NaAlH₄/microporous carbon composite materials for reversible hydrogen storage

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ABSTRACT

Nanoconfinement of NaAlH₄ inside a nanoporous carbon material and its effect on the reversible hydrogen storage has been studied. NaAlH₄ has been deposited into/onto a highly microporous carbon material by solution impregnation method. The structure of the deposited NaAlH₄ and H₂ release from NaAlH₄ after deposition and after 10 dehydrogenation/hydrogenation cycles has been investigated. Materials with smaller NaAlH₄ particles and a higher ratio of amorphous NaAlH₄ phase start releasing hydrogen at ambient temperatures (> 23 °C). Hydrogen release takes place from nanostructured NaAlH₄ with a more even rate over a larger temperature interval. During repetitive cycling, the crystalline NaAlH₄ had been converted into amorphous nanoconfined phase or irreversibly decomposed into bulk phases, crystalline Al and Na₃AlH₆, which have been detected by X-ray diffraction method. Hydrogen release from nanoconfined amorphous NaAlH₄ started already at ambient temperatures. Improved reversibility of H₂ storage has been demonstrated. The data for nanoconfined material has been compared to bulk NaAlH₄.

1. Introduction

Complex metal hydride NaAlH₄ is a potential material for mobile and reversible H₂ storage applications because of the high H₂ content (7.4 wt%). It consists of chemical elements (Na, Al and H) whose compounds are abundant on earth and the good capability to store hydrogen reversibly has been shown [1,2]. However, three hydrogen releasing reactions can take place during NaAlH₄ decomposition:

\[3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \] (1)

\[\text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + 1\frac{1}{2}\text{H}_2 \] (2)

\[3\text{NaH} \rightarrow 3\text{Na} + 1\frac{1}{2}\text{H}_2 \] (3)

Only the first two reactions, starting around 150 °C and 250 °C respectively, are reversible, releasing up to 5.6 wt% of hydrogen from complex metal hydride (i.e. 75% of the total H₂ stored in NaAlH₄) [3,4]. In real conditions, H₂ release from bulk NaAlH₄ is achieved at higher temperatures when NaAlH₄ is already melting (> 183 °C). Decomposition of NaAlH₄ is kinetically hindered at temperatures lower than 183 °C due to slow diffusion of H₂ in a solid phase. Thus, hydrogen is released effectively only from the surface of the solid phase NaAlH₄ [2–5]. The first two decomposition reactions (Eqs. (1) and (2)) are reversible only in principle as the decomposition product, Al, tends to agglomerate into a separate metallic phase. The formed agglomerates decrease the amount of reversibly stored H₂ as the reformation of NaAlH₄ is impossible due to the spatial segregation of Na and Al clusters [5–7].

Baldé et al. [8,9] and Zheng et al. [10] have shown that the hydrogen release temperature decreases with decreasing the particle size of confined NaAlH₄. The hydrogen release temperature is decreased to ambient temperature in the case of particles with size < 10 nm. Confining of NaAlH₄ onto/into a porous supporting material as small clusters prevent segregation of the decomposition products of NaAlH₄ into separate phases and, thus, confined NaAlH₄ improves the amount, kinetics and reversibility of hydrogen release/uptake [10–12].

The decreased temperature and improved reversibility of hydrogen release/uptake have been demonstrated for nanoconfined NaAlH₄ [6,8–13]. Nevertheless, the impact of repeated hydrogen release/uptake cycles on the structure of nanoconfined NaAlH₄ and on the long-term reversibility has not been thoroughly investigated. Only a limited number of cycles have been applied and the degradation of H₂ storage in nanoconfined NaAlH₄ has not been fully described in publications [6,11,13]. In order to improve the reversible hydrogen storage capability by nanoconfined complex metal hydrides it is vital to understand the changes in the structure during repeated dehydrogenation/hydrogenation and how the structural changes in complex metal hydrides...
influence the capability to store hydrogen reversibly.

In this work, the crystallographic structure and hydrogen storage capability of nanoconfined \( \text{NaAlH}_4 \) has been investigated before and after multiple dehydrogenation/hydrogenation cycles. The nanoconfined \( \text{NaAlH}_4 \)/carbon composite material was synthesized through \( \text{NaAlH}_4 \) deposition by solution impregnation from tetrahydrofuran onto/into a high specific surface area microporous carbon material RP-20 with \([14]\). The influence of size and crystallinity of the deposited \( \text{NaAlH}_4 \) crystallites and formation of crystalline deposition products from nonreversible \( \text{NaAlH}_4 \) decomposition on the reversibility of hydrogen storage and irreversible segregation of the decomposition products has been investigated before and after repeated hydrogen release/uptake cycles using X-ray diffraction. Decreasing the hydrogen release temperature under 180 °C would make it possible to use the waste heat from high-temperature proton exchange membrane fuel cells for mobile (transport, etc.) applications, therefore, increasing the efficiency of the overall system \([15,16]\). The impact of the crystallite size of \( \text{NaAlH}_4 \) on the hydrogen release temperature and reversibility over multiple hydrogen release/uptake cycles is compared and discussed. Improved understanding of structural changes in nanoconfined \( \text{NaAlH}_4 \) during dehydrogenation/hydrogenation cycles makes it possible to design and synthesize the hydrogen storage materials with better reversibility and to control the hydrogen release conditions.

2. Experimental

2.1. Synthesis

The \( \text{NaAlH}_4 \)/carbon composite materials were synthesized and stored in a controlled environment under Ar atmosphere. Sodium aluminum hydride (\( \text{NaAlH}_4 \), 90%, Sigma Aldrich) was dissolved in tetrahydrofuran (THF, anhydrous, \( \geq 99.9\%\), Sigma-Aldrich). The prepared solution with a concentration of 0.05 g mL\(^{-1}\) was filtered through a glass microfiber filter (GF/B, Whatman) to remove any insoluble impurities. Dry microporous carbon RP-20 (Kuraray, Japan) was used as a supporting material. The filtered solution of \( \text{NaAlH}_4 \) in THF was added to 1 g dry carbon RP-20 in multiple 2 mL steps. After each step, the mixture was stirred at 0 °C under 1 bar of Ar for 15 min in order to infiltrate the solution into the pores of carbon RP-20. Almost the entire solvent was removed from the composite material during 45 min of stirring in the reaction flask under 1 mbar of Ar pressure at 23 °C. The \( \text{NaAlH}_4 \)/RP-20 composite material was finally dried from residual solvent at 30 °C and 33 μbar Ar pressure for 36 h. The deposited complex hydride was reformed at 140 °C (at hydrogen pressure 180 bars) to regenerate any decomposed \( \text{NaAlH}_4 \). The \( \text{NaAlH}_4 \) wt% in \( \text{NaAlH}_4 \)/RP-20 composite material has been varied from 10 to 60 wt%. Henceforward the synthesized materials are designated as xNaAlH\(_4\)/RP-20, where \( x \) stands for the wt% of \( \text{NaAlH}_4 \) in the composite material. The pure \( \text{NaAlH}_4 \) material was refined through the same preparation route as the described xNaAlH\(_4\)/RP-20 composite materials but without adding any carbon powder.

2.2. Physical characterization

The carbon RP-20 was characterized using \( \text{N}_2 \) sorption method with an ASAP 2020 system (Micromeritics, USA). The specific surface area, \( S_{\text{BET}} \), was calculated according to the Brunauer-Emmett-Teller theory \([17]\), total volume of pores, \( V_{\text{tot}} \), was calculated from the adsorbed amount near the saturation pressure \( (p/p_0) \), surface area of micropores, \( S_{\text{micro}} \), and volume of micropores, \( V_{\text{micro}} \), were calculated according to the t-pot method \([18]\). The pore size distribution of RP-20 (Fig. 1 (b)) was calculated from \( \text{N}_2 \) isotherm (Fig. 1 (a)) with non-local density functional theory based model for carbons with heterogeneous surfaces (2D-NLDTFT-HS) \([19,20]\) using SAIEUS software (v2.02, Micromeritics, USA) \([21]\).

X-ray diffraction (XRD) data were measured using a D8 Advance diffractometer (Bruker, Germany) with CuKα radiation. Measurements were done from \( 2θ = 5° \) to \( 2θ = 90° \) with a total step time of 166 s and a step size of 0.0128° using a LynxEye detector. The powder sample was sealed under an X-ray transparent cap in Ar atmosphere to hinder oxidation during measurements. Crystallite sizes were calculated from the measured diffractograms (Fig. 2) using the with the full profile analysis software Topas 4.1 (Bruker, Germany).

2.3. Hydrogen evolution

The hydrogen evolution from synthesized \( \text{NaAlH}_4 \)/RP-20 composite materials and from pure \( \text{NaAlH}_4 \) was measured with an Autochem 2950HP (Micromeritics, USA) chemisorption analyzer equipped with a thermal conductivity detector. Nitrogen gas (\( \text{N}_2 \), 6.0, AGA) was used as a carrier gas with a flow rate of 50 mL min\(^{-1}\). The sample was held at 0 °C under \( \text{N}_2 \) flow of 50 mL min\(^{-1}\) for two hours prior to measurements to stabilize the baseline. Hydrogen evolution was measured with ramping temperature from 0 to 600 °C with heating up rate of 2 °C min\(^{-1}\) (Fig. 3). The dehydrogenation/hydrogenation cycling was performed on a PCTpro 2000 (Setaram, France) Sievert type instrument. The cycling temperature was fixed for each sample: 170 °C for 10 wt% \( \text{NaAlH}_4 \)/RP-20 and 200 °C for 60 wt% \( \text{NaAlH}_4 \)/RP-20 and for pure \( \text{NaAlH}_4 \). The pressure was cycled from 0.3 to 170 bars. The dehydrogenation/hydrogenation cycling temperature was chosen to cover the temperature region of the first hydrogen release peak for 10 wt% \( \text{NaAlH}_4 \)/RP-20 and 60 wt% \( \text{NaAlH}_4 \)/RP-20 composites. The position of the first hydrogen evolution peak was estimated from the graphs of
3. Results

The N2 sorption analysis shows that supporting material, carbon RP-20, has a high specific surface area: \( S_{\text{BET}} = 1840 \, \text{m}^2 \, \text{g}^{-1} \), a high ratio of micropores by volume: \( V_{\text{micro}}/V_{\text{tot}} = 0.97 \) (Table 1), and most pores are smaller than 2 nm (Fig. 1 (b)). The high volume ratio of micropores \( V_{\text{micro}} \) to the total pore volume \( V_{\text{tot}} \) and high surface area of RP-20 facilitate the confinement of high wt% of NaAlH4, thus, increasing the total volumetric and gravimetric density of hydrogen in composites. Based on the total pore volume value calculated \( V_{\text{tot}} = 0.82 \, \text{cm}^3 \, \text{g}^{-1} \), a NaAlH4 loading of 50 wt% would fill all the pores. The synthesized composite materials were coarse-grained in comparison to supporting carbon material RP-20 and acquired the more of a lighter tint, the higher wt% of NaAlH4 was added, thus, indicating the deposition of NaAlH4 on the surface of RP-20 particles.

XRD peaks of the pure NaAlH4 given in Fig. 2 correspond to NaAlH4 peaks measured by other researchers in previous publications [5,12,13,22] and the calculated average NaAlH4 crystallite size of pure NaAlH4 is 110 nm (Table 2). Sharp NaAlH4 peaks and a wide carbon diffraction peak, 2θ = 43.5°, are visible for composite materials synthesized. The gradual rise in diffraction intensities at 2θ under 30° is caused by the sample holder cap used to seal the sample into Ar atmosphere. NaAlH4 diffraction peak intensities decrease with reducing the wt% of NaAlH4 in the composite material. 10 wt%NaAlH4/RP-20 has only one apparent NaAlH4 diffraction peak at 2θ = 29.5°. Other diffraction peaks for NaAlH4 are hardly recognizable or indeterminable. In addition, the average crystallite size of NaAlH4 decreased with reducing the wt% of deposited NaAlH4 (Table 2). It has been shown previously that nanoconfined NaAlH4 has no diffraction peaks [5,10]. Thus, the decrease in average crystallite size and the lack of diffraction peaks indicate that a higher fraction of NaAlH4 was deposited as nanoparticles (or they are in an amorphous state) into/onto RP-20 rather than bulk NaAlH4 when lower wt% of NaAlH4 was deposited and that most of the NaAlH4 in 10 wt%NaAlH4/RP-20 is nanofacilitated. The nanoconfined NaAlH4 in 10 wt%NaAlH4/RP-20 makes it possible to analyze the effect of NaAlH4 confinement on hydrogen release temperature and reversibility of the hydrogen storage process before and after dehydrogenation/hydrogenation cycles.

The volume of released hydrogen for three xNaAlH4/RP-20 materials is shown in Fig. 3. According to XRD data, these materials are mostly nanoconfined (10 wt%NaAlH4/RP-20), deposited onto/into the supporting carbon as large crystallites (60 wt%NaAlH4/RP-20) and as a constant temperature ramping (Fig. 3). The dehydrogenation/hydrogenation temperature of pure NaAlH4 was chosen to be comparable with 60 wt%NaAlH4/RP-20. During each dehydrogenation cycle hydrogen pressure was decreased by steps of 80 bars and the system was equilibrated for 1 h after each step until 0.3 bars was reached. During hydrogenation, the H2 pressure was increased by steps of 80 bars with an equilibration time of 1 h and until 170 bars was reached. 10 dehydrogenation/hydrogenation cycles were performed for each material. The cycling ended with a hydrogenation step and after that the temperature was gradually decreased to ambient temperature and the sample was retrieved for post-operational XRD and H2 release measurements.
bulk material (pure NaAlH₄). Hydrogen release from composite materials with at least 20 wt% of NaAlH₄ started at temperatures over 160 °C. Four hydrogen release peaks are discernable for pure NaAlH₄, where the second and third peaks overlap. The first hydrogen release peak at 165 °C corresponds to the reaction given by Eq. (1), but it is limited only to the surface of NaAlH₄ particles, i.e. the first reaction step takes place at lower temperatures only at the surface regions of the NaAlH₄ particles, which has been reported before in Ref. [3]. The second and the third hydrogen release peaks correspond to the first two reaction steps (Eqs. (1) and (2)) occurring throughout the NaAlH₄ particles. The second and third peaks are overlapping and have hydrogen release maxima at temperatures of 220 °C and 245 °C, respectively. Fourth hydrogen release peak corresponds to the last reaction step (Eq. (3)) and corresponds to hydrogen release maximum at 315 °C. xNaAlH₄/RP-20 composite materials have a less definite hydrogen release peak corresponding to the last reaction step (Eq. (3)).

Hydrogen release peaks corresponding to the first two reactions (Eqs. (1) and (2)) are expressed at lower temperatures and they are overlapping to a larger degree. Mostly nanoconfined NaAlH₄ in 10 wt% NaAlH₄/RP-20 releases hydrogen evenly from 70 °C up to 160 °C and has only one definite hydrogen release peak thereafter. The larger overlapping or disappearance of definite hydrogen release peaks can be explained in the case of RP-20 supported materials, especially nanoconfined NaAlH₄, through the decomposition of NaAlH₄ directly into NaH, demonstrated previously by Gao et al. [11]. Composite materials xNaAlH₄/RP-20 release hydrogen at lower temperatures compared to pure NaAlH₄. Four times more of the available hydrogen is released at 200 °C from 60 wt%NaAlH₄/RP-20 than from pure NaAlH₄ and over 40 wt% of hydrogen is released under 200 °C from composites with NaAlH₄ loading over 10 wt%. Hydrogen evolution from 10 wt% NaAlH₄/RP-20 starts already at ambient temperature, T = 23 °C, and 45% of the available hydrogen is released below 170 °C. Thus, the nanoconfinement of NaAlH₄ in 10 wt%NaAlH₄/RP-20 is supported by the low temperature of hydrogen release in addition to lack of definite NaAlH₄ diffraction peaks in the XRD spectra. The low temperature of hydrogen release from nanoconfined NaAlH₄ has been demonstrated also by Baldé et al. [9]. The strong effect of nanoconfinement in hydrogen storage applications has also been shown for physical adsorption of hydrogen on carbon and zeolite materials, i.e. when nanosized Pt and Pd particles are used (up to three times the wt% of hydrogen adsorbed), and the effect has been attributed to the hydrogen spillover effect [23–25].

The average crystallite sizes of pure NaAlH₄ (110 nm) and 60 wt% NaAlH₄/RP-20 (80 nm) are comparable. Also, the release of hydrogen starts near the melting temperature (183 °C) of NaAlH₄ for composite materials with NaAlH₄ ≥ 20 wt%. Thus, NaAlH₄ in composite materials with loading over 10 wt% of NaAlH₄ is mostly deposited as too large particles to demonstrate the effect established for nanocoalnainment materials.

In the case of RP-20 supported NaAlH₄, hydrogen is released at decreased temperatures and the hydrogen release peak, discernable for pure NaAlH₄ at 315 °C, is suppressed or indiscernible. This demonstrates the ability of supporting materials to prevent the agglomeration of NaAlH₄ into larger particles during the melting process (183 °C). The agglomeration of NaAlH₄ into larger particles would kinetically hinder the NaAlH₄ decomposition, as it is seen for pure NaAlH₄ [3,4].

The XRD measurements after 10 dehydrogenation/hydrogenation cycles indicate the formation of new crystalline compounds (Fig. 2). Metallic aluminum, the decomposition product of NaAlH₄ (Eqs. (1) and (2)), forms a separate crystalline phase, characterized by the diffraction peaks at 2θ = 38.2°, 2θ = 44.7° and 2θ = 65.0°. In addition to NaAlH₄ and Al new diffraction peaks for Na₃AlH₆ are clearly discernable. The average crystallite size of NaAlH₄ in pure NaAlH₄ decreased slightly from 110 (± 2) nm to 95 (± 3) nm during cycling. The average crystallite size of the decomposition products, Na₃AlH₆ and Al, is almost twice as large as that of NaAlH₄ in pure NaAlH₄ before cycling.

![Graph showing the integrated volume of released hydrogen normalized with the mass of NaAlH₄ vs. temperature plots measured with a temperature ramp rate of 2 °C min⁻¹.](image)

Fig. 4. The integrated volume of released hydrogen (normalized with the mass of NaAlH₄) vs. temperature plots measured with a temperature ramp rate of 2 °C min⁻¹.

Without the supporting material to confine NaAlH₄ the decomposition products Na₃AlH₆ and Al form separate phases, which cannot be reformed back into NaAlH₄ under reasonable temperature and pressure conditions.

Similarly to pure NaAlH₄, 60 wt%NaAlH₄/RP-20 forms separate crystalline phases of Na₃AlH₆ and Al during cycling. Newly formed NaAlH₃ and Al have larger average crystallite sizes in comparison to uncycled NaAlH₄. Although, the intensities for both decomposition products, Al and Na₃AlH₆, are much lower and NaAlH₄ diffraction peaks could even not be detected for 60 wt%NaAlH₄/RP-20 after cycling in comparison to pure NaAlH₄. Only the Al and wide carbon diffraction peaks are discernable for 10 wt%NaAlH₄/RP-20 after cycling. The average crystallite size of formed Al (50 nm) is approximately the same as that of Na₃AlH₆ in 10 wt%NaAlH₄/RP-20 before cycling. Thus, the lower intensities, or the lack thereof, of the decomposition products in diffraction peaks even after many dehydrogenation/hydrogenation cycles of RP-20 supported materials in comparison to pure NaAlH₄ exemplifies the confining ability of the carbon powder RP-20.

The integrated amounts of released hydrogen before and after 10 dehydrogenation/hydrogenation cycles are shown in Fig. 4. Remarkably, the temperature at maximum hydrogen release from 60 wt% NaAlH₄/RP-20 is decreased from 195 °C to 175 °C, corresponding to the maximum hydrogen release temperature of 10 wt%NaAlH₄/RP-20 before cycling. The decrease in temperature of hydrogen release can be explained by the improved confinement of NaAlH₄ during repeated dehydrogenation/hydrogenation cycles at temperatures higher than the melting point of NaAlH₄. This is supported by the lack of well-expressed NaAlH₄ diffraction peaks after cycling. The amount of hydrogen liberated during the intense hydrogen release process, starting at 170 and 185 °C for 10 wt%NaAlH₄/RP-20 and 60 wt%NaAlH₄/RP-20, respectively, decreases considerably. The decrease in the amount of reversibly stored hydrogen is caused by the separation of Al and Na₃AlH₆ into separate bulk phases (Fig. 2) which hinders the reformation of the NaAlH₄, even at high H₂ pressure, up to 170 bars.

Cycling the pure NaAlH₄ increases the temperature of maximum hydrogen release from 220 °C to 245 °C. This is most likely caused by the irreversible decomposition of NaAlH₄ into Na₃AlH₆ and Al, i.e. by the segregation of Na₃AlH₆ and Al into separate crystalline phases as seen from XRD data (Fig. 2). Thus, the maximum release of hydrogen at 245 °C corresponds to the second reaction step (Eq. (2)). Up to 0.9 wt% of hydrogen is released from pure NaAlH₄ when cycled and heated up to 200 °C. Such a low temperature for hydrogen release is most likely connected with the first reaction step (Eq. (1)), being also supported by...
the fact that diffraction peaks for crystalline NaAlH4 are apparent for cycled NaAlH4. The lowered temperature of hydrogen release from cycled NaAlH4 can be caused by activation of the surface layer of NaAlH4, which stored hydrogen reversibly during cycling at temperature of 200 °C.

After cycling the diffraction peaks characteristic of pure NaAlH4 in composite materials are undetectable. Thus, NaAlH4 has reformed as too small crystallites to be detectable or converted into the amorphous state. Based on the amount of released hydrogen from cycled 60 wt% NaAlH4/RP-20, 2.5 wt% and 4.8 wt% of H2 per deposited NaAlH4 at 200 °C and at 450 °C, respectively, and according to the possible reactions of NaAlH4 decomposition (Eqs. (1)–(3)), NaAlH4 should be present after cycling. Thus, the decrease in the temperature of the maximum hydrogen release from 195 °C to 175 °C for 60 wt%NaAlH4/RP-20 is at least partly caused by the conversion of crystalline NaAlH4 into/onto RP-20 in the amorphous state and/or by recrystallization into smaller crystallites. From the integrated hydrogen release vs. temperature data (Fig. 4) it is visible that hydrogen release outside of the maximum hydrogen release temperature region (from 175 to 195 °C) decreases with cycling in a much smaller amount, thus, indicating the developed reversible hydrogen storage capability of amorphous and/or nanosized NaAlH4.

4. Conclusion

Different wt% of NaAlH4 were deposited onto/into highly microporous carbon material noted as RP-20. Hydrogen release from NaAlH4/RP-20 composite materials containing less than 20 wt% of NaAlH4 started at ambient temperature and the average crystallite size of NaAlH4 in these composites was smaller in comparison to pure NaAlH4. Hydrogen release from NaAlH4/RP-20 composite materials with NaAlH4 ≥ 20 wt% started at melting temperature of NaAlH4. At 210 °C more than 50% of releasable hydrogen has been released. X-ray diffraction measurements showed that during 10 dehydrogenation/hydrogenation cycles the crystalline NaAlH4 has been deposited/recrystallized into/onto RP-20 as a nanoconfined and/or amorphous phase. Therefore, the temperature of maximum hydrogen release from NaAlH4/RP-20 composite material with 60 wt% of NaAlH4 loading decreased. During repetitive cycling the amount of reversibly stored hydrogen decreases most apparently for the pure crystalline NaAlH4 phase, thus, showcasing the improved reversibility of amorphous and/or nanoconfined NaAlH4 over many dehydrogenation/hydrogenation cycles. Most importantly, the results show that after multiple dehydrogenation/hydrogenation cycles nanoconfined NaAlH4 released most of the hydrogen under 180 °C. Thus, nanoconfined NaAlH4 in a high surface area carbon supporting material is suitable for application in combination with high-temperature proton exchange membrane fuel cells and other transport applications.

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