Reversibility of the hydrogen desorption from NaBH₄ by confinement in nanoporous carbon†

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NaBH₄ is an interesting hydrogen storage material for mobile applications due to its high hydrogen content of 10.8 wt%. However, its practical use is hampered by the high temperatures (above 500 °C) required to release the hydrogen and by the non reversibility of the hydrogen sorption. In this study, we show that upon heating to 600 °C, bulk NaBH₄ decomposed into Na and Na₂B₁₂H₁₂, releasing the expected 8.1 wt% of hydrogen. Nanosizing and confinement of NaBH₄ in porous carbon resulted in much faster hydrogen desorption kinetics. The onset of hydrogen release was reduced from 470 °C for bulk NaBH₄, and also resulted in the first observation of reversible formation of NaBH₄ from the dehydrogenation products at relatively mild conditions (60 bar H₂ and 325 °C). Reversibility in this system was limited due to partial loss of Na during dehydrogenation. The dehydrogenated boron compounds were almost fully rehydrogenated to NaBH₄ (98%) when extra Na was added to the nanocomposites. To the best of our knowledge, this is the first time that reversibility for NaBH₄ has been demonstrated.

Introduction

Solid state hydrogen storage in metal hydrides attracts much attention due to its potential for application in hydrogen fuel cell cars and its advantages in terms of safety and volumetric hydrogen content when compared to high pressure gaseous hydrogen storage. A class of compounds that is extensively being investigated as potential hydrogen storage material is the metal borohydrides M(BH₄)n. The interest in these materials lies in their stability at room temperature and high hydrogen capacities. NaBH₄ is the first known borohydride and has been widely used as a reducing agent in organic chemistry, especially in the reduction of functional groups like aldehydes and ketones into alcohols and more recently in metal colloid synthesis. NaBH₄ is relatively stable in air, and has gravimetric and volumetric hydrogen contents of 10.8 wt% and 115 kg of H₂ m⁻³ respectively, fulfilling the capacity requirements for onboard hydrogen storage as set by the US department of energy (DOE). Since its discovery, extensive studies

Broader context

For hydrogen to be widely used as fuel for vehicles, a compact, safe and cost effective method has to be developed for onboard hydrogen storage. The use of complex hydrides for reversible hydrogen storage in cars is advantageous in terms of safety and hydrogen densities when compared to pressurized and liquefied hydrogen. For example, NaBH₄ contains 10.8 wt% H₂ which is ideal for onboard hydrogen storage. Unfortunately its use is hindered by high dehydrogenation temperatures and non reversibility. This work reports that when bulk NaBH₄ is heated to 600 °C in Ar flow, it decomposes irreversibly into Na and Na₂B₁₂H₁₂ releasing 8.1 wt% H₂. Nanocrystalline NaBH₄ in nanoporous carbon decreased the onset of dehydrogenation to below 250 °C (470 °C for bulk NaBH₄), and also resulted in the first observation of reversible formation of NaBH₄ from the dehydrogenation products at relatively mild conditions (325 °C and 60 bar H₂). Although these conditions are still far from the requirements for practical application, our work shows that we can fundamentally change hydrogen release temperatures and reversibility in a very stable material like NaBH₄. This demonstrates the strength of nanoconfinement in carbon as an approach towards reversible hydrogen storage materials.
have been undertaken on the use of NaBH₄ as a hydrogen storage material. Most of these studies focused on hydrogen release via catalyzed hydrolysis of NaBH₄. However, DOE recently recommended a no-go for NaBH₄ hydrolysis as a hydrogen source for vehicular applications due to the formation of stable NaBO₂ that can not be recycled efficiently.

An alternative method to release the hydrogen from NaBH₄ is by thermal decomposition into H₂, B and Na (or NaH). However, like most alkali borohydrides, NaBH₄ is thermodynamically very stable (standard enthalpy of formation ΔfH° = -188.6 kJ per mol NaBH₄ and entropy of formation S° = 101.3 JK⁻¹ per mol NaBH₄) and releases hydrogen only when heated to temperatures exceeding 500 °C[12,13,16,17] which is too high for practical applications in hydrogen fuel cell cars. Furthermore, reversibility of the hydrogen desorption which is a very important criterium for a hydrogen storage material, has never been reported for NaBH₄ as far as we are aware.

For LiBH₄, a compound similar to NaBH₄, the thermal hydrogen sorption properties have been widely investigated and the kinetics of its hydrogen release and uptake improved using techniques such as destabilization, nanosizing/ nanoconfinement, and the addition of catalysts. However only few reports in literature exists on the thermal hydrogen sorption properties of NaBH₄ and they mainly focus on mixtures of NaBH₄ and other hydrides, especially MgH₂.[18-20] Martelli et al.[22] recently studied the stability and decomposition of NaBH₄ and reported that the compound decomposes in one step (unlike other complex metal hydrides such as NaAlH₄ and LiBH₄) to Na and an unidentified boron rich phase. However no further report was made on the reversibility of the hydrogen desorption from the bulk NaBH₄.

The reversibility of the hydrogen desorption from metal hydrides can be improved by reducing their particle sizes to the nanoscale,[26] which is usually achieved by mechanical milling.[27] However in the case of NaBH₄, it has been shown that ball milling is not effective in nanostructuring the compound due to its high structural stability even under heavy deformation conditions imposed by milling.[28] Nanosizing and/or confinement in nanoporous materials (especially carbon) is a new approach which has been shown to significantly improve the hydrogen uptake kinetics (and in some cases also the thermodynamics) of complex hydrides.[29,30,31] Recently synthesized NaBH₄/carbon nanocomposites via impregnation of porous carbon with NaBH₄ dissolved in liquid ammonia and showed that the nanocomposites releases hydrogen at lower temperatures than bulk NaBH₄. However, the hydrogen release was associated with ammonia and no reversibility was observed in this nanocomposite.

In this work, we study the thermal hydrogen release from NaBH₄ and investigate how confinement of NaBH₄ in nanoporous carbon using different preparation routes affects the hydrogen sorption properties. Our study reveals that NaBH₄ and investigate how confinement of NaBH₄ in nanoporous carbon resulted in a significant increase in the dehydrogenation kinetics and remarkably enabled the rehydrogenation of the decomposition products to NaBH₄ at relatively mild conditions.

### Experimental

NaBH₄/C nanocomposites were prepared using pore volume impregnation with an aqueous NaBH₄ solution (denoted SI) or melt infiltration (MI). For pore volume impregnation, 1.1g NaBH₄ (98.4% pure, Acros Organics) was dissolved in 2 ml water of pH 13, which was prepared by adding 0.3 g NaOH (Merck 99%) to 10 ml demineralized water. 1g of high surface area carbon (HSAG-500, Timcal Ltd., pore volume 0.66 cm³ g⁻¹, BET surface area 500 m² g⁻¹, broad pore size distribution dominated by 2–3 nm pores) that had been previously dried overnight under vacuum at 200 °C was impregnated with 0.66 ml of the NaBH₄ solution. The water in the impregnated sample was removed by drying overnight at 165 °C under vacuum (~9 mbar). The impregnating and drying were done using a Schlenk technique while NaBH₄ handling and storage was conducted under Ar atmosphere in a glovebox (<0.1 ppm of O₂ and H₂O). For melt infiltration, the required amounts of carbon (which had been dried) and NaBH₄ were mixed in a graphite sample holder and placed in stainless steel autoclave. The mixture was heated under hydrogen atmosphere at 5 °C/min to 520 °C (melting point of NaBH₄ ≈ 500 °C) and dwelled at 520 °C for 25 min at approximately 5 bar H₂. Nanocomposites containing various compositions of NaBH₄ and C were synthesized and labeled according to the weight percentage of NaBH₄ in the composite. As a reference, physically mixed samples of NaBH₄ and C or graphite (BET surface area 7 m² g⁻¹) were prepared by mixing the required amounts in a mortar using a pestle.

Structural characterization was performed using X-ray diffraction (XRD), N₂ physisorption and both ¹B and ²³Na solid-state Nuclear Magnetic Resonance (NMR) spectroscopy. All measurements were done in air tight sample holders. XRD patterns were obtained at room temperature from 18 to 80° 2θ with a Bruker-AXS D-8 Advance X-ray diffractometer setup using CoKα₂ radiation with λ = 1.79026 Å. N₂ physisorption measurements were performed at -196 °C, using a Micromeritics Tristar 3000 apparatus. The pore size distributions of the samples were calculated from the desorption branch using BJH theory with the Harkins and Jura thickness equation. Solid-state NMR experiments were performed on a 600 MHz Varian spectrometer using a 2.5 mm HX MAS probe. ¹B and ²³Na single pulse excitation spectra were obtained using a short hard pulse of 0.20 μs at an effective rf-field strength of 140 kHz after taking pulse rise and decay times into account. Spectra were acquired without proton decoupling. A sample spinning speed of 15 kHz was applied. The ¹B spectra were referenced using an aqueous solution of H₃BO₃ as secondary reference with a chemical shift of δ = 19.6 ppm relative to BF₃ ⋅ OEt₂ (δ = 0 ppm). The ²³Na spectra were referenced with respect to an aqueous solution of NaCl (δ = 0 ppm).

Hydrogen release from the samples was measured by temperature programmed desorption (TPD) using a Micromeritics AutoChem II 2920 apparatus. 100 to 150 mg of sample was heated at 5 °C/min from room temperature to 450–600 °C in 25 ml/min Ar (99.99% purity) flow with a dwell time of 25 min at the maximum temperature. The composition of the desorbed gas was analyzed using a quadrupole mass spectrometer (Pfeifer) attached to the TPD gas outlet. Rehydrogenation of desorbed samples was performed in an autoclave at 60 bar H₂ and 325 °C for 5 h after which the amount of H₂ absorbed by the sample was
determined by a second TPD run. Cycling of the sample was performed in a magnetic suspension balance from Rubotherm. About 100 mg of the sample was loaded in a graphitic cup and inserted into a stainless steel sample holder. The sample was heated at 5 °C/min to 400 °C in 25 ml/min Ar flow. Rehydrogenation of the desorbed sample was performed at 325 °C by increasing the H₂ pressure from zero to 60 bar in 60 min and remaining at this pressure and temperature for 5 h. Hydrogen uptake and release were determined from the weight changes after having corrected for buoyancy effects.

Results and discussion
Structure of the NaBH₄/C nanocomposites

The X-ray diffraction (XRD) patterns of a physical mixture of 25 wt% NaBH₄ and nanoporous carbon, and 25 wt% NaBH₄/C nanocomposites prepared through solution impregnation (SI) and melt infiltration (MI) are shown in Fig. 1. The XRD pattern of the carbon shows two diffraction lines at 31° (002) and around 52° (10) that are typical for turbostratic graphitic materials. After synthesis, all diffraction lines can be ascribed to either carbon or NaBH₄. A comparison of the diffraction patterns of the physical mixture and the nanocomposites show a clear broadening and a huge reduction in the intensity of NaBH₄ diffraction lines in the nanocomposites. A decrease in the amount of NaBH₄ in the nanocomposites to 20 and 15 wt% led to diffraction in the nanocomposites with no detectable diffraction from the NaBH₄ (see Fig. S1 in the electronic supplementary information ESI†). Similar observations have been reported for LiBH₄ confined in porous carbon and silica, and were attributed to a decrease in the long-range order of the compound due to nanozing and confinement in the porous hosts.⁵⁻⁻⁹⁻⁻¹⁰ Hence, we conclude that the NaBH₄ is confined in the porous carbon.

Further evidence for the incorporation of the NaBH₄ into the pores of the carbon is from nitrogen physisorption measurements (Fig. 2) which show that the total pore volume of the carbon decreased from 0.64 cm³/g C in the PM sample to 0.31 and 0.24 cm³/g C in the solution impregnated and melt infiltrated nanocomposites respectively. This decrease in pore volume (0.33 cm³/g C in SI and 0.40 cm³/g C in the MI) is close to the volume of NaBH₄ (0.31 cm³) added in the mixture, in agreement with the fact that the NaBH₄ is in the pores of the carbon. The slight difference is most likely due to minor pore blocking and some pore loss (≈ 0.05 cm³/g) during heat treatment.

Hydrogen release

Fig. 3 shows the hydrogen release from bulk NaBH₄, a physical mixture of 25 wt% NaBH₄ and porous carbon (PM), and the MI and SI 25 wt% NaBH₄/C nanocomposites. Hydrogen release started in the bulk NaBH₄ around 470 °C with two major peaks at 515 °C and 560 °C, in line with literature.¹³ The onset of hydrogen release is significantly lower (about 320 °C) for the PM sample than for the bulk NaBH₄. However, hydrogen release also occurred partially around 500 °C which is the melting point of NaBH₄. For the MI nanocomposite, hydrogen release started at much lower temperatures (below 300 °C) and the majority of the hydrogen was released around 450 °C. Remarkably, for the impregnated sample hydrogen release started below 250 °C, about 220 °C lower in temperature than bulk NaBH₄ and with a maximum release rate at 350 °C which is in agreement with a previous report for NaBH₄/C nanocomposites synthesized via impregnation of NaBH₄/liquid ammonia solution.⁴⁸ These observations clearly demonstrate that nanoconfinement in porous carbon enhances the dehydrogenation of NaBH₄ significantly. The difference in the hydrogen release temperatures of the MI and SI samples suggests the presence of different NaBH₄ feature sizes in the two samples which might be due to differences in the interaction of carbon with molten NaBH₄ and aqueous NaBH₄ solution. Lowering the loading of NaBH₄ in the MI nanocomposites led to hydrogen release at lower temperatures, similar to those for the SI sample (Fig. S2†).

Qualitative analysis of the desorbed gas using mass spectrometry (not shown) proved that hydrogen was released in all cases and if other gases were released, the amount was below the detection limit (5E-11 ion current [A]).
The SI nanocomposite released approximately 6.7 wt% H₂ (normalized to the NaBH₄ content) after heating to 450 °C and dwelling for 25 min, the MI nanocomposites released 7.9 wt% H₂/g NaBH₄ (≈ 2.1 wt% H₂/g sample) with same dwell time at 500 °C, while 8.1 wt% H₂ was released in the physically mixed sample and the bulk NaBH₄ after heating to 600 °C and dwelling for 25 min. The minor difference in hydrogen release for the nanocomposites and the physical mixtures is most likely due to partial decomposition or oxidation of the sample during synthesis and handling. Decomposition of NaBH₄ into NaH and B would release 8.1 wt% H₂ while 10.8 wt% H₂ would be expected for decomposition into elemental Na and B.

Reversibility

Reversibility of the hydrogen desorption in the composites was evaluated by rehydrogenating the dehydrogenated samples in an autoclave at 325 °C and 60 bar H₂ for 5 h. The hydrogen release from the rehydrogenated samples is shown in Fig. 4. About 0.9 wt% hydrogen was released from the rehydrogenated bulk NaBH₄, indicating minor hydrogen uptake during rehydrogenation. Remarkably, the nanocomposites and the physically mixed NaBH₄/porous C released about 3.4 wt% H₂/g NaBH₄, indicating about 43% reversibility under these mild conditions. As far as we are aware, this is the first report of a successful rehydrogenation of NaBH₄ decomposition products. Furthermore, the nanocomposites can be cycled repeatedly as shown in Fig. S3† although the capacity decreases steadily as in the case of nanoconfined LiBH₄. These results show that confinement in the pores of the carbon plays an important role in determining reversibility. The reversibility seen in the physically mixed sample (PM) results from the fact that NaBH₄ melts (500 °C) during the first cycle desorption and infiltrates the pores of the carbon thereby forming nanoconfined products after decomposition that can be rehydrogenated. This is confirmed from nitrogen physisorption measurements which show that the total pore volume of carbon decreased by 0.26 cm³/g after dehydrogenation (Fig. S4†). Such reversibility was not observed for a similar experiment with non-porous carbon or graphite (data not shown).

Notably, all the rehydrogenated nanocomposites released hydrogen in the same temperature range, which means that the desorption temperatures especially for the MI nanocomposites had shifted to lower values. This suggests a possible microstructural change and/or redistribution of the NaBH₄ in the carbon after rehydrogenation. The bulk NaBH₄ shows some reversibility (≈ 0.9 wt% H₂ released) but only if the first desorption cycle is done in a closed system.

To investigate structural changes occurring in the samples during dehydrogenation and rehydrogenation processes, XRD patterns of the dehydrogenated and rehydrogenated samples were acquired (Fig. 5) and compared to the pure NaBH₄. For bulk NaBH₄, we physically observed two distinct solid phases after dehydrogenation as recently reported for dehydrogenated bulk NaBH₄. However XRD showed peaks predominantly from Na, with a minor unidentified phase as evidenced by a small peak at 45° (2θ). After rehydrogenation, two distinct phases were still physically observed but only NaH was detected from the XRD, showing that for the bulk NaBH₄, part of the de- and rehydrogenated material is amorphous.

For both nanocomposites (MI and SI), only C diffraction peaks were observed after hydrogen desorption indicating that the desorption products are amorphous. After rehydrogenation, in addition to the C, diffraction peaks due to NaBO₂ were observed in the impregnated nanocomposites. The NaBO₂ is probably due to reaction between NaOH (used to stabilize the NaBH₄/H₂O solution) and NaBH₄ or its decomposition products at high temperatures. In contrast, no diffraction peaks other than that from the C were observed for the melt infiltrated samples. This shows that for both samples, the hydrogenated phases are amorphous as also reported in literature for LiBH₄ and NaAlH₄ confined in porous carbon.22,28,39,47

Characterization of the non crystalline phases

A convenient technique to investigate the local structure of non-crystalline solids is solid-state magic angle spinning (MAS)
NMR. Fig. 6 shows the $^{11}$B NMR spectra of a physical mixture of NaBH$_4$ and porous carbon, and the nanocomposites after synthesis, dehydrogenation and rehydrogenation. The $^{11}$B spectrum of a physical mixture of NaBH$_4$ and porous carbon shows a well-defined sharp peak at $-42.6$ ppm. For the nanocomposites (both melt infiltrated and volume impregnated), the lineshape of NaBH$_4$ is broadened. As reported previously for NaAlH$_4$/C nanocomposites, this line broadening is explained by distortions of the local field homogeneity because of the magnetic susceptibility of the carbon and/or a higher disorder in the material, which results in a distribution in chemical shift and quadrupolar interaction parameters. The impregnated nanocomposite exhibits a significantly larger linewidth with a full width at half maximum (FWHM) of 17.1 ppm compared to the melt infiltrated sample with a FWHM of 9.4 ppm. This means that the microstructure and/or distribution over the carbon depends on the preparation method as was also clear from the physisorption and hydrogen release measurements.

After dehydrogenation, all NaBH$_4$ disappeared in both MI and SI samples. The dehydrogenated SI sample shows a large resonance peak with a maximum at 16 ppm. For the dehydrogenated SI sample, a large resonance peak with a maximum at 16 ppm is present. $^{11}$B has typical isotropic chemical shifts between 12 and 19 ppm in materials with trigonal B–O coordination. Hence this peak can be assigned to NaBO$_2$ in agreement with the XRD results.

After rehydrogenation, in both samples nanoconfined NaBH$_4$ is reformed. This clearly proves the partial reversibility for these nanocomposites. Clear differences exist between the MI and SI samples. Besides nanoconfined NaBH$_4$, the MI samples show mainly Na$_2$B$_{12}$H$_{12}$ and little NaBO$_2$, while the SI samples show mainly NaBO$_2$ and only a minor amount of Na$_2$B$_{12}$H$_{12}$. The linewidth of the NaBH$_4$ resonance increased slightly after rehydrogenation especially for the MI sample. This suggests a possible change in the structure and/or distribution of NaBH$_4$ in the carbon after rehydrogenation and is most likely responsible for the rehydrogenated MI sample (Reh. MI) when compared to the as synthesized sample (MI).

Na$_2$B$_{12}$H$_{12}$ The smaller contribution at 18 ppm corresponds most likely to NaBO$_2$. In the sample after melt infiltration, a small amount of Na$_2$B$_{12}$H$_{12}$ is also observed which is most likely due to partial desorption, or reaction between NaBH$_4$ and minor impurities in the carbon during melt infiltration. No clear evidence of the formation of elemental boron is found. Boron gives a broad line around 5 ppm and therefore, its resonance might overlap with the resonances of Na$_2$B$_{12}$H$_{12}$ and/or NaBO$_2$.

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Similar to the MI sample, $^{11}$B NMR of the dehydrogenated bulk NaBH$_4$ show a broad resonance that is mainly due to Na$_2$B$_{12}$H$_{12}$ (Fig. S5†) and minor traces of unreacted NaBH$_4$. However in contrast to the nanocomposites, NaBH$_4$ was not reformed after rehydrogenation of the dehydrogenated bulk NaBH$_4$.

$^{23}$Na NMR of the samples was also measured in order to investigate the evolution of the Na phase(s). Unfortunately, for the nanocomposites, $^{23}$Na NMR gave very broad spectra from which no useful information about the Na phases could be extracted. In general, the chemical shift range for $^{23}$Na is relatively small (~30 ppm) compared to $^{11}$B, which results in an overlap of the resonances of different compounds especially when the peaks are broad. This broadening is most likely caused by the high dispersion of Na when confined and in close contact with the carbon. Meanwhile $^{23}$Na NMR for the bulk NaBH$_4$ (Fig. S6†) shows resonances due to elemental Na and Na$_2$B$_{12}$H$_{12}$ after dehydrogenation. After rehydrogenation, the Na resonance disappears while Na$_2$B$_{12}$H$_{12}$ and a peak at a chemical shift due to NaH are clearly seen, in agreement with the XRD results. The formation of NaH (instead of NaBH$_4$) after the rehydrogenation of the bulk NaBH$_4$ explains the differences in the hydrogen release profile from the rehydrogenated nanocomposites and the rehydrogenated bulk sample.

Addition of extra sodium

The reversibility achieved in the nanoconfined NaBH$_4$ is relatively low when compared to that of other complex hydrides such as NaAlH$_4$ and LiBH$_4$ confined in similar carbon materials.$^{22,40,56}$

Apart from partial oxidation of the sample during handling (which also occurs in other nanoconfined hydrides), two major reasons could be responsible for the partial reversibility. Firstly, XRD and NMR measurements clearly show that elemental Na and Na$_2$B$_{12}$H$_{12}$ are the main dehydrogenation products of NaBH$_4$. The predicted high stability of Na$_2$B$_{12}$H$_{12}$ could prevent the rehydrogenation to NaBH$_4$, as recently postulated.$^{54}$

Secondly, since Na is liquid and has a relatively high vapour pressure at 500 °C, the loss of Na through evaporation during dehydrogenation of NaBH$_4$ is likely (Fig S7). In that case there will be insufficient Na to fully form NaBH$_4$ from the dehydrogenated boron compounds. To check if this latter assumption is true, extra Na was added to the melt infiltrated nanocomposites by heating a 20wt% NaBH$_4$/C nanocomposite with 12.5 wt% NaH (95%, Aldrich). The overall composition of the mixture is 17.5, 70 and 12.5 wt% NaBH$_4$, C and NaH respectively (molar ratio Na: B = 2.1). It is expected that Na formed after the dehydrogenation of the NaH will infiltrate the pores of the carbon as previously reported,$^{97}$ thereby providing extra Na to the dehydrogenated nanocomposites. After dehydrogenation, the samples were rehydrogenated at 325 °C and 60 bar H$_2$ for 5 h. Fig. 7 shows the second hydrogen release run. The 20wt% NaBH$_4$/C nanocomposite released approximately 0.7 wt% H$_2$ from NaH sample (3.5 wt% H$_2$/g NaBH$_4$). The nanocomposite containing extra Na released 1.4 wt% H$_2$ from (8.0 wt% H$_2$/g NaBH$_4$), while 8.1 wt% H$_2$/g NaBH$_4$ is expected for fully reversible decomposition to Na$_2$B$_{12}$H$_{12}$.

One has to consider that the additional Na could also have been rehydrogenated, and contribute to the hydrogen release.

However, the additional NaH could contribute a maximum of 0.55 wt % H$_2$ per gram nanocomposite, and hence never fully account for the increase in reversibility. More importantly, $^{11}$B NMR of the rehydrogenated sample (Fig. 6) shows a large increase in the resonance due to NaH in the sample with extra Na, as well as fading of the resonance due to Na$_2$B$_{12}$H$_{12}$. This proves that in these nanoconfined systems neither B nor Na$_2$B$_{12}$H$_{12}$ are intrinsically limiting factors for the reversibility of hydrogen sorption. Nearly full reversibility could be obtained by compensating for the loss of active Na from the system. Alternatively, loss of Na might be reduced by restricting operating temperatures and gas flow.

Discussions

Most alkali metal borohydrides decompose to the metal hydride before further decomposition to the metal, although direct decomposition into the element is also possible. Thus for the dehydrogenation of NaBH$_4$ the following overall reaction equations can be written:

$$2 \text{NaBH}_4 \rightarrow 2 \text{NaH} + 2 \text{B} + 3 \text{H}_2 \quad (1)$$

$$\text{NaBH}_4 \rightarrow \text{Na} + \text{B} + 2 \text{H}_2. \quad (2)$$

Decomposition according to reaction 1 releases 8.1 wt% H$_2$ while reaction 2 yields 10.8 wt% H$_2$. Experimentally, bulk NaBH$_4$ released 8.2 wt% H$_2$ while the MI-nanocomposite and the physically mixed samples released approximately 8.1 wt% H$_2$/[NaBH$_4$] which would suggest that these samples decomposed according to reaction 1. However, the lower stability of NaH compared to NaBH$_4$ implies that NaH should already decompose at lower temperatures than required for the decomposition of NaBH$_4$,$^{28,59}$ especially in the presence of carbon.$^{37}$ Furthermore, the NMR results clearly show that the decomposition products of NaBH$_4$ are mostly Na$_2$B$_{12}$H$_{12}$ and Na. These observations suggest that only partial decomposition of NaBH$_4$ takes place according to the following overall reaction equation:

$$12 \text{NaBH}_4 \rightarrow 10 \text{Na} + 7 \text{Na}_2\text{B}_{12}\text{H}_{12} + 18 \text{H}_2 \quad (3)$$
Interestingly, decomposition according to (3) is expected to yield 8.1 wt% H₂ which is in a good agreement with the amount of hydrogen released from the samples. The presence of two desorption steps in the bulk NaBH₄ and in all the rehydrogenated nanocomposites could be due to either an intermediate decomposition product, or heterogeneity of the NaBH₄.

For the solution impregnated sample, formation of NaBO₂ is observed with both XRD and NMR. As NaOH is present, this can probably be explained by the following reaction:

\[ \text{NaBH}_4 + 2 \text{NaOH} \rightarrow \text{NaBO}_2 + 2 \text{Na} + 3 \text{H}_2 \]  

Since the molar ratio of NaBH₄ to NaOH in the aqueous NaBH₄ solution is 20 : 1, only about 2.5% of the NaBH₄ is consumed in this reaction (except if traces of water are still present in the sample). Unlike for the MI sample, no clear resonance due to Na₂B₁₂H₁₂ was observed with NMR after dehydrogenation. The reversibility seen in the SI sample shows that phases other than oxidation products must be present after dehydrogenation since NaBO₂ cannot be rehydrogenated to NaBH₄. Unfortunately, neither elemental B nor other boron compounds can clearly be identified with solid-state NMR due to possible overlap of these resonances with the broad NaBO₂ resonance. The microstructure and/or distribution of the NaBH₄ over the carbon depend on the preparation method, as seen from NMR and nitrogen physisorption results. Also Fig. 3 shows different hydrogen release profiles for SI and the MI nanocomposites. However, at present we cannot identify which boron species are reversibly formed after dehydrogenation in the SI samples.

Remarkable is the reversible formation of NaBH₄ in these nanocomposites especially at such mild conditions as used in this study since for NaBH₄ reversible hydrogen sorption has not yet been reported. Reversibility in complex hydrides especially borohydrides is typically hampered by the formation of at least two crystalline or amorphous phases after desorption which are the metal or metal hydride phase and boron/boron species. Bulk NaBH₄ forms crystalline Na and amorphous Na₂B₁₂H₁₂ after desorption. Reversibility in such a system is difficult because of the slow solid state diffusion required for the recombination of these macroscopically segregated phases. This is evidenced by the fact that after rehydrogenation, NaH and Na₂B₁₂H₁₂ were seen instead of NaBH₄. This suggests that NaH is first formed during rehydrogenation and since it is a solid at the rehydrogenation conditions, it did not react with the Na₂B₁₂H₁₂ to form NaBH₄. Furthermore, Caputo et al. recently calculated that Na₂B₁₂H₁₂ is very stable (standard enthalpy of formation at 0 K = -1086 kJ/mol Na₂B₁₂H₁₂ or -181 kJ/mol H₂) and cannot be rehydrogenated if formed during dehydrogenation of NaBH₄. However, the results presented in this study clearly showed that NaNBH₄ exhibits partial reversible hydrogen sorption and that full reversibility can be achieved if Na is not lost during dehydrogenation. Therefore the barrier to reversibility in bulk NaBH₄ is not due to the stability of Na₂B₁₂H₁₂ but rather due to the inability of NaH (formed during rehydrogenation) and Na₂B₁₂H₁₂ to react with H₂ to form NaBH₄ at moderate conditions because of phase separation and poor kinetics of solid-state diffusion required for their recombination.

Furthermore, bulk NaBH₄ decomposes above 500 °C and Na loss through evaporation at this high temperatures (except when desorption is carried in a closed system) practically hinders the reversibility of the dehydrogenation reaction. Confining the NaBH₄ in nanoporous carbon reduces these problems. When confined, the dehydrogenated phases are kept together in the pores of the carbon. Therefore the diffusion distance between the Na and Na₂B₁₂H₁₂ is greatly reduced, enabling the reversible formation of NaBH₄ from its dehydrogenated products even at relatively mild conditions without a catalyst.

Our work clearly demonstrate how the kinetics of hydrogen release from NaBH₄ can be greatly enhanced and reversibility enabled by nanosizing and nanoconfinement in carbon. Preliminary investigations also indicate that under 1 bar H₂ pressure, part of the hydrogen is already released starting from 280 °C which is below the temperature at which the dehydrogenation reaction of NaBH₄ would be expected in equilibrium. This indicates that the enthalpy and/or entropy for the decomposition reaction might be different for nanoconfined NaBH₄ compared to bulk material, or the presence of intermediate decomposition steps for NaBH₄ which is different when confined in nanoporous carbon but the details are outside the scope of the present paper.

Despite the fact that the hydrogen release temperatures are lowered and reversibility is observed when NaBH₄ is confined in nanoporous carbon, for practical application in fuel cell cars, further reduction in the desorption temperatures to about 150 °C is required in order to avoid Na loss. In addition, the NaBH₄ loading must be increased to above 60 wt% in order to increase the overall hydrogen content of the nanocomposite. The latter might be achieved by using nanoporous hosts with higher pore volume.

Conclusions

The thermal hydrogen sorption properties of NaBH₄ have been investigated. XRD, solid-state NMR and hydrogen release measurements revealed that NaBH₄ decomposes into elemental Na and Na₂B₁₂H₁₂ when heated to 600 °C, with a release of 8.1 wt % H₂. NaBH₄ was successfully confined into a nanoporous carbon material through impregnation with an aqueous NaBH₄ solution and also by melt infiltration under hydrogen pressure. Confining NaBH₄ in nanoporous carbon material lowers the desorption temperatures significantly, with most of the hydrogen released around 350 °C in Ar flow in the solution impregnated nanocomposites compared to 560 °C for the bulk material. Remarkably, reversible formation of NaBH₄ from its dehydrogenation products was demonstrated for the first time as the dehydrogenated NaBH₄/C nanocomposites can be rehydrogenated to NaBH₄ at relatively mild conditions of 325 °C and 60 bar H₂ for 5h. Reversibility of the system is limited by loss of Na at high temperatures during hydrogen release. Compensations of Na loss by extra Na resulted in almost full rehydrogenation of the dehydrogenated products to NaBH₄. Although at the moment NaBH₄/C nanocomposites do not meet the requirements for onboard applications, our work demonstrates the strength of nanoconfinement in carbon materials as an approach towards reversible hydrogen storage materials.
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Notes and references