Journal of Alloys and Compounds 253–254 (1997) 1–9

# Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials[1]

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## Abstract

New reversible hydrogen storage systems are proposed, based on catalyzed reactions (Eqs. 4–6). The catalytic acceleration of the reactions in both directions is achieved by doping alkali metal aluminium hydrides with a few mol% of selected Ti compounds. The PCI diagrams of the Ti catalyzed systems show an absence of hysteresis and nearly horizontal pressure plateaus. The PCI of the $NaAlH_4$ system reveals two temperature-dependent pressure plateaus, corresponding to the two-step reversible dissociation of $NaAlH_4$. The PCI of the $Na_3AlH_6$ system shows only one pressure plateau; the latter can be lowered by partial substitution of Na by Li. In cyclic tests, reversible $H_2$ capacities of 4.2–3.1 and 2.7–2.1 wt% H have been achieved.

*Keywords:* Reversible hydrogen storage materials; Alkali metal aluminium hydrides; Titanium catalysts; Pressure composition isotherms

## 1. Introduction

One of the major drawbacks of the known reversible metal hydrides applicable for hydrogen storage in comparison to liquid hydrogen is their low gravimetric hydrogen content (expressed in wt% of H in a metal hydride). Magnesium hydride ($MgH_2$, 7.6 wt% H) and hydrides of magnesium alloy (e.g. $Mg_2NiH_4$, 3.8 wt% H) represent in this respect the optimum. However, for their use as storage materials a sufficient amount of heat above ~300°C is necessary for the desorption of hydrogen from the hydride. The disadvantages of the presently known, so-called low- and medium-temperature reversible hydrides [1] are the high costs for intermetallics and alloys applied for the purpose, combined with their 4–5 times lower storage capacities with respect to $MgH_2$ ($LaNi_5H_6$ 1.5, $TiFeH_2$ 1.8 wt% H). As repeatedly emphasized [2,3], the development of low- and/or medium-temperature reversible hydrides having higher then hitherto known storage capacities and lower prices per unit of stored hydrogen, is, therefore, desired. Taking into account their high hydrogen content, complex hydrides of the light metals such as Li, Na and Al have been considered for this purpose [4], although, according to our knowledge, no serious effort has been undertaken in this direction until now.

It has been recognized ever since the early sixties through the work of Ashby [5] and Clasen [6] that sodium aluminium hydride (and other alkali metal aluminium hydrides) can be synthesized directly from sodium hydride (or sodium), aluminium and hydrogen under pressure and in various solvents. The direct synthesis of sodium aluminium hydride from the elements in absence of solvents, in the melt (Eq. (1)), was described by Dymova et al. [7].

$$Na + Al + 2H_2 \xrightarrow[p>175\mathrm{bar}]{T<270-280^\circ\mathrm{C}} NaAlH_4 \tag{1}$$

Sodium aluminium hexahydride, $Na_3AlH_6$, can also be synthesized by a direct process (Eq. (2)) [8], or by heating $NaAlH_4$ with NaH in heptane (Eq. (3)) [9].

$$3Na + Al + 3H_2 \xrightarrow[350\ \mathrm{bar}]{\mathrm{toluene}/165^\circ\mathrm{C}/\mathrm{AlEt}_3} Na_3AlH_6 \tag{2}$$

$$NaAlH_4 + 2NaH \xrightarrow[140\ \mathrm{bar}]{\mathrm{heptane}/160^\circ\mathrm{C}} Na_3AlH_6 \tag{3}$$

It has further been shown that the thermal dissociation of the solid $NaAlH_4$ in NaH, Al and $H_2$ (Eq. (4)) proceeds in two steps: In the first step $NaAlH_4$ dissociates under evolution of hydrogen to $Na_3AlH_6$ and aluminium metal (Eq. (4)a); at higher temperatures $Na_3AlH_6$ decomposes to give NaH, Al and additional hydrogen (Eq. (4)b) [8,10,11]. (The dissociation of NaH in Na and hydrogen occurs at still higher temperatures.) The thermal dissociation of

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[1] Invited paper presented at the International Symposium on Metal–Hydrogen Systems, Les Diablerets, August 25–30, 1996, Switzerland.

0925-8388/97/$17.00
*PII* S0925-8388(96)03049-6

separated $Na_3AlH_6$ takes place in a single-step process (Eq. (5)).

Although the hydrogen dissociation pressures corresponding to thermal dissociation of $NaAlH_4$ (Eq. (4)a, Eq. (4)b) and $Na_3AlH_6$ (Eq. (5)) were experimentally determined by Dymova et al. (see Fig. 2 and [11]), the reverse reactions, i.e. the formation of $NaAlH_4$ or $Na_3AlH_6$ from solid NaH, Al and gaseous hydrogen, have apparently not been experimentally accomplished. As a matter of fact, NaH–Al conglomerates, which upon thermolysis of $NaAlH_4$ or $Na_3AlH_6$ are being obtained in a highly active form, can, under suitable conditions (see below), be hydrogenated with a (partial) restoration of the starting materials [12]. The reactions Eq. (4)a, Eq. (4)b, Eq. (5) can thus be formulated as reversible reactions:

$$NaAlH_4 \overset{(a)}{\rightleftarrows} 1/3Na_3AlH_6 + 2/3Al + H_2\uparrow \overset{(b)}{\rightleftharpoons} NaH + Al + 3/2H_2\uparrow \qquad (4)$$

$$Na_3AlH_6 \rightleftharpoons 3NaH + Al + 3/2H_2\uparrow \qquad (5)$$

In order that the systems discussed here could be utilized for reversible hydrogen storage, the reactions Eq. (4)a, Eq. (4)b, Eq. (5), in both directions, must proceed rapidly under acceptable reaction conditions during many dehydrogenation–rehydrogenation cycles. As it turned out, the reactions given in Eq. (4)a, Eq. (4)b, Eq. (5), as well as the corresponding reaction of $Na_2LiAlH_6$ [13] (Eq. (6)), can effectively be catalyzed by doping the alanates with small amounts of transition metal or rare earth metal compounds, especially with titanium compounds [12]. On the basis of the results achieved, the doped alkali metal alanates can be taken into account as possible candidates for the reversible hydrogen storage. In the present paper we give a preliminary report concerning this work.

$$Na_2LiAlH_6 \rightleftharpoons 2NaH + LiH + Al + 3/2H_2\uparrow \qquad (6)$$

## 2. Experimental details

All reactions and operations with air-sensitive materials (metal hydrides, dopants, doped metal hydrides) were performed under argon using air- and water-free solvents. The elemental analyses were performed by Dornis and Kolbe (Mülheim an der Ruhr, Germany).

### 2.1. Starting materials

The hydrogen was 99.9%, Messer-Grießheim. The $\beta$-$TiCl_3$ was prepared from $TiCl_4$ and $(H_3C)_3SiSi(CH_3)_3$ or $Et_3SiH$ [14]. The $Ti(O\text{-}n\text{-}C_4H_9)_4$ (Aldrich, 99%) was distilled in vacuum before use. The NaH was a commercial product (Fluka).

$NaAlH_4$ (Chemetall) was purified by dissolution in THF, separation from insoluble portions via filtration and precipitation from the solution by addition of ether (according to Clasen [6]) or pentane. Only the purified $NaAlH_4$ was used in all subsequent reactions. The white crystalline $NaAlH_4$ powder obtained after drying under vacuum displays in the IR spectrum (KBr pellet) very broad hydride bands with maxima around 720 and 1670 $cm^{-1}$; absorptions of coordinated THF or ether are not visible in the spectrum (El. analysis, see Table 1).

Ethanolysis/hydrolysis of a sample (0.4 g) of $NaAlH_4$ delivered 99.3% of the calculated amount of $H_2$ (MS analysis). A thermovolumetric analysis [15] of a $NaAlH_4$ sample (~1 g, 4 °C $min^{-1}$, RT→270°C) is reproduced in Fig. 4.

$Na_3AlH_6$ was prepared from $NaAlH_4$ and NaH under $H_2$ pressure in heptane (Eq. (3)) according to [9]. 16.57 g (0.31 mol) of $NaAlH_4$ and 14.87 g (0.62 mol) of NaH were suspended in 120 ml of heptane and the suspension, under intensive stirring, was heated to 162 °C for 72 h under 140 bar of $H_2$. $Na_3AlH_6$ was then separated from the solvent by filtration, washed with pentane and dried in vacuum. $Na_3AlH_6$ (30.90 g) was obtained as a fine,

Table 1
Elemental analyses of undoped and Ti-doped alkali metal aluminium hydrides

| | Elemental composition (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Na | Al | Li | H | C | Ti | Cl |
| $NaAlH_4$ (54.00) | Calc. | 42.75 | 49.96 | – | 7.47 | 0.0 | – | – |
| | Found | 42.71 | 49.46 | – | 7.62 | 0.28 | – | – |
| Ti-doped $NaAlH_4$ (56.99) | Calc. | 40.34 | 47.34 | – | 6.90 | 0.0 | 1.68 | 3.73 |
| ($NaAlH_{3.9}Ti_{0.02}Cl_{0.06}$) | Found | 41.80 | 46.81 | – | 6.95 | 0.28 | 1.46 | 2.79 |
| $Na_3AlH_6$ (102.0) | Calc. | 67.62 | 26.45 | – | 5.93 | 0.0 | – | – |
| | Found | 67.27 | 26.15 | – | 5.84 | 0.88 | – | – |
| Ti-doped $Na_3AlH_6$ (104.98) | Calc. | 65.70 | 25.70 | – | 5.66 | 0.0 | 0.91 | 2.03 |
| ($Na_3AlH_{5.9}Ti_{0.02}Cl_{0.06}$) | Found | 65.92 | 24.75 | – | 5.28 | 0.74 | 1.28 | 1.86 |
| $Na_2LiAlH_6$ (85.95) | Calc. | 53.50 | 31.39 | 8.08 | 7.04 | 0.0 | – | – |
| | Found | 53.98 | 29.87 | 7.88 | 6.50 | 1.56 | – | – |
| Ti-doped $Na_2LiAlH_6$ (88.93) | Calc. | 51.70 | 30.34 | 7.81 | 6.69 | 0.0 | 1.08 | 2.39 |
| ($Na_2LiAlH_{5.9}Ti_{0.02}Cl_{0.06}$) | Found | 51.06 | 30.17 | 7.59 | 5.96 | 1.71 | 1.05 | 2.46 |

slightly grey powder (Table 1) and identified through XRD and IR analyses. In the IR analyses the KBr pellet showed broad absorptions in the regions 500–1000 and around 1350 $cm^{-1}$; absorptions arising from $NaAlH_4$ (~1670 $cm^{-1}$) are lacking in the spectrum.

A thermovolumetric analysis [15] of a sample of $Na_3AlH_6$ (~1 g; 4 °C $min^{-1}$, RT→270°C) gave 96% of the $H_2$ amount calculated according to Eq. (5).

$Na_2LiAlH_6$ was prepared from $NaAlH_4$, LiH and NaH, following the same procedure as given for $Na_3AlH_6$ [9]; it can also be prepared from $LiAlH_4$ and NaH (1:2) in toluene under $H_2$ pressure [13]. 6.79 g (126 mmol) of $NaAlH_4$, 3.04 g (127 mmol) of NaH and 0.97 g (122 mmol) of LiH were reacted in 90 ml of heptane in an autoclave under $H_2$ pressure, and under the same conditions as applied for the preparation of $Na_3AlH_6$. $Na_2LiAlH_6$ (11.08 g) was isolated as a fine, slightly grey powder (Table 1). The IR spectrum of $Na_2LiAlH_6$ was in accordance with that of $Na_3AlH_6$; bands arising from $NaAlH_4$ were not present in the spectrum. A thermovolumetric analysis [15] of a $Na_2LiAlH_6$ sample (~1 g; 4 °C $min^{-1}$, RT→500°C) gave 98% of the amount of $H_2$ calculated according to the equation: $Na_2LiAlH_6 \rightarrow 2\ Na + LiH + Al + 2\frac{1}{2}\ H_2\uparrow$.

## 2.2. Doping procedures

$NaAlH_4$/2 mol% $\beta$-$TiCl_3$/ether: 1.58 g (10.2 mmol) of $\beta$-$TiCl_3$ were added to a stirred suspension of 26.83 g (0.50 mol) $NaAlH_4$ in 150 ml of ether whereby the mixture turned a deep brown colour and evolution of hydrogen began. The evolution of hydrogen was monitored by means of an automatic gas burette [15], connected to the reaction flask. The suspension was stirred until the $H_2$ evolution had ended (~45 min; $H_2$ evolved: 350 ml; 1.43 mol of $H_2$/mol Ti). The ether was evaporated and the residual solid dried under vacuum until a constant weight (28.33 g) was reached (Table 1). The IR spectrum of the Ti-doped $NaAlH_4$ (KBr pellet) was in accordance with that of $NaAlH_4$. $NaAlH_4$/2 mol% $Ti(OBu)_4$/ether: The doping of NaAlH4 (10.96 g, 203 mmol) with 2 mol% of $Ti(OBu)_4$ (1.39 ml) in ether (25 ml) was carried out in the same way as the doping with $\beta$-$TiCl_3$. $H_2$ evolution: 205 ml; 2.1 mol of $H_2$/mol Ti. Ti-doped $NaAlH_4$: 12.40 g.

The doping procedure for $Na_3AlH_6$ (15.99 g, 157 mmol) with 2 mol% of $\beta$-$TiCl_3$ (0.48 g, 3.1 mmol) in ether (30 ml) was the same as that for $NaAlH_4$, described above. $H_2$ evolution: 110 ml; 1.48 mol of $H_2$/mol Ti. Ti-doped $Na_3AlH_6$: 16.46 g (Table 1).

The doping of $Na_3AlH_6$ (9.58 g, 94 mmol) with 2 mol% of $Ti(OBu)_4$ (0.64 ml, 1.9 mmol) in ether (30 ml) was carried out in the same manner as described for the doping of $NaAlH_4$ with $\beta$-$TiCl_3$. $H_2$ evolution: 93 ml; 2.1 mol of $H_2$/mol Ti. The obtained amount of Ti doped $Na_3AlH_6$: 10.13 g.

The doping of $Na_2LiAlH_6$ (5.87 g, 86 mmol) with 2 mol% of $\beta$-$TiCl_3$ (0.22 g, 1.4 mmol) in ether (25 ml) was carried out in the same manner as described for $NaAlH_4$. $H_2$ evolution: 50 ml; 1.49 mol of $H_2$/mol Ti. Ti-doped $Na_2LiAlH_6$: 6.03 g (Table 1).

## 2.3. Determination of pressure-composition isotherms (PCI-s) of Ti-doped alkali metal alanates

The equipment used for the determination of PCI-s, as well as for carrying out the cyclic tests in open systems described below, is schematically represented in Fig. 1. It consisted of a stainless-steel autoclave of 45 ml volume, provided with two thermocouples (for measuring the temperatures inside the hydride sample and within the autoclave) and two valves. The first valve was either connected to a hydrogen pressure cylinder (0.1 l volume) or to a pressure–tension transformer (U/P) for recording the pressure changes within the autoclave. The second valve was joined to a 2 l, automatically registering gas burette [15] which served to measure the hydrogen blow-off from the autoclave each time. The temperatures of the sample and of the autoclave as well as the pressure within the autoclave, or alternatively the level of the burette, were registered by means of a 3-channel recorder. The autoclave was fitted into a heating furnace equipped with a temperature regulator.

A sample (~10 g) of the Ti-doped alkali metal alanate was added to a stainless-steel beaker situated in the autoclave. The valves connecting the autoclave to the burette and to the pressure cylinder were closed and the autoclave then heated and kept at the desired temperature (180 or 211°C) during the entire measurement. When, under isothermal conditions, a constant hydrogen pressure inside the autoclave was attained, a portion of hydrogen (~0.5 l) was blown off the autoclave and measured via the burette. The same procedure was repeated until no more hydrogen evolved from the sample. The autoclave was then successively pressurized with 20–30 bar of hydrogen originating from the pressure cylinder and left standing each time until a constant pressure in the autoclave and a constant temperature of the sample was attained (1/2-6d). The procedure was repeated until no more hydrogen was absorbed by the sample. The respective amount of chemically bound hydrogen in the sample (H/Me) was calculated from the dead volume of the system (32 ml) and the experimentally determined amount of hydrogen present in the system at given pressures and temperatures.

## 2.4. Dehydrogenation–rehydrogenation (cyclic) tests

### 2.4.1. Ti-doped and undoped $NaAlH_4$

Samples (1–2 g) of Ti-doped and undoped $NaAlH_4$ were dehydrogenated under constantly increasing (Fig. 4) or constantly held temperatures (Fig. 5), using the earlier described [15] thermovolumetric apparatus.

Samples (2–3 g) of the above-mentioned materials, dehydrogenated under constantly increasing temperature (Fig. 4), were subjected to rehydrogenation at 170 °C/152 bar (initial $H_2$ pressure). The progression of rehydrogenation in the course of time is shown in Fig. 6.

Cyclic tests with samples of Ti-doped and undoped NaAlH4 (each 2.4 g) were carried out using the equipment represented in Fig. 1. The tests were performed in an open system, i.e. during dehydrogenations, hydrogen was blown off against normal pressure and measured by means of the gas burette and, during hydrogenations, fresh hydrogen was taken from the hydrogen pressure cylinder. Dehydrogenations were implemented by heating the sample to 270 °C at 4 °C $\text{min}^{-1}$, after which the temperature was kept constant until the end of $H_2$ evolution (Fig. 4). Hydrogenations were performed at 170 °C/150 bar (initial $H_2$ pressure; see Fig. 6) over 5 or 21 h. The reversible $H_2$ storage capacities of Fig. 7 are calculated on the basis of the amount of hydrogen liberated during dehydrogenations.

### 2.5. Ti-doped and undoped $Na_3AlH_6$

Cyclic tests of $\beta$-$TiCl_3$ doped and undoped $Na_3AlH_6$ in an open system (Fig. 8) were carried out in a way analogous to that for $NaAlH_4$, except that hydrogenations were performed at 200 °C/60 bar (initial $H_2$ pressure; a pressure drop of 20 bar or less was recorded during hydrogenations).

Dehydrogenations of samples (1.75 g) of $Ti(OBu)_4$ doped and undoped $Na_3AlH_6$ at different, constantly held temperatures using the thermovolumetric apparatus [15] are represented in Fig. 9.

100-cycle test of $Ti(OBu)_4$ doped $Na_3AlH_6$ in a closed system: For the 100-cycle test, the Ti-doped $Na_3AlH_6$ was pressed under argon into ~0.75 g tablets. 10 tablets (7.41 g) were placed into the autoclave depicted in Fig. 1, which was connected to a pressure cylinder of 0.1 l volume via a capillary. The autoclave was alternately heated to 230 °C during a time span of 11/4 h and then kept at 170 °C over a period of 11/4 or 41/2 h to effect dehydrogenations and rehydrogenations, respectively. Variations of the hydrogen pressure and of the temperature of the autoclave were recorded. One section of the chart of the 100-cycle test is reproduced in Fig. 10; the dependence of the reversible hydrogen capacity of the system upon the hydrogenation time and the number of cycles is represented in Fig. 11.

### 2.6. Ti-doped $Na_2LiAlH_6$

A cyclic test with $\beta$-$TiCl_3$ doped $Na_2LiAlH_6$ in an open system (Fig. 12) was performed in the same way as that with $Na_3AlH_6$.

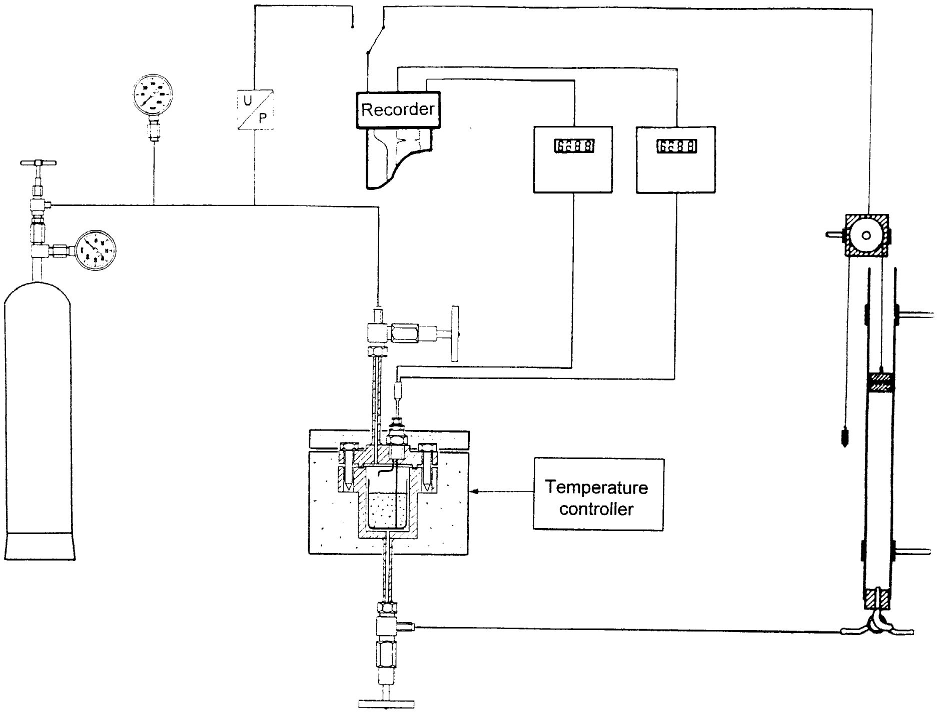

Fig. 1. Schematic representation of the equipment used for the determination of PCIs and for carrying out cyclic tests in an open system.

## 3. Results and discussion

### 3.1. Doping of $NaAlH_4$, $Na_3AlH_6$ and $Na_2LiAlH_6$ with titanium compounds

The doping procedure developed consists of reacting alkali metal alanates in an organic solvent (or in the absence of a solvent) with a small amount of a metal compound used as a dopant. Typically, the doping process was performed with 2 mol% of $\beta$-$TiCl_3$ or $Ti(O\text{-}n\text{-}C_4H_9)_4$ ($Ti(OBu)_4$) in ether or toluene. During the course of the doping reaction, these Ti(+3) and Ti(+4) compounds are apparently reduced to the zerovalent stage, as discernible from the evolution of 1.5 and 2.0 mol of $H_2$/mol Ti, respectively. The nature of the (zerovalent?) Ti-catalyst and its mode of operation are as yet unknown [16].

### 3.2. PCI diagrams of the Ti-doped $NaAlH_4$, $Na_3AlH_6$ and $Na_2LiAlH_6$

For the assessment of reversible metal hydrides as hydrogen storage systems with respect to their attainable hydrogen storage capacity, and conditions under which the hydrogen discharging and recharging are possible from a thermodynamic point of view, the so-called pressure-concentration isotherms (PCI diagrams) are generally used [1,2,4]. The PCI diagram of the undoped $NaAlH_4$ at 210 °C in the desorption mode was previously ascertained by Dymova et al. [11]. Due to the improved dehydrogenation–rehydrogenation rates of the Ti-doped $NaAlH_4$, $Na_3AlH_6$ and $Na_2LiAlH_6$, it was now possible to determine the PCI characteristics of all three systems both under hydrogen desorption and absorption conditions, thus underlining the reversibility of the reactions (Eqs. (4)–(6)) and, in principle, their applicability for reversible hydrogen storage.

The PCI diagram of the Ti-doped $NaAlH_4$ shows at 180 and 211 °C (Fig. 2), clearly discernible, two temperature-dependent pressure plateaus which correspond to the two-step reversible dissociation of the material (Eq. (4)a, Eq. (4)b). The first plateau of the PCI diagram at 211 °C is in good agreement with that determined at 210 °C for the undoped $NaAlH_4$, but the pressure plateau of the second step lies at a significantly higher pressure with respect to that of undoped $NaAlH_4$ [11]. The PCI diagram of the doped $Na_3AlH_6$ at 211 °C (Fig. 3) reveals only one pressure plateau, in accordance with the one-step reversible dissociation of $Na_3AlH_6$ (Eq. (5)). The $NaAlH_4$ system (Eq. (4)) is distinguished from the $Na_3AlH_6$ system (Eq. (5)) by a much higher theoretical hydrogen storage capacity ($3\,H/NaAlH_4 \wedge 5.60$ wt% of H; $3\,H/Na_3AlH_6 \wedge 2.96$ wt% of H). (The reversible hydrogen storage capacities achieved in cyclic tests up to now proved to be dependent upon the reaction conditions and will be discussed in the following section.) On the other hand, the

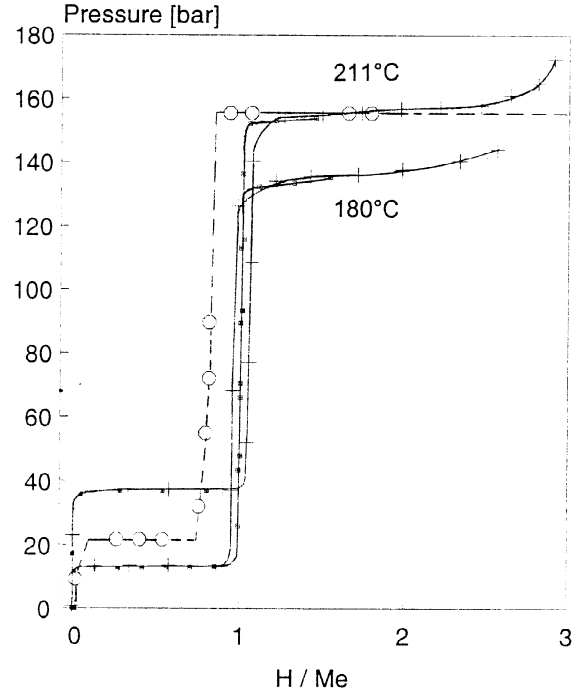

Fig. 2. Pressure-composition isotherms for the Ti-doped $NaAlH_4$ at 180 and 211 °C: ———■———, desorption; ———+———, absorption; ———o——— desorption isotherm of undoped $NaAlH_4$ at 210 °C (reproduced from [11]).

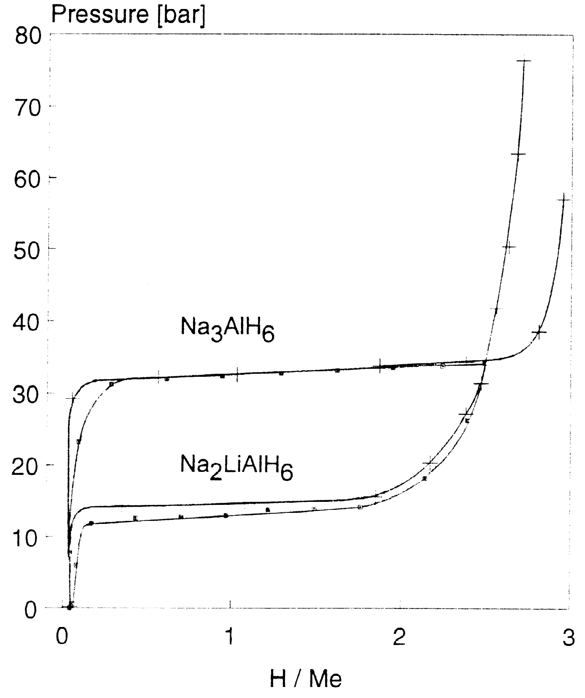

Fig. 3. Pressure-composition isotherms for the Ti-doped $Na_3AlH_6$ and $Na_2LiAlH_6$ at 211°C: ———■———, desorption; ———+———, absorption.

$NaAlH_4$ system is at a disadvantage with respect to the $Na_3AlH_6$ system in that, because of the high dissociation pressure of the first plateau, high hydrogen pressures for the charging of hydrogen (e.g., 130–150 bar at 170 °C) are required. The charging of hydrogen in the $Na_3AlH_6$ system, as can be seen in Fig. 3, can be achieved at much lower hydrogen pressures (e.g., 40–60 bar at 200 °C or lower).

Of particular interest is the PCI diagram of the Ti-doped $Na_2LiAlH_6$ system (Fig. 3). It shows at 211 °C only one distinct pressure plateau, which is about 20 bar lower than that of the $Na_3AlH_6$ system. The existence of a single pressure plateau, different from the plateau of $Na_3AlH_6$, verifies that we are dealing here with a separate and distinct reversible metal hydride system (theoretical capacity amounts to 3.52 wt% H) and not, for example, a mixture of $Na_3AlH_6$ and $Li_3AlH_6$. The PCI diagrams in Fig. 3 suggest that by partial substitution of Na by Li in $Na_3AlH_6$, it should be possible to lower the hydrogen dissociation pressure of the system in a controlled way. Such phenomena are well-known for metal–hydrogen systems, especially for the case of the $MmNi_5H_6$ system [2].

All three PCI diagrams presented here (Figs. 2 and 3) reveal further interesting application-relevant properties of the investigated systems, namely the absence of hysteresis and their almost negligible plateau slope. When the hydrogen dissociation pressures of the two plateaus of the Ti-doped $NaAlH_4$ system, measured at 211 and 180 °C, are extrapolated to lower temperatures by means of the Van't Hoff plots, it can roughly be estimated that the first plateau should have a dissociation pressure of 1 bar below ambient temperature and the second between 100 and 150 °C. According to Buchner's classification [1], the first step of the reversible $NaAlH_4$ dissociation (Eq. (4)a) corresponds to a low-temperature metal hydride system and the second (Eq. (4)b), to a middle temperature system. The Ti-doped $NaAlH_4$ system consists accordingly of a low- and a middle-temperature reversible hydride system, whereas the Ti-doped $Na_3AlH_6$ system can be described as a middle-temperature metal hydride system. According to the present state-of-the-art, those systems can, however, only be operated at temperatures above 140–150°C (see the following section.

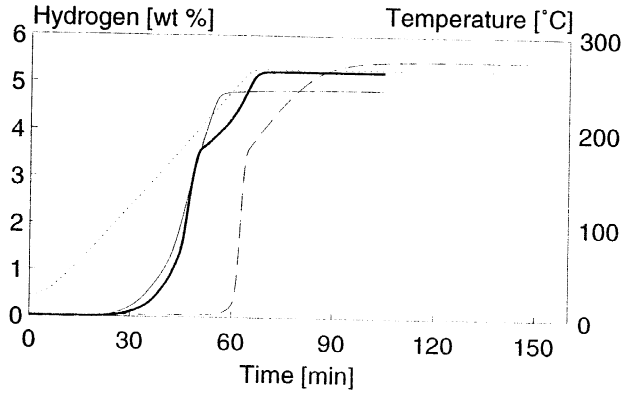

Fig. 4. Thermovolumetric curves for dehydrogenation (4 °C $min^{-1}$, room temperature → 270 °C) of samples of Ti-doped and undoped $NaAlH_4$: - - - - -, undoped $NaAlH_4$; —, doping with 2 mol% of $\beta$-$TiCl_3$ in ether; —, doping with 2 mol% of $Ti(OBu)_4$ in toluene; ·······, temperature of the sample.

### 3.3. Ti-doped and undoped alkali metal alanates in dehydrogenation–rehydrogenation (cyclic) tests

#### 3.3.1. Ti-doped and undoped $NaAlH_4$

The effect of the Ti dopant in catalyzing the thermal dissociation of $NaAlH_4$, generating 1.5 mol of $H_2$/mol of $NaAlH_4$ (Eq. (4)) can be seen in Fig. 4. The thermovolumetric curve [15] of $NaAlH_4$ doped with 2 mol% of $\beta$-$TiCl_3$ in ether (—) or with 2 mol% of $Ti(OBu)_4$ in toluene (—) is shifted to the extent of 80–85 °C to lower temperatures with respect to that of undoped $NaAlH_4$ (- - - -).

The ability of $NaAlH_4$ samples to supply hydrogen at the lowest possible temperatures has been assessed through measuring the rate and extent of dehydrogenation at different constantly held temperatures. As can be seen in Fig. 5, the undoped $NaAlH_4$ sample, at 160 °C, delivers hydrogen at an almost negligible rate and, even at 200 °C, the $H_2$ evolution takes 22–24 h until completion. In contrast, the hydrogen desorption of $NaAlH_4$ doped with 2 mol% of $Ti(OBu)_4$ is completed at 160 °C within 6–8 h and at 180 and 200 °C within 2–3 and 1 h, respectively.

The rehydrogenation of samples of Ti-doped and undoped $NaAlH_4$ dehydrogenated to the NaH + Al stage (Fig. 4) was performed at 170 °C/152 bar (initial $H_2$ pressure). As can be seen in Fig. 6 (cf. also the first cycles in Fig. 7), doping with Ti compounds under these conditions has a dramatic effect on improving the rate and the extent of

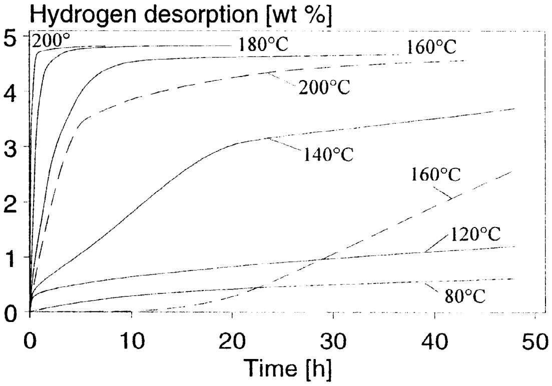

Fig. 5. Progression of hydrogen desorption in the course of time at different temperatures for samples of Ti-doped (2 mol% $Ti(OBu)_4$) and undoped $NaAlH_4$: —, doped $NaAlH_4$; - - - - -, undoped $NaAlH_4$.

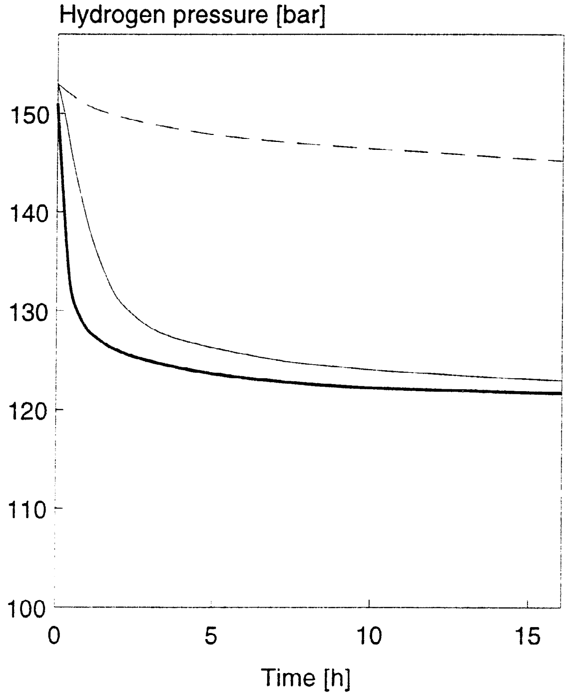

Fig. 6. Progression of rehydrogenation of dehydrogenated (Fig. 4) samples of Ti-doped and undoped $NaAlH_4$ at 170 °C/152 bar: —, $Ti(OBu)_4$ as a dope; —, β-$TiCl_3$ as a dope; - - - - -, undoped $NaAlH_4$.

rehydrogenation. Again, better results (higher initial rate of hydrogenation by a factor of 2–3) are achieved by using $Ti(OBu)_4$ instead of β-$TiCl_3$ as a dopant.

The results of cyclic tests performed with samples of Ti-doped (2 mol% β-$TiCl_3$, 35 cycles) and undoped $NaAlH_4$ (20 cycles) in an open system are graphically represented in Fig. 7. As can be ascertained from the recordings of the corresponding processes, the observed decrease of the hydrogen storage capacity from 4.2 to 3.1 wt% over the course of 35 cycles results from the fall-off in the hydrogenation rate. Further improvements of the applied catalysts are therefore desired.

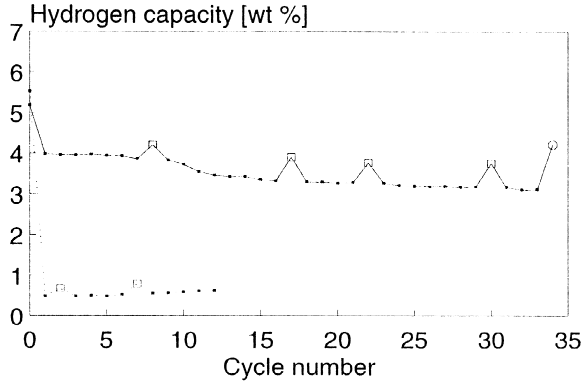

Fig. 7. Cyclic tests for samples of Ti doped (—) and undoped $NaAlH_4$ (·······) in an open system. Dehydrogenation: 4 °C $min^{-1}$, room temperature → 270 °C; Hydrogenation: 170 °C/150 bar (initial $H_2$ pressure)/5 (——■——), 21 (——□——), 100 h (——○——).

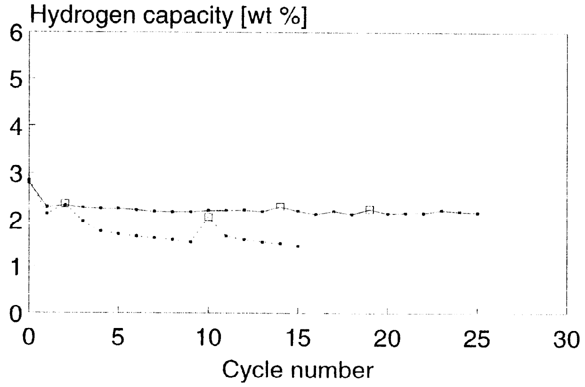

Fig. 8. Cyclic tests for samples of Ti-doped (2 mol% β-$TiCl_3$; —) and undoped $Na_3AlH_6$ (·······) in an open system. Dehydrogenation: 4 °C/min, room temperature → 270 °C; Hydrogenation: 200 °C/60 bar (initial $H_2$ pressure)/$5\frac{1}{2}$ (——■——) or 16 h (——□——).

### 3.3.2. Ti-doped and undoped $Na_3AlH_6$

For comparison with the $NaAlH_4$ system, cyclic tests were also performed with Ti-doped (2 mol% β-$TiCl_3$) and undoped $Na_3AlH_6$. The dependence of the reversible hydrogen storage capacity upon the number of cycles for the first 15–25 cycles in an open system is shown in Fig. 8. Under the conditions applied, the Ti-doped $Na_3AlH_6$ exhibits a higher storage capacity (2.1–2.3 wt% H) and better cyclic stability than the undoped $Na_3AlH_6$.

The dehydrogenations at different temperatures (Fig. 9) and a 100-cycle test (Fig. 10 Fig. 11) were performed with samples of $Na_3AlH_6$ doped with $Ti(OBu)_4$, because in experiments with $NaAlH_4$ (Section 3.3.1) $Ti(OBu)_4$ proved to be a more effective dopant than β-$TiCl_3$. As can be seen in Fig. 9, $Na_3AlH_6$ doped with 2 mol% of $Ti(OBu)_4$ in ether delivers at 160 °C in 4–5 h, and at 180

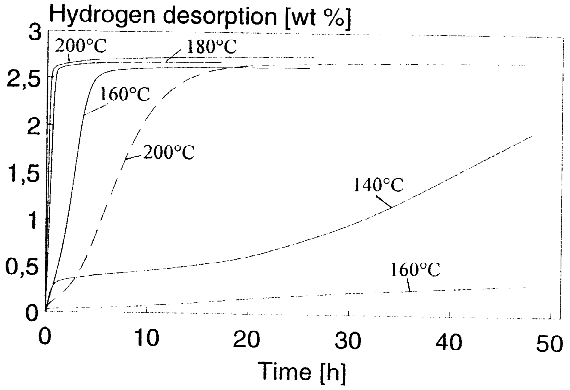

Fig. 9. Progression of hydrogen desorption in the course of time at different temperatures for samples of Ti-doped (2 mol% $Ti(OBu)_4$) and undoped $Na_3AlH_6$: —, doped $Na_3AlH_6$; - - - - -, undoped $Na_3AlH_6$.

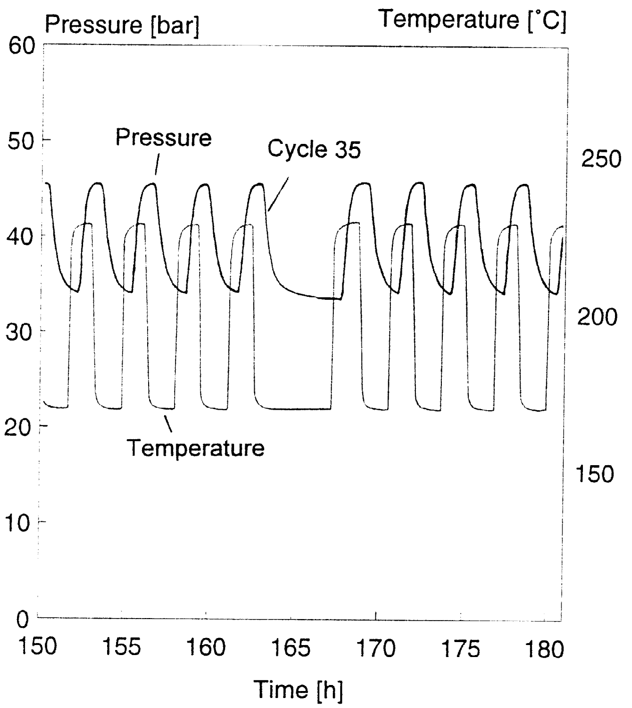

Fig. 10. A section of the chart recording obtained during the 100-cycles test in a closed system with a sample of Ti-doped $Na_3AlH_6$.

and 200 °C in 1 h or less ~2.5 wt% H at a virtually constant rate; Fig. 9 shows also that the dehydrogenation rate is substantially improved in comparison to the undoped $Na_3AlH_6$.

The 100-cycle test (Figs. 10 and 11) was carried out in a closed system, which means under the hydride's own dissociation pressure, whereby the temperature is periodically kept above and below the equilibrium temperature (Fig. 10). During 100 dehydrogenation–rehydrogenation cycles under such conditions only a minor decrease in storage capacity (Fig. 11) is observed.

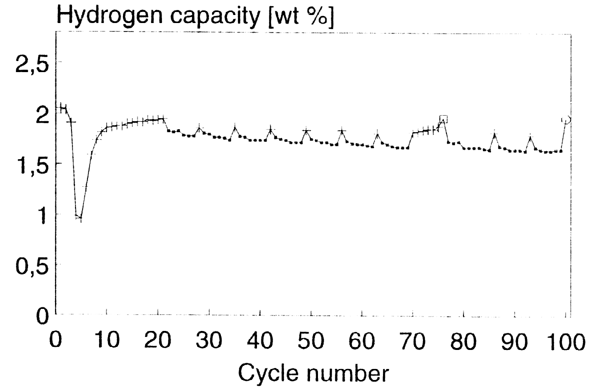

Fig. 11. A 100-cycles test performed with the sample of Ti-doped $Na_3AlH_6$ in a closed system: Dependence of the storage capacity upon the number of cycles. Dehydrogenation: 230 °C/30–42 bar/$1\frac{1}{4}$ h; Hydrogenation: 170 °C/42–30 bar/$1\frac{3}{4}$ (———■———), $4\frac{1}{2}$ (———+———), 12 (———□———), 20 h (———○———).

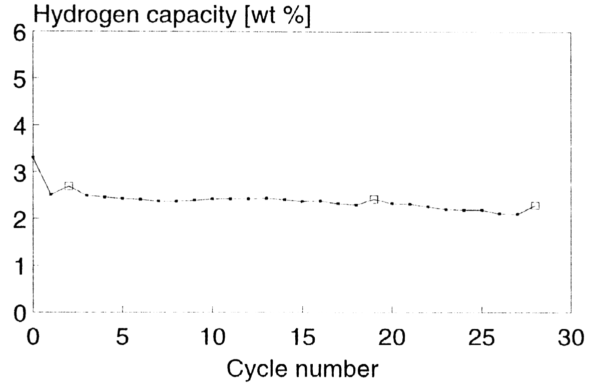

Fig. 12. A cyclic test performed with a sample of Ti-doped (2 mol% $\beta$-$TiCl_3$) $Na_2LiAlH_6$ in an open system. Dehydrogenation: 4 °C $min^{-1}$, room temperature → 270 °C; Hydrogenation: 200 °C/60 bar (initial $H_2$ pressure)/$5\frac{1}{2}$ (———■———) or 16 h (———□———).

### 3.3.3. Ti-doped $Na_2LiAlH_6$

A cyclic test was also carried out with a sample of Ti-doped $Na_2LiAlH_6$ (2 mol% of $\beta$-$TiCl_3$). In a 28-cycle test performed in an open system (Fig. 12) the sample exhibited a comparable cyclic stability and slightly higher storage capacity than the Ti-doped $Na_3AlH_6$ (Fig. 8).

## 4. Conclusion and outlook

The results presented here indicate that reversible low- or middle-temperature metal hydride–hydrogen storage systems based on complex hydrides of the light metals Na, Li and Al are feasible. Their current disadvantages include the still unsatisfactory rates of the Ti-catalyzed dehydrogenation–rehydrogenation—and the resulting necessity of operating at relatively high temperatures (~>150 °C) and hydrogenation pressures (60–150 bar)—and cyclic instability. Further improvements of the systems can be expected by variation of the catalysts and of the hydride compositions.

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[16] Of interest in this connection is a recent work by Buhro et al. describing the synthesis of titanium and nickel aluminides from the metal chlorides and lithium aluminium hydride in refluxing mesitylene and subsequent heating of the precipitates in the solid state at 550 °C: J.A. Haber, J.L. Crane, W.E. Buhro, C.A. Frey, S.M.L. Sastry, J.J. Balbach and M.S. Conradi, *Adv. Mater., 8* (1996) 163.