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How carbon affects hydrogen desorption in NaAlH₄ and Ti-doped NaAlH₄

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Abstract

The hydrogen storage properties of doped and undoped NaAlH₄ samples are studied after mixing them with different percentages of high surface carbon. Manually mixed samples are compared with ball milled ones; it was found that manual mixing was a simple and effective way to dope NaAlH₄. A morphological and micro-structural analysis has been carried out in order to understand the effect of carbon. Carbon added samples show a marked enhancement of hydrogen desorption rate. The desorption temperature and the total hydrogen content remain almost unchanged for undoped sample. The desorption temperatures of Ti-doped samples increase with carbon content. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Hydrogen storage for vehicle application is still an open challenge. Different routes have been followed but a satisfying solution has not achieved yet. Liquid hydrogen shows good volumetric and gravimetric density but its production cost is relatively high. Compressed hydrogen suffers for low volumetric hydrogen density whilst the use of traditional metal hydride is detrimental in terms of gravimetric hydrogen density. High amount of hydrogen (about 7 wt.%) can be absorbed at very high temperatures ($350-450 \,^{\circ}$ C) in light weight metals or metal nitrides (i.e. Mg or LiN₃) [1,2]. The desorption enthalpy (about 80 kcal/mol) can be supplied burning part of the stored hydrogen. In such a way the available hydrogen content is reduced to about 5wt.%.

Complex metal hydrides represent a good compromise between hydrogen content, desorption temperature and reaction enthalpy. Ti-doped NaAlH₄ is emerging as one of the most interesting candidate to efficiently store hydrogen since the discovery of its reversibility in hydrogen desorption.

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.09.025 Different techniques and precursors have been used to prepare Ti-doped NaAlH₄. A solution chemistry was followed by Bogdanovic and Schwickardi [3] and by Jensen and co-workers [4] to prepare the Ti-doped material. A solution of TiCl₃ or Ti(OBuⁿ)₄ in THF was added to a solution or a suspension of the hydride in the same solvent. The doped material was obtained by removing the solvent under vacuum.

The theoretical hydrogen content of NaAlH₄ is 5.6 and 5.1 wt.% hydrogen was desorbed from NaAlH₄ at 225 °C [5]. Material modifications induced by ball milling strongly decrease the desorption temperature. The rate of decomposition of 2 h milled sampled was so fast to release about 3.0 wt.% hydrogen in 2 h at 160 °C [6]. Impressive results were obtained with Tidoped NaAlH₄. Three weight percent hydrogen was desorbed in 4 h from the 0.9 mol% doped sample at temperature as low as 125 °C and still faster desorption rates have been observed increasing the doping level [5]. Since part of the hydride reacts irreversibly with the dopant, high dopant levels are detrimental from gravimetrical point of view. Thus, the very positive benefits on kinetics of Ti-catalyst are seriously offset by losses in reversible H-capacity [5,7]. It has been shown that many types of dopant precursors including non-titanium based compounds result in enhancing sorption kinetics, among them carbon and graphite. Zaluska et al. [6] modified NaAlH₄ and Na₃AlH₆ by mechanical grinding with or without carbon. Milled materials

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showed enhanced desorption kinetics, and the addition of carbon in the milling process remarkably improved their performance. The amount of added carbon varied from 7 to 18 wt.%. It was found that in the case of activated carbon or powdered graphite the results did not significantly depend on the initial form of carbon, whilst carbon nanotubes (CNT) admixed NaAlH₄ shows higher performances [8]. In a recent study, the positive synergistic effect of 10 wt.% graphite powder as co-dopant of 2 mol% Ti-doped NaAlH₄ was reported [9].

The observed phenomena were interpreted in mechanical and electronic terms. Graphite can serve as lubricant or microgrinding agent through the formation of titanium carbide. The electronic interaction of graphite π -electrons with Ti could also facilitate Ti-hydrogen bond formation and consequently enhancing Al-hydrogen bond cleavage. In the same work it was shown that graphite in absence of titanium is essentially inactive as a catalyst [9].

In this work the effect of high surface carbon on dehydrogenation and re-hydrogenation of NaAlH₄ was investigated. Hydrogen desorption properties of manually mixed and high energy milled materials were compared. The effect of carbon as a co-dopant on the de-hydrogenation kinetics of Ti-doped NaAlH₄ was also studied.

2. Experimental

Sodium aluminum hydride (NaAlH₄, Aldrich, tech. 90%) and hydrogen titanium ortobutylate (Ti(OBu)₄, Aldrich, purity \geq 97%) were used as received. High surface area carbon (Carbon Ketjen Black, Akzo Nobel, specific surface 1250 m²/g) was dried at 120 °C for 12 h. The amount of added carbon varied from 2 to 20 wt.%. Carbon was added following two methods, namely ball milling or manual mixing. In a typical ball-milled sample NaAlH₄ and carbon were weighed to form 0.5g-batches which were loaded in a stainless steel vial together with two stainless steel balls. The vial was evacuated and filled with hydrogen. It was mounted in a shaker mill (SPEX 8000, CertPrep, Metuchen, NJ) and milled for 30 min. Manually mixed samples were prepared by grinding the powders in a mortar for 5 min. Doped samples were obtained by gently mixing the mixture with titanium ortobutylate in its liquid form for additional 5 min. The amount of added titanium varied from 0.5 to 4 mol%.

The materials were characterized by X-ray diffraction (XRD) analysis (Miniflex Rigaku diffractometer) using Cu K α radiation.

Powders morphology was studied by scanning electron microscopy (SEM, JEOL JSM-5510LV). Energy dispersive X-ray (EDS) analysis was performed with an IXRF EDS-2000 System. The conditions were: accelerating voltage 25 kV, spot size 21 and working distance 21 mm.

Thermal decomposition was monitored by the home-made apparatus illustrated in Fig. 1. The sample (about 200 mg-batches) was introduced in a cylindrical glass holder. Before each measurement the sample holder was evacuated and filled with nitrogen for three times and finally connected to the measure apparatus. This latter consists in a BronkHorst F-100 flow-meter, 30 nl/h range. The volume of desorbed hydrogen was calculated by numerical integration. A thermocouple positioned on the sample holder was used to record the temperature. When the set temperature was reached, the sample was introduced into a B-585 Buchi Glass Oven. Both the signals from thermocouple and flow-meter were recorded.

Hydrogenation/de-hydrogenation cycles at various temperatures were carried on in a specifically designed pressure composition isotherm apparatus (PCI) from DeltaE, University of Calabria, Italy (www.deltae.it). About 1.0 g of sample was loaded in a cylindrical SS reactor (1.0 cm inner diameter). In order to achieve identical starting condition, the reactor was heated at the operative temperature and evacuated at low pressure (300 Pa) using a turbomolecular pump before each hydrogenation process.



Fig. 1. Apparatus for desorption rate measurements.

The reactor was heated by an external oven. To monitor the temperature a thermocouple was connected to the reactor. When the thermal equilibrium was reached hydrogen was injected into the sample holder at constant flow and pressure changes have been quantified by a calibrated 8 MPa range pressure transducer. An additional 0.08 MPa pressure transducer was used for a good resolution at low pressure fields. The flow was accurately monitored by a flow controller. The signal from the flow-meter was recorded and the volume of flowed hydrogen obtained by numerical integration.

3. Results

Ball-milled Ti-doped samples showed a very high reactivity with air: the powder burned immediately after the evacuated vial was opened, even if this operation was carried out in a glove box. The reactivity of ball-milled samples induced us to find an alternative method to prepare Ti-doped alanate. It was found that manually grinding of the NaAlH₄ powder together with the Ti precursor was an effective method to prepare air-stable Tidoped alanate. There are several practical merits related to the dry approach since it is very easy to produce large amounts of doped material and it avoids the handling of solvents.

3.1. SEM analysis results

A morphological investigation has been carried out to detect modifications in the alanate structure due to addition of carbon or to ball milling, before and after de-hydrogenation. In Fig. 2, SEM images of the NaAlH–0.5mol% Ti sample are shown before (Fig. 2a) and after (Fig. 2b) de-hydrogenation. The very small amount of Ti has not been revealed by micro-analysis.

In Fig. 3a and b, the mortar grinded 10% carbon sample is shown, before and after de-hydrogenation, respectively. The carbon clusters can easily be recognized in Fig. 3a since their grain size is smaller, as compared to the smoother NaAlH₄ grains.

The sample with the same C content as Fig. 3 but prepared by ball milling is shown in Fig. 4. The structures of both the NaAlH₄ and C grains are no more distinguishable, the ball milling had



Fig. 2. SEM images of Ti-doped samples (a) before and (b) after de-hydrogenation.



Fig. 3. SEM images of 10% C added samples (a) before and (b) after de-hydrogenation.

the effect of "flattening" the hydride; in reality, as the XRD analysis showed (Section 3.3), the macroscopic loss of granularity corresponds to a loss of microscopic cristallinity. The same picture at a larger view shows a columnar stratification of planes, Fig. 4b.

The "flat aspect" disappears after the first de-hydrogenation, and the de-hydrogenated product appears similar to the non-ball milled one (Fig. 5).

3.2. Hydrogen desorption in carbon added samples

A plot of the hydrogen flow, normalized to the sample weight, versus time, released by un-doped, carbon added samples with

different carbon percentage, is shown in Fig. 6. The temperature was kept constant at 220 °C for several hours. The effect of the carbon content on desorption kinetic is evident: passing from 2 to 20% carbon, the hydrogen flow increases by a factor of 4.

In Fig. 7, the plot of the hydrogen yield versus time at 220 °C for various carbon content samples is shown. Again it is evident that increasing carbon content has the effect of speeding up the hydrogen dissociation: after 150 min the 20% carbon samples attained the maximum hydrogen yield, 5.1 wt.%, whilst lower percentage carbon samples are still desorbing.

The weight percentage refers to the alanate weight only; if we calculate the hydrogen yield with respect to the sample weight,



Fig. 4. SEM images of 10% C added ball-milled samples before de-hydrogenation at two magnifications.



Fig. 5. SEM images of 10% C added ball-milled samples and after de-hydrogenation at two different magnification.



Fig. 6. Desorbed hydrogen flow of different C content NaAlH₄ samples at 220 $^{\circ}$ C; the flow is normalized to the alanate weight.

the 10% C sample shows better results in terms of gravimetric hydrogen density than the 20% C still at a reasonable desorption rate.

The behavior of the manually grinded samples compared to the ball milled one with the same carbon content is shown in Fig. 8. The hydrogen flow is reduced in the just grinded sample, although the hydrogen amount and the desorption temperature of the two samples are very similar.

The Arrhenius plot of the flow versus temperature for the non-doped 20% carbon added sample (Fig. 9) shows a single decomposition step characterized by an activation energy of 158 kJ/mol/K and a pre-exponential factor of 5.3E18. The effect



Fig. 7. Desorbed hydrogen of various C content NaAlH₄ samples at $220 \degree$ C; the hydrogen weight percentage is referred to the alanate weight.



Fig. 8. Comparison between hydrogen flow released from a ball milled and a just grinded 10% C added samples.

of carbon is to increase the pre-exponential factor, and consequently to increase the kinetics of the reaction, with respect to the undoped NaAlH₄ [5].

It is well known that the decomposition of NaAlH₄ is a twostep reaction described by the following formula:

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \tag{1}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + \frac{3}{2}H2$$
⁽²⁾



Fig. 9. Arrhenius plot of an undoped 20% C added sample.



Fig. 10. XRD spectrum of a 10% C added sample after decomposition at 195 °C.

To detect only the first decomposition step of NaAlH₄ we set the temperature at 195 °C and analyzed the decomposition reaction products by XRD. The hydrogen released by the first step of reaction was 3.7 wt.%.

3.3. X-ray diffraction of carbon added samples

The progressive turning from NaAlH₄ into two different Na₃AlH₆ phases, the α -Na₃AlH₆ and β -Na₃AlH₆, and successively into Al and NaH, was clearly detected by X-ray analysis.

In Figs. 10 and 11, the X-ray diffraction of the desorption products of the 10% carbon ball-milled sample after decomposition, respectively at 195 and 220 °C, are shown. In the low-temperature reaction (Fig. 10) the NaAlH₄ completely decomposed into Al and Na₃AlH₆ (α and β phases) following Eq. (1); after a further increase in temperature (Fig. 11), together with a small amount of Na₃AlH₆, the peaks of Al and NaH appear, as predicted by Eq. (2).

The spectra for the ball-milled sample, before any dehydrogenation process, evidences that the macroscopic amorphous structure seen by SEM corresponds effectively to an absence of microscopic structure: the peak intensity related to NaAlH₄ was strongly decreased and Al was found in the spectrum. The presence of Al evidences that some decomposition reaction occurred during the ball milling.



Fig. 11. XRD spectrum of a 10% C added sample after decomposition at 220 °C.

3.4. X-ray diffraction in carbon-added Ti doped samples

X-ray diffraction spectra for a mixture of NaAlH₄ containing 5 wt.% carbon and doped with 0.5 mol% Ti shows exclusively crystalline NaAlH₄. The absence of the peaks related to titanium metal does not allow to recognize whether Ti is in its crystalline state or not. The absence of peaks attributed to carbon is not surprising since the carbon we used is amorphous.

3.5. Hydrogen desorption in Ti-doped carbon added samples

As stated by different authors [4,5], Ti doping is a very effective way to improve performance and de-hydrogenation kinetic. We tested therefore if the beneficial effect found by adding carbon to the alanates is effective also for Ti-doped samples.

In Fig. 12a, the desorbing curves of four 0.5 mol% Ti samples added, with 0, 5, 10 and 20 wt% carbon are compared. According to Sandrock et al. [5] the Ti-doped sample without carbon shows two well defined decomposition step. The addition of carbon results in an increase of flow that again reaches its maximum for the sample containing 10 wt.% carbon. At the same time the second decomposition step disappeared and it seems that the reaction follows a single decomposition pathway.



Fig. 12. Ti-doped, C added NaAlH₄ samples in: (a) the desorbed hydrogen flow is shown for different C percentages; (b) the corresponding hydrogen content is plotted. Temperature of measurement: 200 °C.



Fig. 13. Arrhenius plot of 0.5 mol% Ti-doped samples for different C added percentages; the 0% carbon curve shows the typical behavior with two different activation energies corresponding to the two decomposition steps.

The total amount of hydrogen evolved versus time is plotted in Fig. 12b. The temperature was raised up to 200 °C, so only the first reaction step is likely to occur; the hydrogen yield is therefore only 3.8%.

The Arrhenius plots for three 0.5 mol% Ti-doped samples at various carbon content, 0, 5 and 20 wt%, are plotted in Fig. 13. By increasing the carbon content both the activation energy and pre-exponential factor are increased with respect to the no-carbon, Ti-doped samples.

Differently from the un-doped sample, the desorption temperatures are strongly affected by carbon content. The effect of the carbon content on the doped sample desorption temperature can be argued from Fig. 14, where the flow curves of Fig. 12a are plotted versus temperature: increasing the carbon percentage from 0 to 20% has the effect to move the desorption onset at higher temperatures, from 140 to 160 °C.

3.6. Hydrogenation and cyclability

The PCT apparatus has been used with P = 80 bar maximum pressure, F = 40 ncc/min hydrogen flow, temperatures in the 200–230 °C range. Before any subsequent re-hydrogenation,



Fig. 14. Desorption temperatures for doped C added NaAlH₄.



Fig. 15. Hydrogen absorbed by a 10% C sample during a PCT cycle, with a constant pressure ramp up to 80 bar at various temperatures.

the sample was completely de-hydrogenated by pumping it at $230 \,^{\circ}$ C till a 0.1 mbar pressure was attained.

The absorption and desorption curves of the 10% C added sample at various temperatures are shown in Figs. 15 and 16, respectively, the sample absorbed reversibly about 5 wt.%hydrogen. It is worth to note that the pure alanate do not exhibit any re-hydrogenation property at those conditions. For the 2.5 h charging time, the rate of hydrogenation as well as the total amount of H₂ absorbed does not seem to be affected by temperature. A little change in the absorption rate is observed at the end of process and it causes a little variation in the amount of absorbed hydrogen with temperature. The desorption curves show a more pronounced dependence on temperature: the des-



Fig. 16. Hydrogen desorbed by a 10% C sample during a PCT cycle, with a constant pressure ramp down from 80 bar at various temperatures.

orbed hydrogen amount is larger at higher temperature, and larger is also the desorption rate.

4. Discussion

Beneficial effects in both hydrogen desorption rate and desorption temperature due to carbon presence have been detected by different authors [6,8]. How the carbon could enhance the alanate performance is anyway still an open question. Morphological analysis shows that the aggregate structure of the de-hydrogenated samples has been modified by carbon. The presence of carbon produces rough particles. By examining every single particle it is possible to observe that it is an aggregation of particles of smaller diameter (few micron); anyway X-ray spectra after de-hydrogenation show that no modification occurred in the crystalline structure of alanate. The role of carbon could be more "physical" than "chemical" in the sense that it modifies the grain surface of the de-hydrogenated phases probably due to the inhibition of grain aggregation. The increase of the surface/volume ratio upon the first de-hydrogenation could enhance the second de-hydrogenation step. This is in accordance with the obtained results, which show that only the desorption rate is improved by carbon addition, being the desorption temperature and the hydrogen yield only slightly affected.

The effect of carbon to increase the hydrogen desorption rate is noticeable for carbon content as high as 10 wt.%. By doubling this amount only a slight change in the hydrogen rate was observed. The amounts of hydrogen desorbed from 10 to 20 wt.% carbon added samples was almost the same. It is easy to recognize a "threshold" behavior appearing when the carbon content lies between 5 and 10%. By considering that large amount of dopant is detrimental in term of gravimetrical hydrogen density, the 10 wt.% sample can be considered the best compromise between the de-hydrogenation rate and the hydrogen yield.

Also in Ti-doped materials the rate of the second dehydrogenation step is increased after carbon was added. As a result the two desorption steps clearly visible in the Ti-doped material, disappeared in presence of carbon (Figs. 12 and 13) and a single desorption process was observed in carbon added titanium-doped NaAlH₄ samples. The temperature of the first desorption step is slightly increased by increasing the amount of carbon. This could be explained by considering that Ti-doped samples are very sensitive to the amount of Ti used as catalyst [5]. Carbon inhibits the effect of the titanium through an increase of the activation energy of the process. It could be due to some interaction of Ti with carbon that decreases the amount of "active" titanium or reduces Ti mobility. As stated for nondoped samples, the presence of carbon on doped samples inhibits the grain aggregation of NaAlH₄.

With respect to what previously found [9] our results pointed out that the effect of carbon, independently from its allotropic state, has beneficial effect on both Ti-doped or undoped NaAlH₄ decomposition. The main differences between what has been found by Wang et al. by adding graphite instead of high surface carbon [9] and our results are in the lower decomposition temperature; a very light effect on it should be ascribed to the ball milling of the sample.

5. Conclusions

In this paper, the positive effect of carbon on hydrogen absorbtion/desorption process has been shown. Carbon acts with a threshold behavior and 10 wt.% carbon was found the best carbon content. The 10% carbon sample, obtained by manual mixing carbon and NaAlH₄, showed to reversibly desorption of hydrogen to 4 wt.% in the temperature range between 200 and $300 \,^{\circ}$ C. The smaller grain size noted for carbon-doped materials could enhance the rate of the second de-hydrogenation and the following hydrogenation/de-hydrogenation steps. Synergism was found between carbon and Ti in double-doped samples. It follows that the two dopants act with different mechanisms. The higher desorption temperature showed from Ti-doped samples mixed with carbon was related to a decrease of the amount of available titanium.

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