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Sodium alanates for reversible hydrogen storage

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Abstract

In this paper we show that sodium alanates may be used for reversible hydrogen storage, with the advantage of having high storage capacity combined with low cost. Both $NaAlH_4$ and Na_3AlH_6 have been investigated for this application, and two complementary techniques have been used: improvement of the reaction kinetics by mechanical grinding, and chemical modification of the alloys. By these methods remarkable desorption/absorption kinetics are obtained. Sodium alanates so modified are capable of reversible hydrogen storage at the relatively low temperatures of around 80–140°C, with a capacity of between 2.5 and 3.0 wt.%. The hydrides have an even higher reversible capacity of about 4.5–5 wt.% when operated at temperatures around 150–180°C.

Keywords: Reversible hydrogen storage materials; Alkali metal aluminium hydrides; Metal hydrides; Ball milling

1. Introduction

Sodium alanates (i.e. complex hydrides of aluminum and sodium: sodium tetrahydroaluminate–$NaAlH_4$ and trisodium hexahydroaluminate–Na_3AlH_6) have been known for decades as reducing agents in organic chemistry. $NaAlH_4$ was first synthesized in the late 1940s by Finholt et al. [1], and Na_3AlH_6 about 15 years later by Zakharin and Gavrilenko [2]. Although a good source of hydrogen, sodium alanates were not considered appropriate for reversible hydrogen storage, because hydrogen release was extremely slow, and more importantly, because the rehydrogenation after decomposition was in practice impossible.

$NaAlH_4$ and Na_3AlH_6 contain large amounts of hydrogen (7.4 and 5.9 wt.%, respectively). However the release of hydrogen does not occur in a single-step reaction. According to Ref. [3] (and references within), the decomposition of $NaAlH_4$ proceeds as follows:

$$3\,NaAlH_4 \rightarrow Na_3AlH_6 + 2\,Al + 3H_2\uparrow$$
$$Na_3AlH_6 \rightarrow 3\,NaH + Al + 3/2\,H_2\uparrow$$
$$NaH \rightarrow Na + 1/2\,H_2$$

The first reaction releases 3.7 wt.% of hydrogen and starts at a temperature between 185°C (where melting of $NaAlH_4$ is also suggested [4,5]) and 230°C [3]. The second reaction occurs at about 260°C, with a further desorption of 1.85 wt.% of hydrogen (relative to the starting material, $NaAlH_4$). Finally, the decomposition of NaH occurs at a much higher temperature, with the total hydrogen release of 7.4 wt.%.

For hydrogen storage, only the first two reactions (with total hydrogen release of 5.55 wt.%) need to be considered, because the decomposition of NaH occurs at too high a temperature for practical storage systems. (The Merck Index gives the temperature of decomposition of 425°C for commercial NaH). As mentioned above, the reversibility of these two reactions is a critical factor for the usability of sodium alanates in hydrogen storage devices. Reversibility means the ability to form $NaAlH_4$ and Na_3AlH_6 directly from NaH and Al (i.e. from the products of the second stage of decomposition), under hydrogen pressure. However, so far methods for the direct formation of $NaAlH_4$ and Na_3AlH_6 use sodium in elemental form rather than in the form of sodium hydride, NaH. It has been reported that $NaAlH_4$ can be formed by the following reaction [4,6,7]:

$$Na + Al + 2H_2 \rightarrow NaAlH_4$$

According to Ref. [6], the reaction should be performed for several hours in a solvent, tetrahydrofuran (THF), at a temperature of about 140–160°C. It requires high pressure

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of hydrogen (140–350 atm.) and the use of activated aluminum. The activation of the aluminum consists of treating it in powder form with triethylaluminum. In another method developed by Dymova et al. [4], hydrogen pressure of 200–400 atm. is used to hydrogenate Na in the presence of aluminum. The reaction is performed at higher temperature (240–260°C) allowing sodium to melt, which is the key to the process. The liquid form of the reagent is advantageous because the reaction can be performed without organic solvents. The above methods are, however, not very effective when using NaH instead of Na. As reported in Ref. [4], only traces of $NaAlH_4$ were formed from NaH and Al after hydrogenation at temperatures between 180 and 240°C and under hydrogen pressures between 100 and 400 atm., although the same conditions were sufficient for the formation of $NaAlH_4$ from Na and Al. In the work of Ashby et al. [6], the reaction with NaH was indicated to occur under hydrogen pressure of 350 atm. in a 'quantitative yield', but no further data were given. The above direct methods of the formation of $NaAlH_4$ do not therefore solve the problem of reversibility of the hydriding/dehydriding reactions. Still, from the thermodynamic point of view, formation of sodium alanates from Al and NaH under gaseous hydrogen *is* possible, but perhaps requires either extreme pressures of hydrogen or the presence of special solvents or catalysts. Recent work of Bogdanović and Schwickardi [8,9] showed for the first time that reversibility is indeed possible in sodium alanates. It was confirmed that sodium alanates are extremely difficult to rehydrogenate, but a new method of catalysis (by doping with a special Ti-based catalyst) improved kinetics of hydrogenation/dehydrogenation in such a way that cycling was feasible. Although the reaction still required the use of high hydrogen pressure, at least 150 atm., and took several hours at 170°C, the results showed that formation of $NaAlH_4$ from NaH and Al under gaseous hydrogen was at least possible. The work of Bogdanović and Schwickardi [8] initiated new interest in sodium alanates as prospective hydrogen-storage media (e.g. [10–12]). An obvious advantage of sodium alanates is their high hydrogen capacity, combined with the low cost of sodium and aluminum. Our efforts have been focused recently on enabling sodium alanates to operate reversibly, with improved kinetics and in the range of moderate temperatures. We have investigated both $NaAlH_4$ and Na_3AlH_6, and have adopted two complementary approaches: firstly, improvement of the reaction kinetics by mechanical grinding, and secondly, chemical modification of the alloys. These methods result in a great enhancement of the hydrogenation/dehydrogenation performance of sodium alanates. In many aspects the results surpass the catalytically enhanced alloys from Ref. [8]. More importantly however, this work indicates possible new directions for the development of sodium alanates (to be exploited independently of, or concurrently with catalytic methods) leading to viable and inexpensive materials for hydrogen storage.

2. Experimental

The starting material, $NaAlH_4$ (sodium aluminum hydride), was purchased from Sigma-Aldrich Canada, with a nominal purity of 90%. Na_3AlH_6 was fabricated by mechano-chemical synthesis through solid-state reaction, as described in Ref. [10]. It involved direct reaction of $NaAlH_4$ and NaH in a vibratory ball mill. The process was performed in a laboratory apparatus from SCP Sience (Model SP-2100). Appropriate amounts of the reagents ($NaAlH_4$ and 2NaH, in the form of powders or granules) were ball milled in the stainless steel vials, with stainless steel balls.

Ball milling was performed under an inert atmosphere of argon [10]. Sodium hydride, NaH, was purchased from Sigma-Aldrich Canada, having a nominal purity of 95%. Ball milling was also used to improve kinetics of the sorption properties of the hydrides. In this case the milling time was shorter: between 0.25 and 2 h, performed in argon, in stainless steel vials. The mass ball-to-powder ratio (ξ) was between 1.7 and 15.

Chemical modification of sodium alanates was performed by ball milling $NaAlH_4$ and Na_3AlH_6 with other elements or compounds. Various additives have been studied, as will be presented in upcoming papers. In this work we describe results obtained with carbon as an additive and chemical modificator. The amount of carbon added to $NaAlH_4$ was varied from 1:3 to 1:1 in molar ratio. This was equivalent to a content of 7–18 wt.% of carbon in the sample. It has been found that the results did not depend significantly on the initial form of carbon. For example, similar results were obtained when using either activated carbon or powdered graphite as a starting material.

The materials were characterized by an automated Nicolet-Stoe powder diffractometer with CuKα radiation.

Hydrogenation experiments from the gas phase were performed by using a volumetric method. A computerized gas titration system was used to determine the absorption/desorption kinetics and to measure the pressure–concentration isotherms. The system operates over the temperature range from room temperature to 500°C.

Alkali metal hydrides are very sensitive to exposure to air, and any contact with water results in their hydration. Therefore exposure to air and humidity was carefully avoided. All the material handling (including weighing and loading) was performed in a glove box with a carefully controlled atmosphere, with low oxygen and water vapour content. Also, X-ray diffraction (XRD) samples were specially prepared. The samples were covered with a plastic tape, which had a negligible or easily deductible contribution to the diffraction pattern.

Commercially available $NaAlH_4$ and NaH have relatively low purity (90% and 95%, respectively). The use of such materials obviously results in lower hydrogen capacities than the nominal values. Moreover, as will be explained in the following section, $NaAlH_4$ is in fact thermodynamically unstable when stored at room temperature and under hydrogen pressure lower than several tens of atm. Although $NaAlH_4$ decomposes extremely slowly at low temperatures (which is a serious disadvantage for practical cycling) it can be expected that after prolonged storage the actual content of $NaAlH_4$ in the sample may be even lower than that claimed by the manufacturer. In particular, it is difficult to determine how long the material has been stored by the supplier after the fabrication, and whether it deteriorated because of the residual humidity in the storage atmosphere, etc. For this reason, hydrogen capacities in the purchased alanates depend not only on their initial purity but also on their ‘freshness’. One way to overcome this problem is to purify sodium alanates before the hydrogenation experiments. There are methods allowing effective purification of $NaAlH_4$ (see for example [7,8]), which consist of solvation in THF, filtration of the solid impurities and then precipitation in ether, toluene or pentane. Although purification allows us to regain hydrogen capacities in the hydride, it is possible that this treatment may by itself change the hydriding/dehydriding properties of $NaAlH_4$.

Traces of organic media (if not carefully removed) may decompose during heating (as indicated for example in [13]) and contribute to the measured weight-loss of the sample, or to an apparent pressure increase when measured by volumetric methods. Moreover, THF (even in small amounts) can strongly affect hydriding/dehydriding kinetics, as shown by Imamura et al. [14,15] for Mg–Pd–C composites. It was suggested that in this case THF was involved in the formation of a charge-transfer complex, having a high ability of catalytic activation [14,15]. Moreover, for some alanates, cleavage of THF occurs at low temperatures, and opening of the THF ring was observed even at room temperature for example in a THF–AlH_3 complex [3]. These effects may cause the first desorption after purification to produce apparently more hydrogen than can be obtained in the subsequent, reversible cycles.

For the above reasons, the effects of synthesis and purification of $NaAlH_4$ perhaps require a more detailed study. We avoided any contribution of these effects, in particular the eventual catalytic action of the purifying media, by performing experiments on a batch of commercial $NaAlH_4$, untreated and unpurified. As a result, the hydrogen capacities were reduced (in some cases by as much as 20 wt.%), but they can be regained if purification is applied. In consequence, the results demonstrate the effects of ball milling and chemical additives on the sorption properties of sodium alanates, without the interference with organic media being used for purification.

3. Results and discussion

3.1. Characteristics of the Na–Al–H system

As indicated above, the Na–Al–H system exhibits multistep dehydrogenation, with the following hydride phases involved: $NaAlH_4$, Na_3AlH_6 and NaH. In order to determine the usability of the system for practical hydrogen storage, temperature–pressure conditions for each of these reactions should be determined. There are, to date, two reports providing thermodynamic data for these reactions, namely the early paper of Dymova et al. [5] and the more recent work of Bogdanovič and Schwickardi [8]. In the work of Dymova et al. [5] thermodynamic properties of $NaAlH_4$ and Na_3AlH_6 were determined from the dissociation pressures, which have been measured at temperatures between 190 and 240°C. In the work of Bogdanovič et al. [8] several *P–C* isotherms for both $NaAlH_4$ and Na_3AlH_6 have been also reported. These literature results are plotted in Fig. 1 and allow us to draw the following conclusions about the Na–Al–H system:

1. Over a very wide range of temperatures (even below room temperature), $NaAlH_4$ is thermodynamically unstable and should spontaneously decompose (although

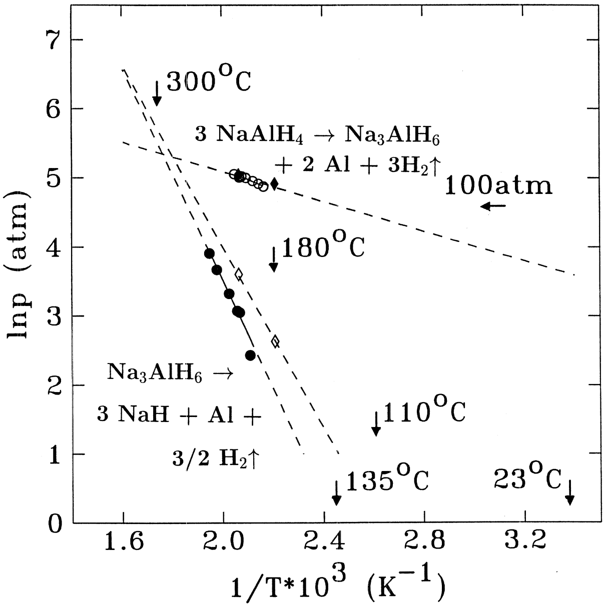

Fig. 1. Equilibrium pressures for the decomposition of $NaAlH_4$ and Na_3AlH_6 in dependence on temperature: (◦) from Ref. [5] and (◇) from Ref. [8]. (Blank and filled symbols are used to differentiate the decomposition of $NaAlH_4$ and Na_3AlH_6).

in practice very slowly), if hydrogen pressure is lower than about several tens of atmospheres. If simply extrapolated from the literature data [5,8], the equilibrium pressure at room temperature should be equal to about 30–40 atm. In consequence gaseous synthesis of $NaAlH_4$ is thermodynamically possible only if hydrogen pressure exceeds these pressures, for example 130 atm. at 180°C, or 155 atm. at 210°C, as measured in Refs. [5] and [8], respectively. (It should be noted that in practice even higher pressure has to be applied in order to produce a meaningful driving force for the reaction and to give usable kinetics).

2. At room temperature, Na_3AlH_6 is very stable and in practice cannot decompose. As estimated from Fig. 1, this hydride has equilibrium pressure of 1 atm. at about 110°C [8] or 135°C [5]. Therefore in practice one cannot expect decomposition of Na_3AlH_6 below these temperatures, unless the kinetics of desorption are excellent.
3. In the range of intermediate temperatures (above ~110–135°C and below ~300°C), the decomposition of $NaAlH_4$ proceeds in two steps and involves firstly decomposition into Na_3AlH_6, and subsequently into NaH, consistent with the reactions cited above. At lower temperatures $NaAlH_4$ cannot be fully decomposed because Na_3AlH_6 remains stable at these temperatures.
4. The reaction: $NaH + Al \rightarrow NaAlH_4$ (proposed in the literature as a possible path for direct formation of $NaAlH_4$ e.g. [6]) is in fact not substantiated thermodynamically. Under gaseous hydrogen, formation of $NaAlH_4$ has to be also a stepwise process, involving formation of Na_3AlH_6 as an intermediate phase. Direct synthesis of $NaAlH_4$ without the formation of Na_3AlH_6 may eventually occur, but only at high temperature and under very high hydrogen pressure. As can be deduced from Fig. 1, this can be probably effected at temperatures above 300°C and under hydrogen pressure exceeding about 250 atm., where possibly Na_3AlH_6 becomes less stable than $NaAlH_4$. In this context, one comment should be made regarding the formation of $NaAlH_4$. In previous papers [4,6] it has been established that direct synthesis of $NaAlH_4$ from Na and Al always required a substantial excess of aluminum (up to as much as 100 at.%). The excess of aluminum ‘‘has been used to exclude formation of Na_3AlH_6’’ [4], being interpreted as an unwanted by-product of the reaction which perhaps indicated insufficient amount of aluminum in the process. It turns out that Na_3AlH_4 is actually a necessary, intermediate stage of the reaction. Therefore, in the case of an incomplete synthesis, Na_3AlH_4 can indeed be seen among the reaction products, and its amount simply depends on the stage of the reaction.

It should be stressed that the above interpretation of Fig. 1 is based on an arbitrary assumption that the data of Dymova et al. [5] and Bogdanović and Schwickardi [8] can be extrapolated beyond the measured temperature ranges. Also, we do not know the effect of melting of $NaAlH_4$ (suggested to occur at 185°C) on its thermodynamics of dehydrogenation/hydrogenation. (After submission of this paper we learned that recent results indeed confirm that melting changes the slope of the van’t Hoff plot [16,17]). Although the above basic characteristics can be derived from Fig. 1 alone, evidence for these properties has also been found in the course of the present work, as described below. The most characteristic feature of the Na–Al–H system is that the kinetic curves for both decomposition and synthesis of $NaAlH_4$ always exhibit two steps, reflecting the two stages of the reaction. This is illustrated in Fig. 2, which shows the kinetics of the decomposition of $NaAlH_4$ (ball milled for 15 min). The first reaction, $3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2\uparrow$, occurred when $NaAlH_4$ was heated from room temperature up to 160°C, as shown in Fig. 2a. Further hydrogen desorption ceased after about 16 h because the temperature was too low for the decomposition of Na_3AlH_6. Subsequent heating of the sample up to the temperature of 220°C resulted in the decomposition of Na_3AlH_6. Two steps are also seen in Fig. 2b, which shows the decomposition of $NaAlH_4$ at 180°C, with both reactions occurring, but at different rates. Fig. 3 shows the XRD patterns taken at each stage of the reaction: before the decomposition, after the first reaction, and after the second reaction. In the first pattern, the structure of $NaAlH_4$ is shown, with some aluminum impurity. The second XRD pattern shows Na_3AlH_6 formed as an intermediate stage of the decomposition, with an

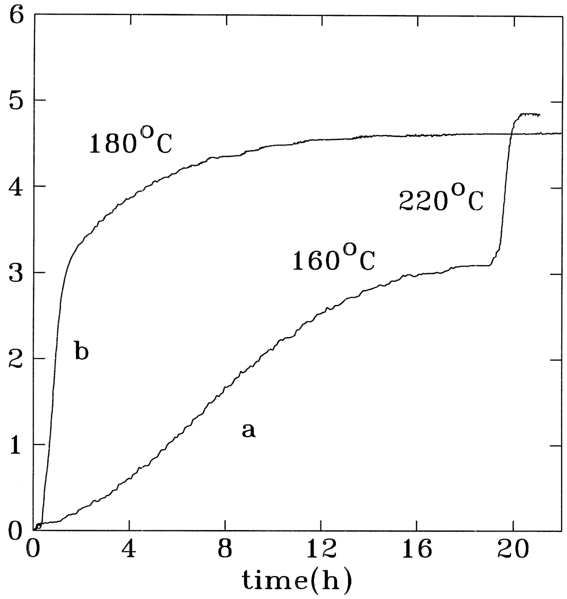

Fig. 2. Decomposition of $NaAlH_4$ (ball milled for 15 min., $\xi = 1.7$): (a) during heating from RT to 160°C (first decomposition stage: $NaAlH_4 \rightarrow Na_3AlH_6$) and subsequent heating to 220°C (second decomposition stage: $Na_3AlH_6 \rightarrow NaH$); (b) during heating from RT to 180°C. Heating rate: ~5°C/min, first desorption of the unpurified material.

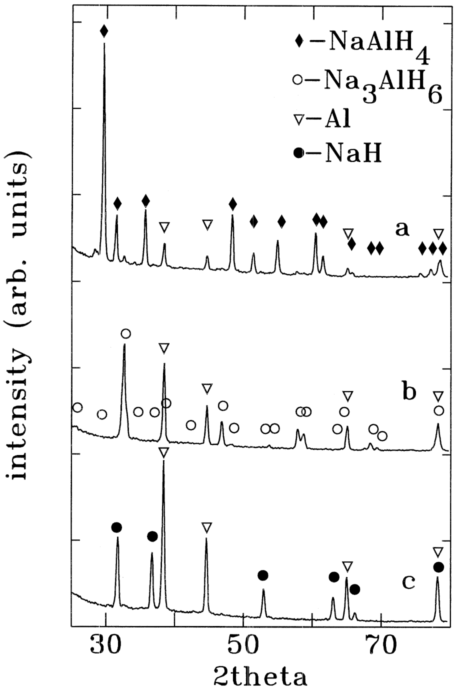

Fig. 3. X-ray diffraction patterns illustrating decomposition of $NaAlH_4$: (a) before decomposition: $NaAlH_4$ with Al impurity; (b) after the first reaction: Na_3AlH_6 + Al; (c) after the second reaction: NaH + Al.

increased amount of aluminum, resulting from the first reaction. At the final stage of the decomposition, the material consists only of sodium hydride, NaH, and aluminum, as presented in the third XRD pattern in Fig. 3.

3.2. Effects of ball milling on the kinetics of decomposition

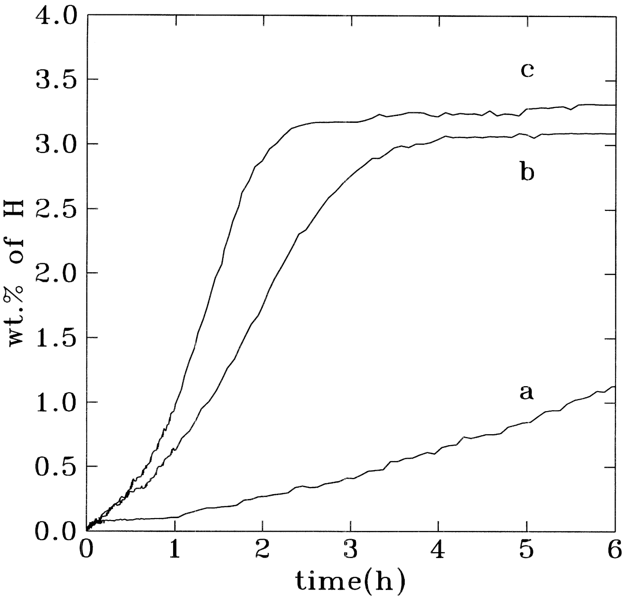

Fig. 4. Rates of decomposition (first hydrogen desorption) for $NaAlH_4$ ball-milled for various periods of time: (a) 15 min, $\xi = 1.7$, during heating from RT to 160°C (shown in full in Fig. 2); (b) 1 h, $\xi = 15$, desorption at 160°C; (c) 2 h, $\xi = 15$, desorption at 160°C.

Commercial $NaAlH_4$ is usually provided in the form of granules. As-purchased, the hydride does not exhibit any significant desorption of hydrogen up to about 180°C. According to Ref. [8], after purification $NaAlH_4$ decomposes very slowly at 160°C. It was shown that a desorption of about 2 wt.% required more than 50 h at this temperature, and for the first 15–20 h almost no desorption was observed [8]. It has been found in the present work that $NaAlH_4$ decomposes much more easily after ball milling. The rate of decomposition depends on the milling intensity (milling energy) and on the milling time, as illustrated in Fig. 4. However, even samples milled for a very short period of time (15 min.) and at a low energy (i.e. a mass ratio of ball-to-powder $\xi = 1.7$) exhibited a much faster decomposition at 160°C than that shown by Bogdanović and Schwickardi [8] for the purified (but non-catalysed) sample. Fig. 4a presents a portion of the plot, which is shown in full in Fig. 2a. Prolonged milling with higher energy (i.e. $\xi = 15$) resulted in even faster desorption. In this case the first reaction can be completed within 1–2 h, which is comparable with the rates reported in Ref. [8] for the catalyzed $NaAlH_4$. The decomposition of ball-milled Na_3AlH_6 (fabricated by solid state reaction [10]) also occurs at a higher rate than the same hydride prepared by conventional methods, described in [2,18,8]. The rate of hydrogen desorption shown in Fig. 5 is for example almost ten times faster at 200°C than that presented by Bogdanović and Schwickardi [8] for the Na_3AlH_6 prepared in a solvent, and is similar to that for the catalyzed hydride. Thus, even with no catalysts and activators, ball-milled

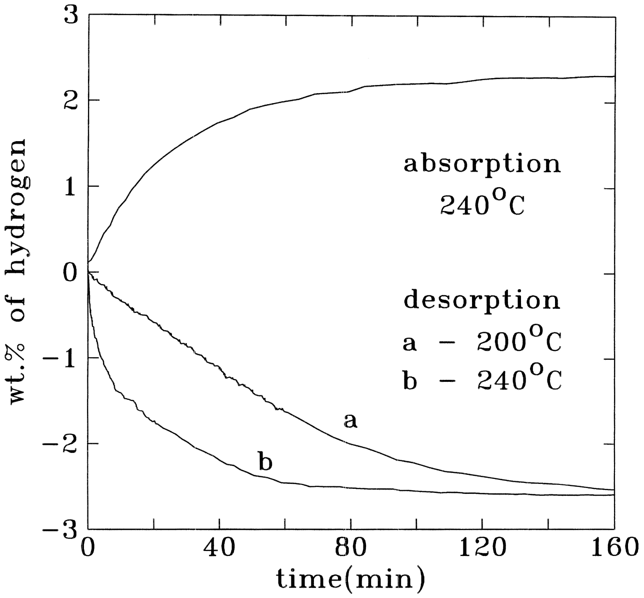

Fig. 5. Rates of hydrogen desorption and absorption for Na_3AlH_6 synthesized by the solid-state process; (temperatures of desorption: 200 and 240°C; temperature of absorption: 240°C; absorption pressure: 58 atm.).

Na_3AlH_6 is able to absorb and desorb hydrogen relatively quickly, e.g. within ~1 h at a temperature of 240°C (Fig. 5).

3.3. Carbon as activator

The hydrogen sorption properties of hydrides are in general changed by alloying with other elements or compounds. For the present hydrides, the most effective method of such alloying is by using mechanical grinding (ball milling) of the hydride in the presence of additives. Various mechanisms may be involved in this process, such as thermodynamic modification of the hydride (by changing hydrogen bonding through substitution by atoms of the additive) or kinetic modification (for example by catalysis). Sodium alanates can be effectively modified by such processes and one of the most efficient additives is carbon. In most samples the amount of added carbon was 10 wt.%, but samples with 7 and 18 wt.% C were also studied. The optimum (i.e. the lowest) content of carbon still needs to be determined. Too much carbon reduces the hydrogen capacity by increasing the total weight of the material; on the other hand, too little carbon produces insufficient enhancement. All samples with carbon were ball milled with a mass ball-to-powder ratio ξ of 15.

Fig. 6 compares the rates of decomposition at 160°C for $NaAlH_4$, milled with and without carbon (10 wt.%). With the addition of carbon, $NaAlH_4$ decomposes much faster than any previous sample: either ball milled without carbon or catalyzed (as reported in the literature [8]). Fig. 6b and c shows also the difference between the first and subsequent decomposition rate. The first desorption is the slowest one, and in the subsequent cycles the rates are always faster and reproducible. It should be noted that the difference between the samples milled with and without carbon is not limited to the rate of the first reaction, i.e. $NaAlH_4 \rightarrow Na_3AlH_6$. In a more significant way, the second reaction (i.e. the decomposition of Na_3AlH_6) is also affected. The sample without carbon does not exhibit at 160°C any noticeable hydrogen desorption within several hours after completion the first reaction. In contrast, the sample milled with carbon exhibited a decomposition of Na_3AlH_6 at 160°C. This reaction was however significantly slower than the first reaction, and was completed only within about 12 h in the first dehydrogenation, and within about 2–3 h in the subsequent cycles. The total amount of hydrogen released reached ~4.5 wt.% (which is beyond the time scale in Fig. 6). A similar effect of enabling the decomposition of Na_3AlH_6 at lower temperatures has been also observed in the case of the catalyzed $NaAlH_4$ [8,11].

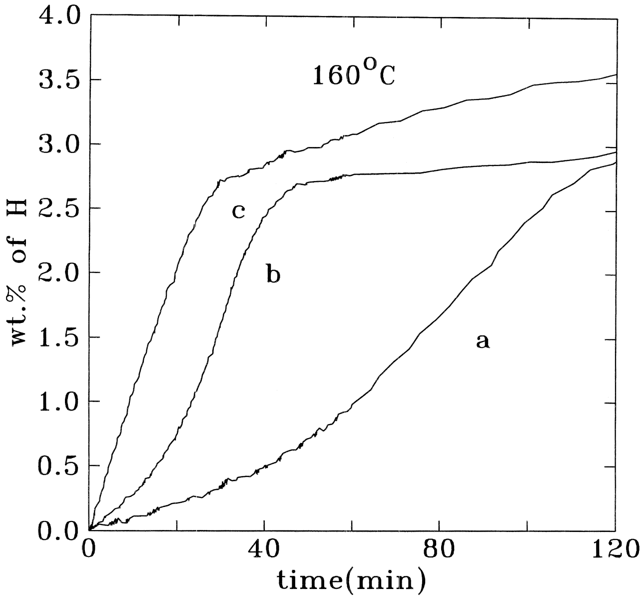

Fig. 6. Decomposition of $NaAlH_4$ at 160°C: (a) ball milled for 2 h without carbon, first decomposition (b) ball milled for 2 h with 10 wt.% of carbon, first decomposition (c) ball milled with 10 wt.% of carbon, second decomposition.

After the decomposition of $NaAlH_4$ (modified with carbon), absorption experiments have been performed. According to Fig. 1, the first stage of hydrogen absorption (i.e. formation of Na_3AlH_6) should not require high hydrogen pressures at moderately elevated temperatures, for example about 100°C. In practice however, formation of Na_3AlH_6 can occur only at higher temperatures because of the kinetic limitations. For example, Bogdanović and Schwickardi [8] used a temperature of 200°C and a hydrogen pressure of about 60 bar for the rehydrogenation of the catalyzed Na_3AlH_6. The formation of $NaAlH_4$ (i.e. the second stage of the reaction) requires much higher hydrogen pressures. It was indicated by Dymova et al. [4] that a pressure of about 175 atm. represents the 'threshold pressure', below which $NaAlH_4$ cannot be synthesized, but only Na_3AlH_6. However, in the work of Bogdanović and Schwickardi [8], the absorption of $NaAlH_4$ was accomplished, through the catalytic action of the chemical dopant. In the case of the catalyzed $NaAlH_4$, the absorption was performed under hydrogen pressure of 152 bar, at 170°C. Without catalysis only a negligible absorption was observed.

Sodium alanates activated by our technique (i.e by ball milling with carbon) cannot only be rehydrogenated without the use of catalysts, but may also be rehydrogenated under more practical conditions. For example, the formation of $NaAlH_4$ has been effected under a hydrogen pressure of about 75–90 atm., instead of the 150 atm. used in Refs. [8] and [11]. As a result, the synthesis of $NaAlH_4$ can be performed using regular cylinders with compressed hydrogen, with no need for its additional compression. In addition, as shown in Fig. 7, hydrogen absorption can be completed under this pressure within 3–5 h at an even lower temperature of 130°C. Because of the good kinetics resulting from our method of synthesis of $NaAlH_4$, the process can be performed even at temperatures below

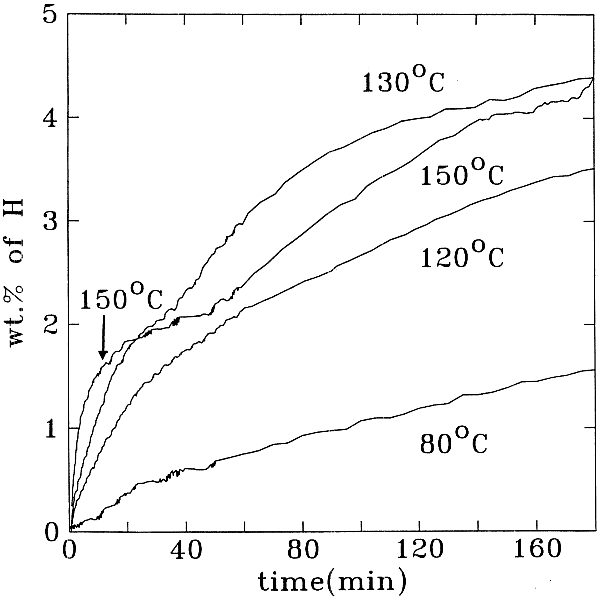

Fig. 7. Rehydrogenation of the decomposed $NaAlH_4$ at various temperatures. Initial hydrogen pressure: 88 atm.

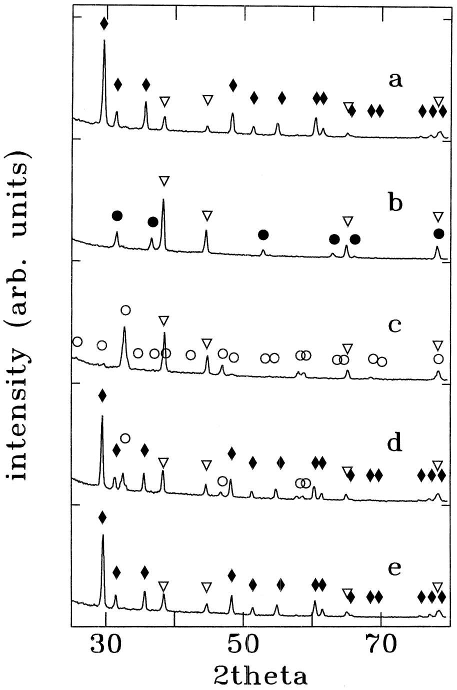

Fig. 8. X-ray diffraction patterns for $NaAlH_4$ ball milled with 10 wt.% of carbon: (a) after ball milling (b) after full decomposition into NaH and Al (c) after the first stage of absorption: Na_3AlH_6 formed (d) intermediate stage of absorption: both Na_3AlH_6 and $NaAlH_4$ are present (e) completed absorption: $NaAlH_4$, with Al impurity only. Phases are marked with the same symbols as in Fig. 3.

100°C (Fig. 7), although at these temperatures the reaction takes more than 20 h to complete.

All kinetic plots for the hydrogen absorption exhibit a two-step reaction: firstly the relatively fast formation of Na_3AlH_6 and then the slower synthesis of $NaAlH_4$. This reaction route is confirmed by XRD measurements, as shown in Fig. 8. The first XRD pattern represents the structure of $NaAlH_4$, ball milled for 2 h with the addition of 10 wt.% of carbon. The pattern is substantially similar to that presented in Fig. 3, which was obtained for $NaAlH_4$ milled for a very short time (15 min) and without carbon. However, the reflections are broader, as is seen more clearly when patterns with similar intensities are compared. The broadening indicates a refinement of the structure (perhaps even a nano-structure), and a possible contribution from strain and defects. Another observation is that carbon cannot be seen in the diffraction pattern, either in the form of crystalline or amorphous contribution. In Fig. 8, the second XRD pattern shows the same material after complete decomposition into NaH and Al, and is similar to that shown in Fig. 3c. The next three patterns represent different stages of the rehydrogenation: the formation of Na_3AlH_6 (Fig. 8c; the pattern taken after the 'fast' portion of the absorption curve), an intermediate stage (both Na_3AlH_6 and $NaAlH_4$ are present, Fig. 8d) and the final formation of $NaAlH_4$ (taken after the completion of the slower process; Fig. 8e).

It is interesting to note that the kinetics of absorption reflect a competition between different kinetic factors at different temperatures. For the formation of Na_3AlH_6, the driving force of the reaction (i.e. the difference between the actual hydrogen pressure and the equilibrium pressure) is large enough for the reaction to exhibit the usual, simple kinetic behaviour, with a higher rate occurring at a higher temperature. For the second reaction however (i.e. for the formation of $NaAlH_4$) the driving force is more critical. The applied hydrogen pressure of above 80 atm. (which decreases during the absorption by several atm.) represents a much greater driving force for the reaction at 130°C than at 150°C, so that under these conditions absorption is actually slower at 150°C than at 130°C. We conclude that the optimum temperature for the formation of $NaAlH_4$ in the pressure range of 80–90 atm. is between 120 and 140°C.

In parallel with the excellent kinetics of hydrogen absorption, alanates modified with carbon also desorb hydrogen at much lower temperatures. Figs. 9 and 10 show decomposition rates of the modified $NaAlH_4$ at various temperatures. The most important result is again the ability of $NaAlH_4$ to decompose even at temperatures below 100°C, and with kinetics still better than these for catalyzed $NaAlH_4$ at 140°C [8]. As shown in Fig. 11, $NaAlH_4$ can also desorb hydrogen in two steps: first a low-temperature desorption, then, as a result of heating the sample to higher temperature, a second desorption corresponding to the decomposition of Na_3AlH_6. In this two-step process, high hydrogen capacities can be obtained without excessive heating of the material.

As shown above, ball milling alone has a significant effect on the improvement of the kinetics of absorption and

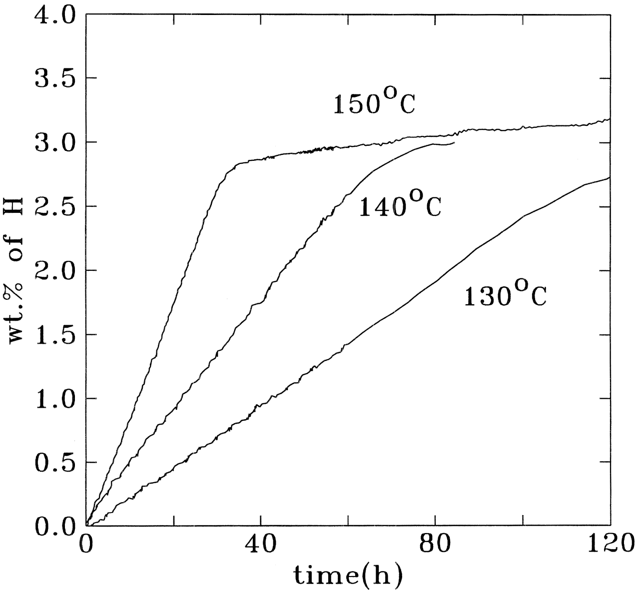

Fig. 9. Hydrogen desorption from $NaAlH_4$, ball milled with 10 wt.% of carbon, at medium temperatures.

desorption, but the addition of carbon improves it even more remarkably. How carbon modifies sodium alanates is an interesting question. To study possible thermodynamic contribution to these modifications, pressure–composition isotherms of $NaAlH_4$ were measured at various temperatures between 130 and 230°C. Fig. 12 shows a *P–C* isotherm for hydrogen desorption taken at 150°C. The isotherm has two-plateaus, the higher plateau corresponding to the decomposition of $NaAlH_4$ into Na_3AlH_6 and Al, and the lower plateau corresponding to the decomposition of Na_3AlH_6. It should be noted that our volumetric system provides good accuracy only for the lower plateau. At pressures much over 60 atm. the system is less accurate and the measured values of the desorption pressure could be as much as 10–15% lower than the true equilibrium values. This must be borne in mind when we compare our measured desorption pressures with previous results in the literature, as is shown in Fig. 13. For the first reaction (i.e for the higher plateau) our measured desorption pressures are significantly lower than indicated by the extrapolation of the results of both [8] and [5]. Absorption experiments provide further support that the first plateau really is occurring at a lower pressure. The absorption

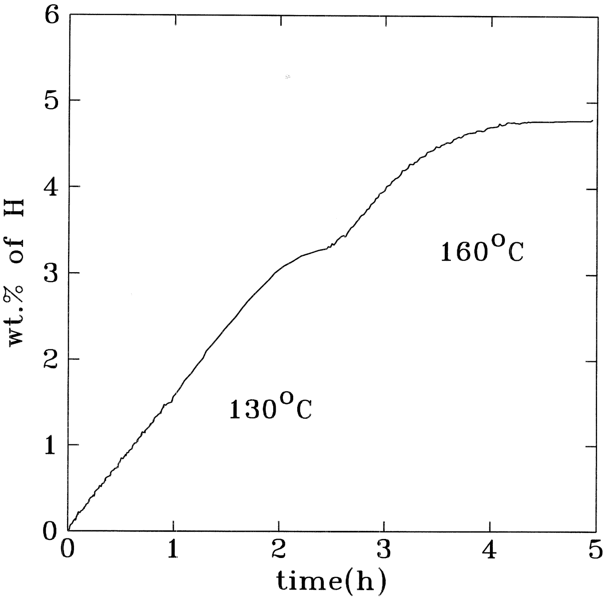

Fig. 11. Two-step decomposition of $NaAlH_4$ at 130 and 160°C.

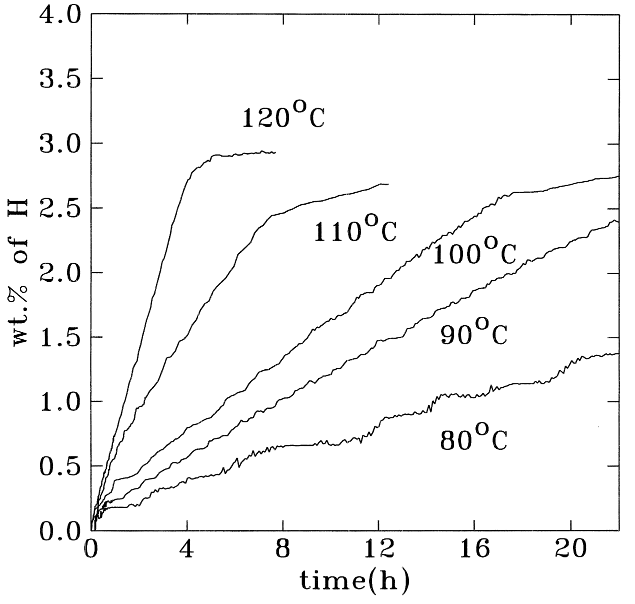

Fig. 10. Hydrogen desorption from $NaAlH_4$, ball milled with 10 wt.% of carbon, at low temperatures.

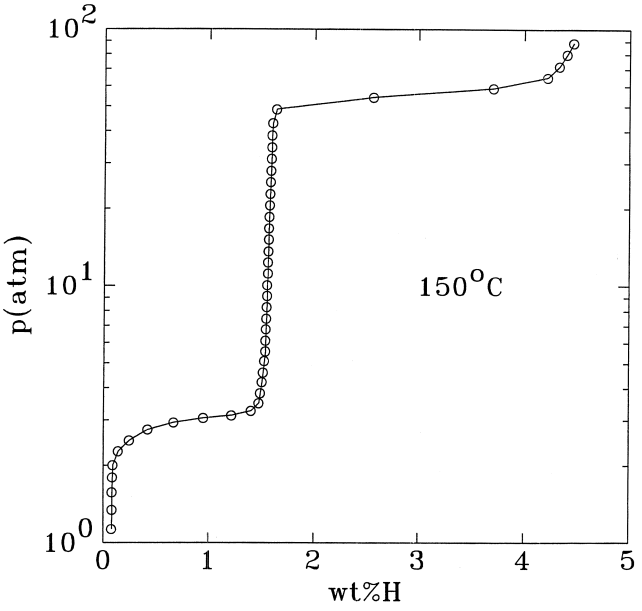

Fig. 12. Pressure–composition isotherm for $NaAlH_4$, taken for hydrogen desorption at 150°C.

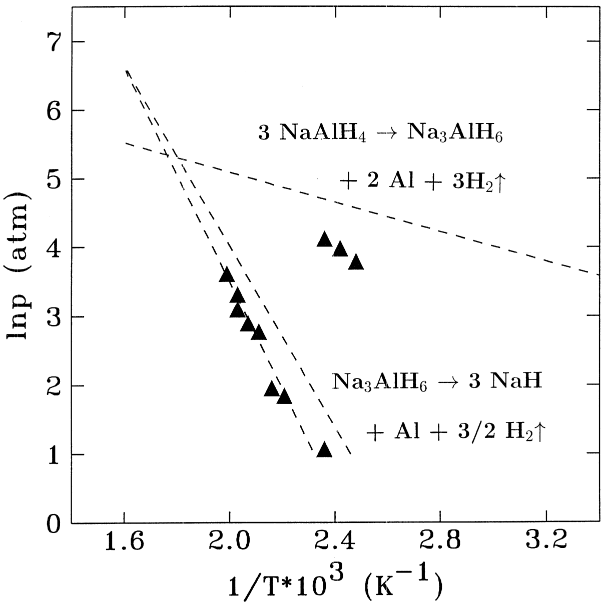

Fig. 13. Van't Hoff plot (temperature dependence of equilibrium pressure for hydrogen desorption) for the decomposition of $NaAlH_4$ ball milled for 2 h with 10 wt.% of carbon. Dashed lines represent literature results as in Fig. 1.

experiments proved a complete rehydrogenation (as shown both by kinetic measurements and by XRD) under the initial pressure of 80–90 atm. at 150°C. One possible explanation of this apparent discrepancy could be that simple linear extrapolation of the data of Refs. [8] and [5] to lower temperatures is in fact not justified and that the thermodynamic behaviour of the Na–Al–H system is more complex (involving the effect of melting). Extrapolation of the present results gives much more usable equilibrium pressures at room temperature for the decomposition of $NaAlH_4$, i.e. several atm. only.

Unfortunately we are not at present able to resolve the question of the role of carbon directly (i.e. by comparing samples milled with and without carbon). At low temperatures the hydrogen absorption in samples without carbon occurs too slowly for the equilibrium pressure to be reliably measured, and at higher temperatures (for example above 180°C), too high pressures are required, for which our system is not best suited. We shall be addressing this problem in more detail in the future.

In Fig. 13, the equilibrium pressures for the second plateau (reflecting the decomposition of Na_3AlH_6) are also lower than the results from Ref. [8], and overlap with the results from Ref. [5]. The discrepancies between the results obtained in [5] and [8] have been already pointed out in [8]. However, there is no indication whether these differences reflect changes in the hydrides, or instrumental differences. In this context, it is worth mentioning that the hydrides of Dymova et al. [5] (and also our materials) were not purified before the hydrogenation experiments and contained aluminum, whereas the hydrides of Bogdanović and Schwickardi [8] were chemically purified and had all the excessive aluminum removed from the samples. It is not clear in what way this could affect the equilibrium pressures. However, if the higher plateau pressure is indeed a result of purification of the alloys, then it could explain the easier decomposition of Na_3AlH_6 at lower temperatures in the purified alloys (as in [8,11]) and also points to an easy way to improve the decomposition of Na_3AlH_6.

4. Conclusions

Sodium alanates have been modified by mechanical grinding without and with an addition — carbon. Milled $NaAlH_4$ or Na_3AlH_6 exhibited great enhancement of the kinetics of absorption and desorption, and the addition of carbon in the milling process improved their performance even more remarkably. Mixtures of $NaAlH_4$ with carbon are capable of reversible dehydrogenation/hydrogenation at much lower pressures and with much faster kinetics than conventional compounds. The kinetics of dehydrogenation/hydrogenation cycling are many times faster even than those seen in catalysed $NaAlH_4$ and Na_3AlH_6 [8,9]. The desorption behaviour is remarkable in that it can be performed even at the relatively low temperature of 80°C. Rehydrogenation can be effected at 75–90 atm. instead of 150 atm., as is reported necessary for the rehydrogenation of catalysed $NaAlH_4$ [8,9,11,12]. Also, hydrogen absorption can be affected at much lower temperatures, even below 100°C. In conclusion, these hydrides show a good potential for hydrogen storage applications, being capable of operation in the temperature range required for PEM fuel cells, and having high hydrogen capacity at low price.

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