

NaBH₄ in solidified aluminosilicate gel: a new hydrogen storage with interesting properties

J.-Ch. Buhl, L. Schomborg and C. H. Rüscher

*Institute of Mineralogy, Leibniz University Hannover, Callinstr. 3
D-30167 Hannover, Germany, j.buhl@mineralogie.uni-hannover.de

ABSTRACT

NaBH₄ exhibits a high gravimetric storage capacity. However, rapid hydrolysis reaction already under air moisture, connected with hydrogen release (2.4 l H₂/g in the reaction with H₂O), prevent easy technical applications (uncontrollable loss of hydrogen and risk of self ignition). Solidified NaBH₄- gel provides a new and safe way of hydrogen storage on the basis of moisture protection of boranate by an aluminosilicate composite matrix.

Details of synthesis and principal hydrogen release properties of this new boranate gel will be presented in this contribution. The composite compound has a high hydrogen storage capability with maximum enclosure of up to 72 wt% of NaBH₄. Besides its simple preparation method, a controlled H₂ release on demand is possible by addition of very few amount of slightly acid diluted solution. A pH-controlled total hydrogen release up to 1.7 l H₂/g is realized from the gel according to the reaction NaBH₄+2H₂O → NaBO₂+4H₂.

It can be concluded that the NaBH₄-aluminosilicate gel provides a new and safe way of hydrogen storage.

Keywords: hydrogen storage, material synthesis, sodium boranate, partial crystalline solids

1 INTRODUCTION

The hydride salt sodium boranate NaBH₄ with its high gravimetric storage capacity of 2.4 l H₂/g could be a suitable solid hydrogen reservoir. However problems arise due to strong reactivity with water. Rapid hydrolysis connected with hydrogen release occurs already under air moisture according to the reaction NaBH₄+2H₂O → NaBO₂+4H₂. This uncontrollable loss of hydrogen as well as the risk of self ignition prevents easy technical applications. Attempts to overcome these difficulties by the enclathration of boranate anions inside the cavities of microporous materials like microcrystalline or nanocrystalline sodalites were successfully tested, but the gravimetric hydrogen storage capacity of these materials is only about 1/10 of that of pure NaBH₄ [1, 2].

The rather save handling of NaBH₄ in alkaline media during synthesis obtains, however, the possibility to easily store NaBH₄ in certain types of solidified aluminosilicate gels [3], protecting the enclosed

NaBH₄ and providing a hydrogen storage capability as high as 1.7 l H₂/g.

This new type of safe storage of NaBH₄ of high hydrogen density concerns not only protecting of the boranate from reactions with moisture but also enables an easy and fully controllable hydrogen release by adding a very small amount of diluted acid like 1 M HCl. Details of synthesis and principal hydrogen release properties of this new solidified boranate aluminosilicate gel will be presented in this contribution.

2 EXPERIMENTAL

The NaBH₄-containing gel is obtained by an easy two step process: firstly the gel precipitation and secondly the solidification by simply drying the gel in an oven. Gel formation is achieved at room temperature from aqueous sodium-silicate and sodium-aluminate solutions under addition of NaBH₄ salt. 250 mg NaAlO₂ were dissolved in 1.5 ml H₂O before certain amounts of NaBH₄ (we investigated amounts between 100 - 850 mg) were added. The mixture must be stirred until a clear solution forms. The silicate solution is prepared by dissolving 310 mg Na₂SiO₃ in 1.5 ml water before the same amount of NaBH₄ as for the aluminate solution is added under stirring, until even here a clear solution arises. Afterwards the silicate solution must be added dropwise to the silicate solution whereby gel precipitation starts rapidly.

For the second step of preparation the gel has to be exposed to drying procedure at 80-110 °C for 0.5-4 h. This process, to performed in a muffle type furnace under open conditions, leading to the solidification of the gel without any loss of NaBH₄.

After this solidification procedure the boranate gel is characterized by XRD, FTIR, REM/EDX and temperature depending IR (TIR). XRD was performed 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 WinXpov software (STOE) and the TOPAS software (Bruker) were used for data evaluation.

SEM investigations combined with EDX-analysis were performed on a JEOL JSM-6390A scanning electron

microscope coupled with a JED 203 energy disperse X-ray analysis system.

FTIR was carried out on a Bruker Vertex 80 FTIR spectrometer using KBr pellets (1 mg of sample and 200 mg KBr). Monitoring BH_4^- -anions is easy possible this way according to their characteristic IR active absorption bands.

Temperature dependent IR-measurements (TIR) were taken in situ on a Bruker IFS66/FTIR spectrometer equipped with a heating device. The samples were diluted in dry NaCl (1mg sample in 200 mg NaCl), pressed into pellets and measured in relation to a NaCl reference pellet.

For the investigation of a controlled hydrogen release experiments a special glass apparatus equipped with a gas syringe for measuring the gas volume was used. A 1% solution of hydrochloride acid was added to the gel at room temperature. Gels with different amounts of NaBH_4 were therefore examined.

3 RESULTS

3.1 Synthesis and SEM/EDX analysis

Figure 1 shows a SEM-image of the NaBH_4 gel solidified at 110°C for 1 h and EDX analysis of the sample, obtained in the full area of image. Strong sodium content as a result of high amounts of NaBH_4 as well as separation of NaOH during gel precipitation and alteration process becomes obvious.

Therefore the alkalinity during solidification remains very high, thus preventing the BH_4^- anions within the starting gel from decomposition by hydrolysis before hardening is finished. This subsequent process of drying at $80 - 110^\circ\text{C}$ for times between 0.5 h – 4.0 h causes rapid gel hardening according to the withdraw of water molecules. A solidified NaBH_4 containing strong alkaline aluminosilicate gel results. This product evaluation starting with gel precipitation and the alteration during gel drying for up to two hours was followed by X-ray powder diffraction.

3.2 XRD, FTIR and TIR

Figure 2 summarizes the X-ray powder patterns of NaBH_4 gel just after precipitation at room temperature; (a), the solidified NaBH_4 composite after gel drying for 1 h at 110°C (b) and pure dried NaBH_4 salt (c). Directly after precipitation of the NaBH_4 gel the product has the state of an amorphous sodium aluminosilicate, containing the whole amount of BH_4^- anions from the inserted NaBH_4 becoming obvious from the XRD pattern (Figure 2 a). The broad signal around $20-60^\circ 2\theta$ with a maximum near $30^\circ 2\theta$ indicates short range order (related to more or less) Si-O-Al bonds within the gel.

Partial crystallization occurs hand in hand with the gel drying process, depending on temperature and time of drying procedure. The XRD pattern after 1 hour of drying at 110°C shows strong reduction of the broad signal and the formation of crystalline species according to evaluation of a

powder pattern consisting of broader as well as sharp signals (Figure 2 b).

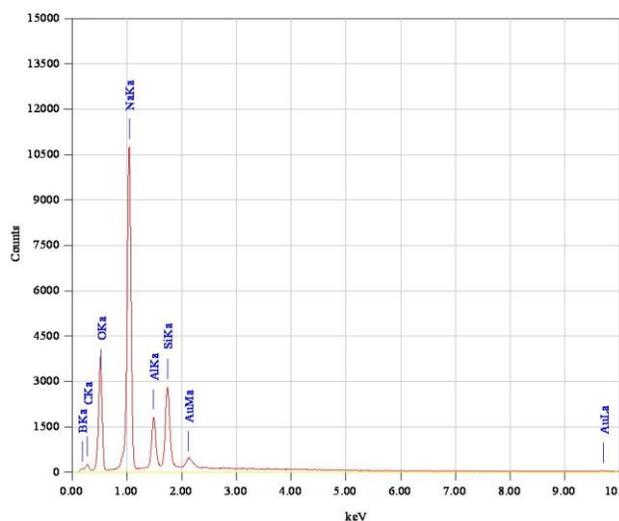
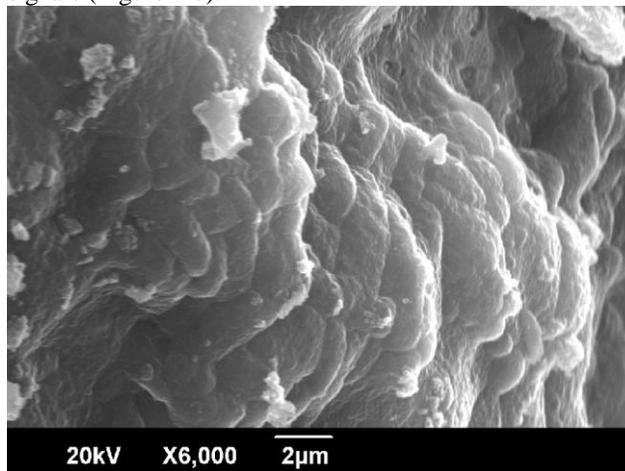


Figure 1: SEM-image and full area EDX analysis of solidified NaBH_4 -gel as synthesized after solidification at 110°C for 1h.

Re-crystallization of NaBH_4 can be clearly seen by comparison of the very sharp peaks in Figure 2 b with the pattern of pure NaBH_4 salt in Figure 2 c. Besides NaBH_4 the formation of a low crystalline second phase can be derived from this pattern. Here the main reflections of an aluminosilicate sodalite type phase can be observed, broadened according to low degree of crystallinity together with a strong and sharp new peak at $6.5^\circ 2\theta$. The latter signal indicates probably a sheeted type of long range order of this sodalite related aluminosilicate.

Furthermore a reduced amount of the amorphous material remains in the solidified gel as can be seen from the background contribution of the pattern in Figure 3c. Thus the new solidified NaBH_4 gel can be regarded as a solid composite of an amorphous body containing partial crystalline aluminosilicate and high amounts of re-crystallized NaBH_4 .

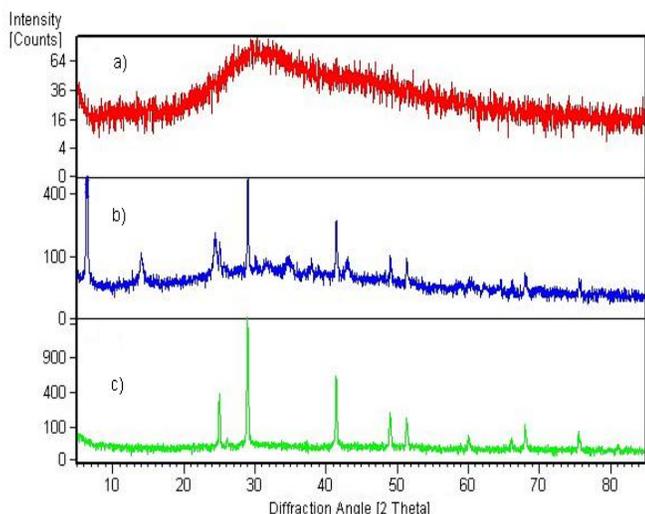


Figure 2: X-ray powder pattern: NaBH₄ gel just after precipitation at room temperature; (a), NaBH₄ composite after gel drying for 1 h at 110°C (b) and pure dried NaBH₄ salt (c).

The NaBH₄ within the solidified gel and its stability by protection of the gel matrix over weeks is further confirmed by infrared absorption spectroscopy, as shown in Figure 3. As an example here the spectrum of the composite material, as synthesized as well as exposed to air for three weeks are given, compared with the spectrum of the pure NaBH₄ salt.

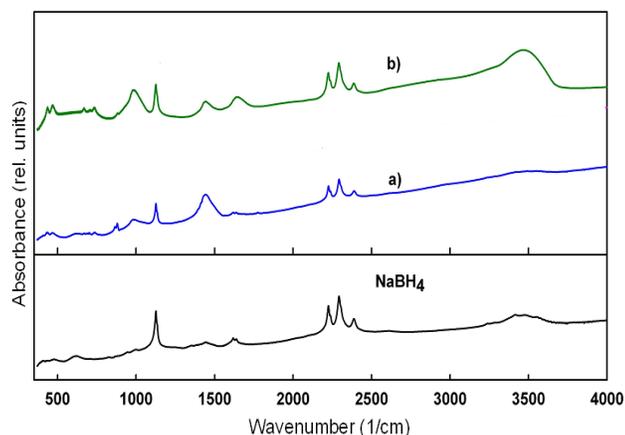


Figure 3: FTIR spectra of NaBH₄ aluminosilicate gel as synthesized (a), gel kept 21 days under open conditions (b) and of NaBH₄ salt (bottom).

A significant uptake of water molecules can further derived from Figure 3 b due to increasing bending and stretching modes of water (signal at 1630 cm⁻¹: bending mode and the broad band around 3500 cm⁻¹: stretching mode [11]). As a further indication for the protection effect of the gel on NaBH₄ it can be concluded that these water molecules are not causing any hydrolysis reactions of the

NaBH₄. No other borate species can be found in the spectrum of Figure 3 b [12-14].

Formation of sodium carbonate on the gel surface as the result of reaction with CO₂ from the air under alkaline conditions can further derived from Figure 3 (mode around 1450 cm⁻¹ and a weak one at 880 cm⁻¹ of CO₃²⁻ anions [11, 15]).

The BH₄⁻ anions of NaBH₄ inside the composite material can be monitored by the strong vibration modes at 1143 (ν₄), 2286 (2•ν₄), 2241 (ν₃) and 2390 (ν₂+ν₄) ([4-8], i.e. at the same positions as in the spectrum of the pure NaBH₄ salt). It could be shown that this new material is stable over many weeks under open conditions possessing not any alteration in the spectra.

The vibration modes of the sodalite-like weak crystalline compound of the solidified NaBH₄ gel can be further seen in the spectra of Figure 3 a and 3 b being more pronounced in the 3 week old sample. Here the aluminosilicate framework modes of sodalite appear by a more stronger broad absorption band around 1000 cm⁻¹ caused by the asymmetric T-O-T vibrations (T= Si, Al) and the weaker triplet of symmetric stretching modes ν_s of the sodalite framework in the 660 cm⁻¹- 740 cm⁻¹ range, entitled as “sodalite fingerprint” as well as the two framework bending modes in the 400 cm⁻¹- 500 cm⁻¹ region [9-10].

TIR spectra were recorded to test the thermal stability of the NaBH₄ gel. The results are given in Figure 4. Under the conditions of the NaCl pellet matrix used in TIR the gel is stable up to 400°C. Further experiments by heating the material in an oven under open conditions reveal somewhat lower stability. Decomposition was found to start here just above 300°C.

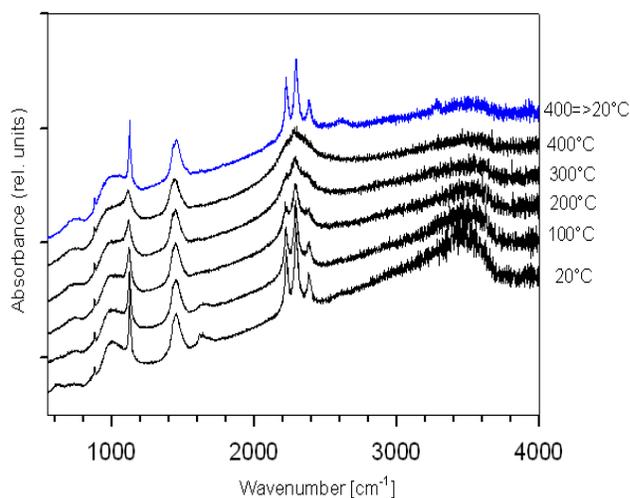


Figure 4: TIR spectra of NaBH₄ gel inside a NaCl matrix.

3.3. Hydrogen release

A controlled H₂ release on demand from the gel is simply possible by addition of very few amount of slightly

diluted acid solution. As mentioned above NaBH_4 -salt reacts with water uncontrollable to hydrogen and different borates. Mild increased temperatures of 40°C are therefore necessary, because NaBH_4 first forms a stable hydrate phase $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ in contact with water. $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ dehydrates at about 40°C to water and NaBH_4 leading to the uncontrollable reaction [8].

Thus we used a 1% solution of hydrochloride acid for a controllable hydrogen release at room temperature. The experiment was performed in a special glass apparatus equipped with a gas syringe for measuring the gas volume. Five gels were tested synthesized with different total mass of NaBH_4 of 200, 500, 800, 1200 or 1700 mg according to NaBH_4 /solid ratios 0.26, 0.47, 0.59, 0.68 and 0.75. With a linear regression the volume of released hydrogen per 100 mg sample could be calculated and compared to the pure NaBH_4 -salt

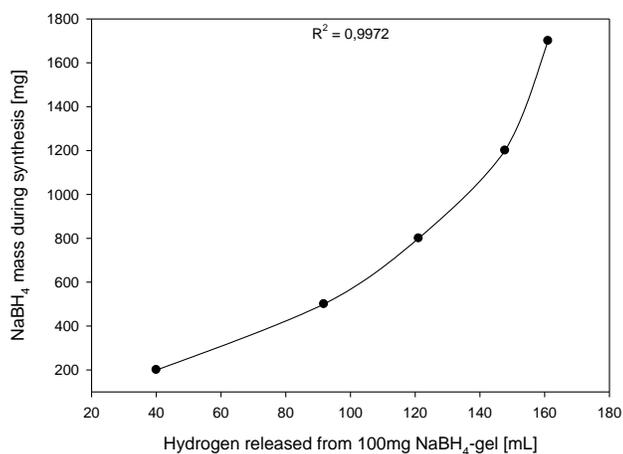


Figure 5: Hydrogen release from NaBH_4 gels with different amounts of NaBH_4 during synthesis solidified at 110°C

The results are plotted in Figure 5. From this figure it can be estimated, that a high amount of 161 ml H_2 per 100 mg gel is obtained from a gel synthesized with the highest NaBH_4 /solid ratio of 0.75. This released hydrogen volume is equivalent to 72 % of the pure NaBH_4 -salt.

4. CONCLUSIONS

Compared with the micro- or nanocrystalline sodalite host matrix [1, 2] the new solidificated NaBH_4 -aluminosilicate gel has a much higher hydrogen storage capability. Our hydrogen release experiments suggest that up to 72 wt% of NaBH_4 could be enclosed. This total amount of NaBH_4 can be used for hydrogen generation according to the reaction $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$. Beside a high storage capacity and the simple production method, compared with sodalite [1, 2] the following points will demonstrate some further goals of the new boranate gel:

(1) Whereas sodalite is only encapsulating a few percent of the high boranate excess being necessary for its preparation the gel takes up the whole amount of NaBH_4 salt, inserted for synthesis.

(2) Hydrogen release on demand can be obtained from the gel by addition of very few amount of slightly acid diluted solution. Hydrogen release by this way can be controlled by the pH-value.

(3) The hydrogen content of the solidified aluminosilicate gels can be varied with the amount of NaBH_4 salt inserted during gel precipitation.

(4) Till now the amount of 161 ml H_2 per 100 mg gel is obtained from a sample synthesized with the highest NaBH_4 /solid ratio of 0.75.

Summarizing all facts it can be concluded that the NaBH_4 -aluminosilicate gel provides a new and safe way of hydrogen storage which can simply be prepared and allows an easy and save fully controlled hydrogen release.

REFERENCES

- [1] J.-C. Buhl, F. Stemme and I. Poltz, *Microp. Mesop. Mat.* 126 (2009) 276-282.
- [2] J.-C. Buhl, L. Schomborg and C. H. Rüscher, *Microp. Mesop. Mat.* 132 (2010) 210-218.
- [3] J.-C. Buhl, *Z. Krist. Suppl. Issue No. 31* (2011) 23-24.
- [4] T. C. Wadlington, *J. Chem. Soc.* 4783, 1958.
- [5] J. Goubeau and H. Kallfass, *Z. Anorg. Allg. Chem.* 299 (1959) 160-169.
- [6] C. J. H. Schutte, *Spectrochim. Acta* 16 (1960) 1054-1059.
- [7] A. Ketelaar and C. J. H. Schutte, *Spectrochim. Acta* 17 (1961) 1240-1243.
- [8] Y. Filinchuk and H. Hagemann, *Europ. J. Inorganic Chemistry* 20 (2008) 3127-3133
- [9] E. M. Flanigen, H. Khatami and H. A. Szymanski, *Advan. Chem. Ser.* 101 (1971) 201-209.
- [10] C. H. Rüscher, *Microp. Mesop. Materials* 86 (2005) 58-68.
- [11] J. Weidlein, U. Müller and K. Dehnicke, "Schwingungsfrequenzen", Georg Thieme Vlg. Stuttgart/New York, 1981.
- [12] I. C. Hisatsune and N. H. Suarez, *Inorg. Chem.* 3 (1964) 168-174.
- [13] G. Kessler and H. A. Lehmann, *Z. Anorg. Allg. Chem.* 338 (1965) 179-184.
- [14] H. H. E. Pietsch, M. Fechtelkord and J.-C. Buhl, *J. Alloys Compd.* 257 (1997) 168-174.
- [15] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, New York, 1978