the Teflon liner before a homogeneous dry powder mix of 1,25 g of very fine grained sodium-metasilicate (Fluka 2299129) and 1,25 g sodium aluminate (Riedel-de Haen 13404) was added over the boronhydride salt without further mechanically mixing. At last 20 ml of a 5-molar freshly prepared sodium hydroxide solution (Merck 1.06467) cooled down to room temperature, was carefully added. The autoclave was heated at 333K for reaction times between 4h – 12 h periods. After these times the products were washed with 500 ml water and dried at 383 K for 48 hours. To compare the nanocrystalline low temperature products with microcrystalline material the latter was hydrothermally grown at 393K for 24 hours heating time according to the method described in [2].

All samples were characterized by X-ray-powder diffraction on a Philips PW-1800 powder diffractometer

(CuK α 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. The X-ray powder pattern of the 12 h product was further analysed to estimate the average particle size as well as the ratio between crystalline material and amorphous material.

SEM investigations together with EDX-analysis were performed on a JEOL JSM-6390A scanning electron microscope coupled with a JED 203 energy disperse X-ray analysis system.

Infrared spectra were taken on a Bruker Vertex 80 FTIR spectrometer using KBr pellets (1 mg of sample and 200 mg KBr). Monitoring of a successful enclathration of the BH $_4^-$ -anions is easy possible this way according to their characteristic IR active absorption bands.

A first investigation of thermal decomposition behaviour of the enclathrated BH $_4^-$ anions, connected with hydrogen release was performed under open conditions on air. Therefore the nanocrystalline sample obtained after 12 h reaction time and the microcrystalline sample synthesized by alkaline hydrothermal transformation of kaolinite, described in [2] were heated at 723 K for 30 minutes in a muffle furnace under open conditions in air. The products of these heating experiments were analysed by XRD and FTIR using the same measurement conditions as for the “as synthesized” phases. In addition thermogravimetric measurements were carried out for the nanocrystalline sample of the 12 h experiment on a Setaram Setsys evolution 1750 thermoanalyzer up to 773 K at a heating rate of 2 K/minute under flowing He atmosphere (20ml/minute).

For more detailed informations on the behaviour of the nanoparticles compared to the microcrystalline sample the hydrogen release was detected via nitrate reduction test reaction in temperature dependent IR (TIR) experiments with temperatures up to 873 K. A Bruker IFS 66v FTIR spectrometer equipped with a special heating device (NaCl pellets, 1 mg of sample and 200 mg NaCl) was used for the TIR studies.

3. RESULTS

2.1 Synthesis

Nanocrystalline NaBH $_4$ sodalite of suitable size and sufficient crystallinity was successfully synthesized after a reaction time of 12 h. The X-ray powder pattern of this sample is shown in Figure 1 a) compared to the pattern of the microcrystalline sample (Figure 1b) obtained according to the procedure in [2]. The pattern of the nanocrystalline 12 h sample shows sodalite type reflexes as the only crystalline contribution. Using the “TOPAS” software the cubic cell parameter of 893.51(8) pm was refined and an average crystal size of 25 nm was calculated. The lattice parameter of this nanocrystalline sodalite is slightly enlarged compared to the 891.61(2) pm cell of the microcrystalline

phase, described in [2]. This could be due to imperfections in the cage fillings. Intercalations of impurities like CO $_3^{2-}$, (OHH $_2$ O) and water molecules in some of the sodalite cages are well-known from each synthesis of salt-filled sodalites in NaOH solutions [11].

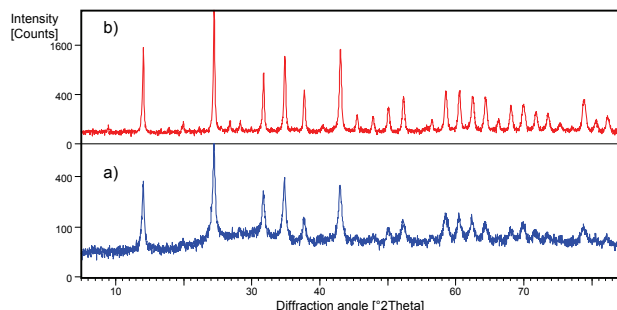


Figure 1: XRD powder pattern of the nanocrystalline sample, observed after 12 h reactions time (a) and the microcrystalline sample according to [2] (b).

Additionally a certain amount of amorphous material becomes obvious from the background features of Figure 1 a). Thermogravimetry of the nanocrystalline sample yielded a total weight loss of 8.0 % which is mainly attributed to a very high content of water molecules inside the amorphous phase. Back-measurements by TG of the same sample after exposing for 24 hours under normal atmospheric conditions reveal that again 7.3 percent by weight are lost. There seems to be very close resemblance of the amorphous phase to a very poor crystalline expanded hydrosodalite, described in [7] and the amorphous material can be regarded as a precursor of hydrosodalite. Hydrosodalite is known to reload water immediately under open air conditions as shown here by TG remeasurement. The amount of amorphous material is estimated to be about 50 % for the 12 h sample using the “TOPAS” Rietveld software for estimation.

Figure 2 shows a SEM-image of the nanocrystalline sample obtained after 12 hours reaction time. Very fine grained material was found consisting of sodalite nanocrystals of ~25 nm size “glued” by amorphous material to spherical agglomerates of about 100 nm beside a few bigger agglomerates. Quantitative evaluation of the EDX-analysis of the sample obtained from the JED-2300 analysis system, yields to a Si:Al ratio of 1,07 for the batch obtained in the full area of Figure 2.

The IR spectra obtained in the mid-infrared regions of the nanocrystalline and microcrystalline samples are summarized in Figure 3a – b) compared with the spectrum of pure NaBH $_4$ salt (Merck 8.06373). The spectrum of the microcrystalline sample coincides with that given in [2]. In the range of the framework modes all the spectra show the strong broad absorption band around 1000 cm $^{-1}$ due to of the asymmetric T-O-T vibrations (T= Si, Al). The somewhat weaker three symmetric stretching modes ν_s of the sodalite framework in the 660 cm $^{-1}$ - 740 cm $^{-1}$, called the

“sodalite fingerprint” vibrations, can be clearly seen from Figure 3 a-b) together with the two framework bending modes in the 400 cm⁻¹ - 500 cm⁻¹ range.

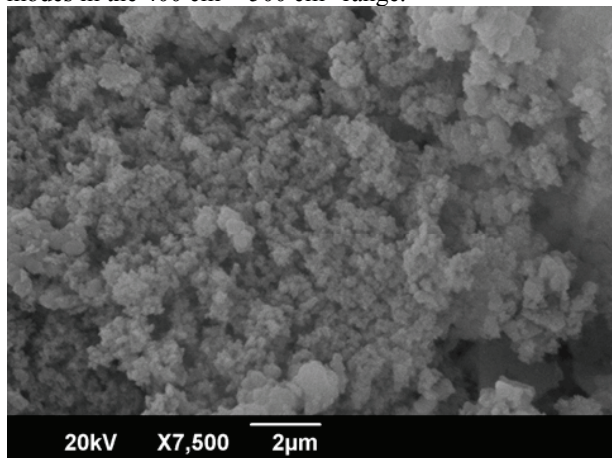


Figure 2: SEM-image of the nanocrystalline NaBH₄-sodalite agglomerated by very poorly crystalline material of hydrosodalite

The amount of enclathrated BH₄⁻ anions can be clearly estimated according to the absorption peaks of NaBH₄ salt at 1143 cm⁻¹ (ν₄), 2241 cm⁻¹ (ν₃), 2286 cm⁻¹ (2*ν₄), and 2390 cm⁻¹ (ν₂+ν₄) as given in the literature [8-11]. These bands are found only slightly shifted when enclathrated in the microcrystalline sodalite (at 1134, 2238, 2287 cm⁻¹ for the main peaks) and appear to be broader and again shifted for BH₄ groups enclathrated in the nanocrystals (2242, 2295 cm⁻¹ for the main peaks) This may be due to a lower degree of perfection of the nanocrystalline sample. Consequently the ν₄-mode at 1143 cm⁻¹ appears as shoulder at the broad asymmetric stretching mode of framework T-O-T atoms around 1000 cm⁻¹. Beside the vibrations of the BH₄⁻ anions the high water content mainly enclathrated in the amorphous phase as discussed above, can be seen in the spectra of the nanocrystalline sample by the vibration modes of water molecules at 1650 cm⁻¹ and a broad band in the 3100 cm⁻¹ – 3600 cm⁻¹ region which is in contrast to the spectrum of the microcrystalline sodalite (Figure 3 b) showing no remarkable amounts of water molecules. Here a small signal at 3640 cm⁻¹ can be stated according to enclathration of some (OH·H₂O)⁻ anions which were not exchanged by water during washing according to the high degree of crystallinity of the sample, as already discussed above. In the spectrum of the tetrahydroborate sodalite nanoparticles (Figure 3a) some cage fillings with other borate species beside BH₄⁻ can be seen by an additional weak band at about 1300 cm⁻¹, i.e. in the region proposed in [2] for hydrolysis products of BH₄⁻. Hydro/hydroxoborate species, termed species A in [2] were expected formed by intra-cage reaction of some BH₄⁻-anions with water impurities during the drying period of 48 h at a temperature of 383 K according to the thermal induced reaction

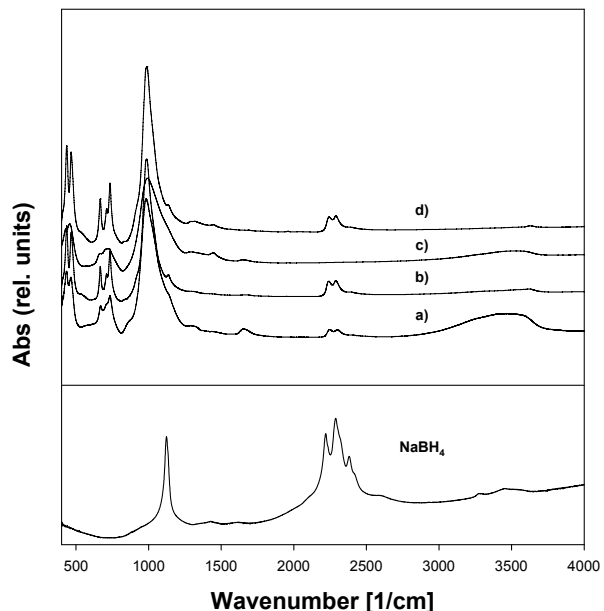
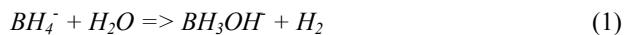


Figure 3: IR spectra of the nanocrystallites (a) and microcrystallites (b) as synthesized and nanocrystallites (c) and microcrystallites (d) after heating at 723 K for 30' under open conditions. The spectrum of the pure NaBH₄ salt (Merck 8.06373) is inserted below for comparison.

Within microcrystalline sodalite, washed with 250 ml water and dried at 353 K over night this reaction was found to start at higher temperature above about 473 K [2]. For comparison the microcrystalline sample used in the present study was washed with 500 ml water and dried at 383 K for 48 h too, as the nanocrystalline sample. The IR spectrum of this microcrystalline sample in Figure 3 b shows no additional borate formation, the nanocrystalline sample (Figure 3 b) evolves a weak band at about 1300 cm⁻¹. This behaviour is a hint that decomposed BH₄ species are enclathrated within the sodalite nanocrystals. Water as the reactant initiating the decomposition reaction is available in higher amounts at elevated temperatures and intra cage hydrolyses will be accelerated already at 383 K.

Further heating experiments were performed to investigate if there are also differences in the thermal decomposition of the BH₄⁻ anions at elevated temperatures. The nanocrystalline and the microcrystalline samples were heated at 723 K for 30 minutes under open conditions in a muffle furnace, the spectra are given in Figure 3 c) and d). In the case of the microcrystalline sample it can be seen due to the high and nearly the same BH₄ absorption intensity Figure 3 b) and 3 d) that a very high amount of the BH₄ anions remains stable during heating. Some new borate species were formed by hydrolysis with water impurities revealing the signal around 1300 cm⁻¹ as well as in the 1400 – 1500 cm⁻¹ region. Furthermore a very weak signal at 2000 cm⁻¹ indicates the formation of metaborate according to the

“dry” conditions at 723 K. In contrast different thermal reaction behaviour of the enclathrated BH_4^- groups can be derived from Figure 3 a) and c) in the case of the nanocrystalline sample. Here a complete disappearance of the BH_4^- modes and formation of new borate species (signal around 1300 cm^{-1} and in the $1400 - 1500\text{ cm}^{-1}$ region) can be stated. The decomposition of BH_4^- is already finished without the formation of metaborate species in the cages under the used reaction conditions. A loss of crystallinity of the nanocrystalline sample could be further derived from Figure 3 d) due to decreasing intensities of the framework vibrations which is consistent with a slight decrease in XRD peak intensity with respect to the “background” contribution (pattern not shown).

TIR experiments gave a deeper insight in the reaction mechanism. The reaction of the BH_4^- -groups in the sodalite cages is mainly thermally controlled as shown in the upper part of Fig. 4 for the integrated intensities deduced from TIR experiments. Two important results were obtained: firstly hydrogen release from the nanocrystalline sample already starts significantly above about 373 K. i.e. about 100K lower compared to the microcrystalline material. Secondly a 100% conversion rate was found for the BH_4^- anions in the nanocrystalline sample instead of only 40% under the same experimental conditions for the microcrystalline material.

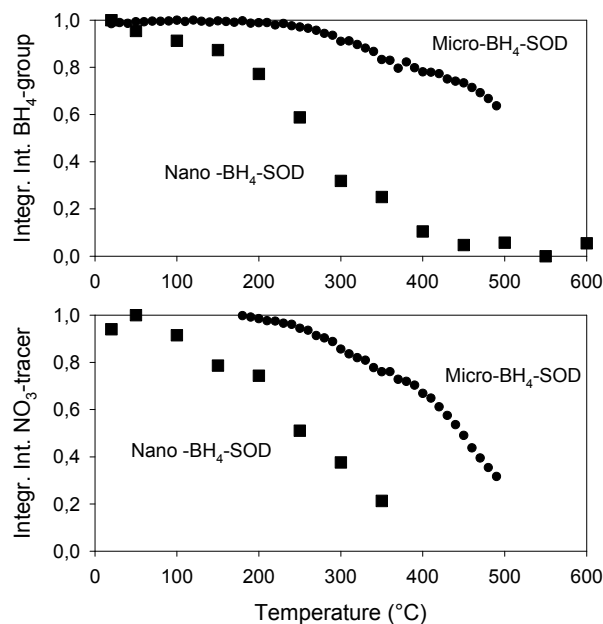


Figure 4: Integrated intensities of the BH_4^- absorption (upper part) and the NO_3^- -tracer absorption (lower part) obtained from TIR experiments of the nanocrystalline sample (squares) and the microcrystalline sample (circles).

As reported in [12] the release of hydrogen from the microcrystalline BH_4^- -sodalite could be measured by a nitrate reduction reaction in TIR experiments with the addition of trace amounts of NaNO_3 . Thus we applied a

similar TIR experiment for the nanocrystalline BH_4^- -sodalite here. Fig. 4 (lower part) shows the integrated intensities of the NO_3^- -tracer absorption for the nanocrystalline sample (squares) and the microcrystalline sample (circles). A gradual increase in NaNO_3 reduction with increasing temperature can be stated and the progression of the curves is well correlating with the differences of BH_4^- decomposition reaction also shown in Fig. 4 (upper part). A more detailed spectroscopic study with suggestion of intermediate step reaction equations from BH_4^- to BO_2^- is given in a forthcoming paper [13].

4. CONCLUSIONS

Nanoparticle formation of NaBH_4 -sodalite is an important step of tailored materials synthesis as matrix for secure long time protecting of boronhydrides. The new material exhibit a low hydrogen release temperature and a high hydrogen release rate.

From the presented results we conclude that the small particle size and also the amount of water, available from the poorly crystalline hydrosodalite parts of the whole sample controls the complete hydrogen release reaction: $\text{BH}_4^- + 2\text{H}_2\text{O} \Rightarrow 4\text{H}_2 + \text{BO}_2^-$.

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