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Mechanochemical preparation and investigation of properties of magnesium, calcium and lithium–magnesium alanates

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Abstract

Ball milling of MgCl₂ and CaCl₂ with NaAlH₄ or LiAlH₄ can be used for the preparation of magnesium, calcium and lithium–magnesium alanates in mixture with NaCl or LiCl. Using wet chemical separation methods, it was possible to obtain these alanates in nearly pure state. The alanates were characterized by X-ray diffractometry, solid-state ²⁷Al NMR and IR spectroscopy and thermovolumetric (TV) and differential scanning calorimetry (DSC) measurements. Mg(AlH₄)₂ dissociates thermally in one step to MgH₂, Al and hydrogen; at a higher temperature, MgH₂ and Al transform to Mg–Al alloy and hydrogen. Thermal dissociations of Ca(AlH₄)₂ and of LiMg(AlH₄)₃ (in mixture with NaCl or LiCl) proceeds in several steps, of which the first two can be assigned to the formation of CaH₂ and of a MgH₂/LiH mixture, respectively, in addition to Al and H₂. Possible intermediates of these two steps are CaAlH₅ and LiMgAlH₆. Higher temperature dissociations include formation of MgH₂ (LiH) and Ca–Al alloys from CaH₂, CaH₂ and Al, respectively. Upon ball milling of MgCl₂ or CaCl₂ with NaAlH₄ or LiAlH₄ in the presence of Ti catalysts, only the thermal dissociation products of the expected alanates are obtained. This indicates that dehydrogenation discharge of earth alkali metal alanates can be catalyzed by Ti. According to DSC measurements, the thermodynamic stability of Mg(AlH₄)₂ (ΔH = 1.7 kJ/mol) is too low for the purpose of reversible hydrogen storage. Determination of ΔH values for the second, endothermal step of calcium and lithium–magnesium alanate dissociations gave values of around 31.6 and 13.1 kJ/mol, respectively.

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1. Introduction

The reversible dissociation of Ti-doped sodium alanate (NaAlH₄) is presently widely investigated as a potential hydrogen storage system, which offers high capacity at moderate temperatures [1,2]. With respect to this, the question arises, if other than sodium-based alanates or other complex hydrides, e.g. boranates can be applied for hydrogen storage.

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Stimulated by this question, in the last years, considerable research work has been done on preparation and characterization of alkaline earth metal alanates, a group of compounds, which in the past, had attracted little attention. Along these lines, the highest yet known reversible hydrogen storage capacity of more than 8 wt.% was reported by Zaluska et al. [3] by employing lithium beryllium hydrides. A detailed procedure for the preparation of solvent free magnesium alanate has been described by Fichtner and Fuhr [4]. In addition, the compound has been characterized by physical methods such as, thermal and catalyzed hydrogen release [5]. Fichtner et al. [6] have performed a quantum chemical calculation of the Mg(AlH₄)₂ structure on the density functional theory (DFT) level. The calculated pattern was found to be congruent with experimental data. A series of partially as yet unknown Mg,

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Ca and Sr alanates have been obtained by Dymova et al. [7–10] by application of the ball milling method. Novel barium and strontium alanates have been discovered and their structures elucidated by neutron diffraction by Akiba and coworkers [11,12].

In context of our investigations on alkaline earth metal alanates, we report here about the mechanochemical preparation and characterization of magnesium, calcium and lithium–magnesium alanate via X-ray diffraction (XRD), infrared spectroscopy (IR), solid-state nuclear magnetic resonance (NMR) and thermovolumetric (TV) and differential scanning calorimetry (DSC) measurements. On the basis of DSC measurements, an attempt was made to evaluate thermodynamic stabilities of the investigated alanates.

2. Experimental

All operations in the described experiments were performed under argon as a protecting atmosphere, using a glove box or Schlenk techniques.

Starting materials: NaAlH₄ (Chemetall) was recrystallized by addition of pentane to a NaAlH₄ tetrahydrofurane (THF) solution [13]. LiAlH₄ (Aldrich) was purified by dissolving it in diethyl ether, filtering the solution and evaporating the diethyl ether (purity 99% according to TV). Anhydrous MgCl₂, CaCl₂ and TiCl₃ (99%; Aldrich) were used without further purification. A sample of colloidal Ti nanoparticles (Ti^{*}) has been kindly left to us by the group of Prof. Bönnemann [14,15]. Pentane and diethyl ether were dried over K–Na alloy, toluene over sodium aluminum tetraethyl and THF was purified over magnesium anthracene.

Ball milling: Retsch ball mill 200 MM (30 Hz), 25 ml milling vial and two steel milling balls of 6.3 g each; a description of the set-up and measuring of hydrogen evolution during ball milling are described in Ref. [16].

XRD: The X-ray powder patterns for qualitative phase analysis were collected at room temperature on a Stoe STADI P transmission diffractometer in Debye-Scherrer geometry (Cu K α_1 : 1.54060 Å) with a primary monochromator (curved germanium (111)) and a linear position sensitive detector. For the in situ high-temperature experiments, a capillary furnace and a 40° position sensitive detector were attached to the diffractometer. Data were collected in the range between 20 and 90° 2θ with a step width of 0.01° 2θ . For the measurements, the samples were filled into \emptyset 0.5 mm glass capillaries (for the high-temperature measurements, quartz-glass capillaries were used) in a glove box, which were sealed to prevent contact with air. During the in situ experiment, the sample was held under argon. The sample was heated from room temperature to 470 °C in temperature steps of 10 °C. The heating rate was 4 °C/min. The measured patterns were evaluated qualitatively by

comparison with entries from the PDF-2 powder pattern database.

NMR: The solid-state NMR spectra were measured on a Bruker Avance 500 WB instrument using a 4 mm MAS probe. The experimental conditions for ²⁷Al MAS NMR were 1 s recycle delay, 4000 scans, 13 kHz spinning rate and 0.6 μ s $\pi/12$ pulse and those for ²³Na MAS NMR were 10 s recycle delay, 4000 scans, 12 kHz spinning rate and 0.9 μ s $\pi/8$ pulse. The ²⁷Al NMR spectra without MAS were recorded with a spin-echo pulse sequence consisting of two 0.6 s pulses with a spacing of 200 s and an appropriate phase cycling.

IR: A few milligrams of the samples were grinded with dry KBr under Ar and pressed to pellets. Solid-state infrared spectra of the alanates were recorded in the range of $400-4000 \text{ cm}^{-1}$ at ambient conditions in air using a Nicolet Magna-IRTM 750 spectrometer.

DSC: The DSC measurements were done on a METTLER-TOLEDO DSC 27HP instrument, using a fully automated program for evaluation of DSC data. The peak areas of DSC curves are expressed in mJ units. Before measurements, the peak areas were calibrated on the basis of averaged heats of fusion of In, Sn and Bi as standards.

2.1. Magnesium alanate

2.1.1. Mechanochemical preparation of

 $Mg(AlH_4)_2 + 2Na(Li)Cl mixtures (Scheme 1)$

0.567 g (10.5 mmol) of NaAlH₄ or 0.399 g (10.5 mmol) of LiAlH₄ and 0.500 g (5.25 mmol) of MgCl₂ were weighted in the vial of the milling apparatus and the mixture was milled for 3 h.

2.1.2. Isolation of $Mg(AlH_4)_2$ from the mixture with NaCl

Each one of the four batches of NaAlH₄/MgCl₂, 2:1 mixtures was milled for 3 h as described above to yield altogether ~8 g of a Mg(AlH₄)₂ + 2NaCl mixture. Separation of Mg(AlH₄)₂ from NaCl was carried out using the Soxhlet extraction method, described in Ref. [4]. The Mg(AlH₄)₂ + 2NaCl mixture was suspended in 150 ml of Et₂O and extracted for several days using a Soxhlet apparatus, which led to crystallization of the Mg(AlH₄)₂·Et₂O adduct from the solvent. The solvent was evaporated and the solid Mg(AlH₄)₂·Et₂O heated to 40 °C for 3–4 h in vacuum. Upon further heating of the solid to 60 °C for 6 h in high vacuum, no loss of weight was detected (yield ~ 1 g).

2.1.3. Hydrogen evolution during ball milling of $MgCl_2$ with NaAlH₄ in the presence of Ti^* (Scheme 1)

 $0.567 \text{ g} (10.5 \text{ mmol}) \text{ of NaAlH}_4, 0.500 \text{ g} (5.25 \text{ mmol}) \text{ of MgCl}_2 \text{ and } 0.012 \text{ g} (2 \text{ mol}\%) \text{ of Ti}^* \text{ were milled in the Retsch mill equipped with a set-up for recording of hydrogen evolution [16].}$

2.2. Calcium alanate

2.2.1. Mechanochemical preparation of Ca(AlH₄)₂ + 2Na(Li)Cl mixtures (Scheme 2)

Ca(AlH₄)₂ + 2Na(Li)Cl mixtures were prepared in the same way as the corresponding Mg analogs (Section 2.1), starting from 0.486 g (9.0 mmol) of NaAlH₄ or 0.342 g (9.0 mmol) of LiAlH₄ and 0.500 g (4.5 mmol) of CaCl₂.

2.2.2. Wet chemical preparation and isolation of (nearly) pure $Ca(AlH_4)_2$

Following Ref. [17], 1.00 g (9.01 mmol) of CaCl₂ was suspended in 100 ml of THF and stirred for 1 h with a high-speed stirrer. The suspension was then added to a solution of 0.97 g (18.0 mmol) of NaAlH₄ in 200 ml THF and the mixture was stirred for 1 h with a high-speed stirrer. The reaction mixture was filtered. A portion of the clear filtrate was concentrated in vacuum to \sim 75 ml and thereupon, 200 ml of pentane added under stirring, resulting in separation of Ca(AlH₄)₂.4THF as a fine precipitate. The suspension was cooled in dry ice for 1 h and then filtrated at low temperature, the precipitate was washed with pentane and solid-dried for 4 h in vacuum (yield = 1.3 g).

2.3. Lithium–magnesium alanate

2.3.1. Mechanochemical preparation of the LiMg(AlH₄)₃ + 2LiCl mixture (Scheme 3)

The LiMg(AlH₄)₃ + 2LiCl mixture was prepared in the same way as the Mg(AlH₄)₂ + 2LiCl mixture (Section 2.1), starting from 0.611 g (16.0 mmol) of LiAlH₄ and 0.500 g (5.25 mmol) of MgCl₂.

2.3.2. Ti-catalyzed dissociation of the

$LiMg(AlH_4)_3 + 2LiCl mixture (Scheme 3)$

A 3:1 mixture of LiAlH₄, MgCl₂ (1.10 g) and 2 mol% Ti^{*} was milled for 3 h. Upon heating of the product to 150 °C, no hydrogen was evolved.

2.3.3. Separation of $LiMg(AlH_4)_3$ from the mixture with LiCl (following Ref. [18])

2.0 g of the LiMg(AlH₄)₃ + 2LiCl mixture was suspended in 150 ml of diethyl ether and the suspension stirred for 50 min with a high-speed stirrer (~2500 rpm). The precipitate of LiCl formed was separated by filtration and 200 ml of toluene were added to the filtrate. During continuous removal of the solvent by heating on an oil bath at 80 °C, LiMg(AlH₄)₃ began to crystallize from the solution. The suspension was kept for 10–15 min at the same temperature. The plate-like crystals were separated from the mother liquor by filtration, washed with pentane and dried in vacuum (10⁻² mbar) at 70 °C, yielding 0.9 g of LiMg(AlH₄)₃.

3. Results and discussion

3.1. Magnesium alanate

Magnesium alanate ether adducts have been formerly prepared from magnesium halides and lithium or sodium alanates in diethyl ether or THF [19–21]. Fichtner and Fuhr succeeded in isolation of neat Mg(AlH₄)₂ via Soxhlet extraction followed by heating of the etherate to 90 °C in high vacuum [4]. A mechanochemical preparation of magnesium alanate–magnesium chloride mixtures by ball milling (Eq. (1)) has been described by Dymova et al. [10].

$$2MgH_2 + AlCl_3 \xrightarrow{\text{b.m.}} 0.5Mg(AlH_4)_2 + 1.5MgCl_2$$
(1)

We have found that Mg, Ca and Li–Mg alanate–Na(Li)Cl mixtures can be prepared by ball milling of sodium or lithium alanate in conjunction with the corresponding alkaline earth metal chlorides (Schemes 1–3). In the case of the Mg(AlH₄)₂–2NaCl mixture, isolation of the neat Mg(AlH₄)₂ was carried out according to Ref. [4].

The X-ray powder patterns of thus prepared $Mg(AlH_4)_2 + 2NaCl$ or 2LiCl mixtures (Scheme 1) are shown in Fig. 1(a and b). The full width at half maximum









(FWHM) of the reflections in the patterns point to particle sizes of the Mg(AlH₄)₂ phase of 18 ± 2 nm. Furthermore, the presence of a high background between 20 and $30^{\circ} 2\theta$ in the patterns indicates that a part of the material might be present in X-ray amorphous form. Apart from this and apart from the presence of diffraction lines of NaCl or LiCl, both diagrams show reflections, which are in accordance with those of $Mg(AlH_4)_2$ prepared from $MgCl_2$ and $NaAlH_4$ in ether [4,6,22]. Since in both patterns, no diffraction lines belonging to the starting materials and only those of Mg(AlH₄)₂, NaCl and LiCl can be observed, it is reasonable to assume that the ball milling reaction proceeds until completion. The XRD pattern of the Mg(AlH₄)₂ obtained after separation from NaCl (Fig. 1(c)) is in accordance with that from Refs. [4,6,23]. Weak absorption bands in the IR spectra of the compound at 1262 and 2963 cm^{-1} show that small amounts of the ether adduct are (still) present. $Mg(AlH_4)_2 + 2Na(Li)Cl$ mixtures and the neat compound were further characterized by solid-state NMR spectroscopy. All the ²⁷Al NMR spectra show a pronounced doublet with maxima at 169 and -1 ppm, which can be assigned to the ²⁷Al resonance signal of Mg(AlH₄)₂. The ²⁷Al NMR spectrum of Mg(AlH₄)₂ (Fig. 2) shows a line shape characteristic of strong quadrupolar coupling. From the total width of the line (26 kHz), a quadrupole coupling constant of about 10 MHz can be deduced. The ²³Na MAS NMR spectrum of the Mg(AlH₄)₂ + 2NaCl (not shown) exhibits a strong resonance line of NaCl (7.2 ppm) and a very small one of NaAlH₄ at -9.3 ppm.



Fig. 1. X-ray powder patterns of: (a) $Mg(AlH_4)_2 + 2NaCl$; (b) 2LiCl mixtures; (c) $Mg(AlH_4)_2$ after separation from NaCl; the base diffraction lines are those from the Refs. [4,6,22], PDF-data base number 47-980.

The thermal dissociation behavior of $Mg(AlH_4)_2 + 2Na(Li)Cl$ mixtures and of $Mg(AlH_4)_2$ was investigated by in situ high-temperature X-ray diffraction (HTXRD), TV and DSC measurements (Section 3.4). As evident from Fig. 3(a),







Fig. 3. The two-step thermal hydrogen evolution curves of: (a) $Mg(AlH_4)_2 + 2NaCl$ mixture and (b) neat $Mg(AlH_4)_2$ (---) temperature in °C and curve of hydrogen evolution recorded during ball milling of $MgCl_2$ with $NaAlH_4$ (molar ratio 1:2) in the presence of 2 mol.% of Ti^{*} (c).



Fig. 4. X-ray powder patterns collected in situ at different temperatures: (a) $Mg(AlH_4)_2 + 2NaCl$; (b) $MgH_2 + Al + NaCl$; (c) $Al_2Mg_3 + Al + NaCl$.

the thermal dissociation of the Mg(AlH₄)₂ + 2NaCl mixture proceeds in two steps, the first step being completed at 150 and the second at 310 °C. The amounts of hydrogen liberated (in wt.%) in the two steps (Scheme 1) are in good agreement with calculated ones (in brackets). However, thermal dissociation of neat Mg(AlH₄)₂ at 150 °C (Eq. (2), Fig. 3(b)) resulted reproducibly in evolution of only 50–60% of the expected amount of hydrogen. Probably, a part of hydrogen together with Et₂O is lost during heating the compound to 40 °C in vacuum and then to 60 °C in high vacuum.

$$Mg(AlH_4)_2 \xrightarrow[(a)]{50^{\circ}C} MgH_2 + 2Al + 3H_2$$

$$\xrightarrow[(b)]{310^{\circ}C} Mg-Al \text{ alloy} + H_2$$
(2)

The HTXRD of the Mg(AlH₄)₂ + 2NaCl mixture is presented in Fig. 4. For clearness, only the patterns collected at r.t., 150 and 370 °C are shown. Between 120 and 130 °C Mg(AlH₄)₂, decomposes and reflections belonging to MgH₂ and aluminium appear. In the temperature range of about 250 °C, the reflections of MgH₂ decrease successively and new reflections in the range between 34.5 and 38.9° 2 θ appear. The reflections are assigned to an alloy with a composition very similar to Al₂Mg₃ [5]. The alloy is stable up to 450 °C, before it starts to melt. The shift of reflections with temperature to lower diffraction angles is due to the thermal expansion of the material.

An enhanced kinetics of dehydrogenation of $Mg(AlH_4)_2$ promoted by ball milling of the compound with 2 mol% of TiCl₃ has been reported [5]. While the uncatalyzed $Mg(AlH_4)_2 + 2NaCl$ mixture (Scheme 1; Fig. 3(a)) dissociates at 150 °C to MgH₂, Al, NaCl (Fig. 4(b)) and H₂, during ball milling of MgCl₂ with NaAlH₄ in the presence of 2 mol% Ti^{*} [15,16,23] at ambient temperature, hydrogen evolution takes place (Fig. 3(c)), giving the amount of hydrogen expected according to the Scheme 1. The product after milling displays an X-ray diffraction pattern identical with that of the Mg(AlH₄) + 2NaCl mixture after being heated to 150 °C (Fig. 4(b)). This indicates a Ti^{*}-catalyzed dissociation of the in situ formed Mg(AlH₄)₂.

3.2. Calcium alanate

Ca(AlH₄)₂·(THF)_{*x*} has been earlier prepared from CaH₂ and AlBr₃ or AlCl₃ in dimethyl ether/THF or THF [24–27] or from CaCl₂ and NaAlH₄ in THF [17]. As found by Dymova and co-workers [9], solvent free Ca(AlH₄)₂, admixed with CaAlH₅ (see below), is formed upon heating or ball milling of CaH₂/AlCl₃ mixtures (Eq. (3)) [9]:

$$2\text{CaH}_{2} + \text{AlCl}_{3} \xrightarrow{\text{b.m.}}_{\text{or heating}} 0.5\text{Ca}(\text{AlH}_{4})_{2}(+\text{CaAlH}_{5}) + 1.5\text{CaCl}_{2}$$
(3)

For the thermal dissociation of $Ca(AlH_4)_2$, prepared according to Eq. (3), on the basis of hydrogen amounts released upon thermolysis (3:3:2), DTA and XRD, the following sequence of reactions was proposed:

$$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 1.5H_2 \tag{4}$$

$$CaAlH_5 \xrightarrow{260-550^{\circ}C} CaH_2 + Al + 1.5H_2$$
(5)

$$CaH_2 + Al \xrightarrow{600-700} Ca_4Al + H_2$$
(6)

The DTA trace for the ball milled $CaH_2/AlCl_3$ mixtures was found to display well-defined exotherms at 130–140 and 330 °C [9].

In the present work, $Ca(AlH_4)_2$ in mixture with NaCl or LiCl was prepared by ball milling of $CaCl_2$ with NaAlH₄ or LiAlH₄ (Scheme 2). Additionally, following Ref. [17], a nearly pure $Ca(AlH_4)_2$ could be obtained from $CaCl_2$ and NaAlH₄ in THF and subsequent desolvation of the THF adduct at 60 °C in high vacuum (Eq. (7)).

$$CaCl_{2} + 2NaAlH_{4} \xrightarrow{\text{IHF}} Ca(AlH_{4})_{2} \cdot 4THF + 2NaCl$$

$$\stackrel{60^{\circ}C/HV}{\longrightarrow} Ca(AlH_{4})_{2}$$
(7)

A composition of IR spectra of $Ca(AlH_4)_2$ before and after desolvation (Fig. 5(a and b)) shows that complete removal of the complexed THF could not be achieved. The X-ray powder patterns of $Ca(AlH_4)_2$ in mixture with NaCl or LiCl and of the wet chemically prepared one after desolvation (Eq. (6)) are shown in Fig. 6(a–c). The FWHM of the reflections in the patterns assigned to the mechanochemically prepared $Ca(AlH_4)_2$ (Fig. 6(a and b)) indicates small particle sizes. Furthermore, the high background suggests that a large part of the material might be present in X-ray amorphous form. Apart from this, the X-ray diffraction patterns of



Fig. 5. IR spectra of: (a) Ca(AlH₄)₂·4THF and (b) Ca(AlH₄)₂ after removal of THF in high vacuum/60 $^{\circ}$ C, trace shifted by 40% transmission for clarity.

Ca(AlH₄)₂ shown in Fig. 6(c) and of the mixtures Fig. 6(a and b) are showing diffraction lines mainly at 18.8, 25.5, 27.2, 29.9, 31.0 and $32.7^{\circ} 2\theta$, which can tentatively be assigned to Ca(AlH₄)₂. The exact assignment of observed reflections is speculative. The diffraction lines of Ca(AlH₄)₂.4THF Fig. 6(d) differ significantly from those ascribed to solvent-free Ca(AlH₄)₂ Fig. 6(c). The ²⁷Al MAS NMR spectrum of the Ca(AlH₄)₂ + 2LiCl mixture in Fig. 7 shows a relatively narrow line at 104.6 ppm. The intense spinning side bands are mainly caused by the inner satellite transition.

Thermal dissociation of the Ca(AlH₄)₂ + 2NaCl mixtures (Scheme 2), as well as that of neat Ca(AlH₄)₂ (Eq. (8)), was observed via TV upon heating the sample from r.t. to 250 °C at 4 °C/min (Fig. 8(a and b)). As evident from the figure, the dissociation takes place in two steps with approximately equal amounts of hydrogen released in both steps. The total amounts of hydrogen liberated are in good agreement with calculated ones (given in brackets). The expected thermolysis



Fig. 6. X-ray powder patterns of $Ca(AlH_4)_2 + 2Na(Li)Cl$ mixtures (a and b), $Ca(AlH_4)_2$ (after removal of THF) (c) and $Ca(AlH_4)_2 \cdot 4THF$ (d).



Fig. 7. Solid-state ²⁷Al MAS NMR spectrum of Ca(AlH₄)₂.

products, CaH₂ and Al, apart from NaCl, could be identified by the XRD patterns (Fig. 9(a and b)). The two-step dissociation of Ca(AlH₄)₂ is in accordance with the findings of Dymova and co-workers [9] (Eqs. (4) and (5)) and can be assigned to the formation of the CaAlH₅ intermediate (Section 3.4).

On the example of the $CaCl_2 + 2NaAlH_4$ mixture, it could be demonstrated that, apparently, also the dissociation of $Ca(AlH_4)_2$ (of 3.1) can be catalyzed by titanium. As shown in Scheme 2, ball milling of $CaCl_2$, $NaAlH_4$ and 2 mol% of TiCl₃ produced an amount of hydrogen (Fig. 8(c)), approximately equal to that resulting from heating the $Ca(AlH_4)_2 + 2NaCl$ mixture to 250 °C.

$$Ca(AlH_4)_2 \xrightarrow{250^{\circ}C} CaH_2 + 2Al + 3H_2, \quad 5.0(5.5) \text{ wt.}\%$$
 (8)



Fig. 8. Course of thermal dissociations of: (a) $Ca(AlH_4)_2 + 2NaCl$ mixture (0.5 g sample); (b) neat $Ca(AlH_4)_2$ (0.18 g sample); (c) hydrogen evolution recorded during ball milling of a $CaCl_2/2NaAlH_4/2$ mol% TiCl₃ mixture; (---) temperature in °C.



Fig. 9. X-ray powder patterns of thermal dissociation products of: (a) $Ca(AIH_4)_2 + 2NaCl$ and (b) $Ca(AIH_4)_2$.

3.3. Lithium-magnesium alanate

The only source of data on preparation and properties of lithium–magnesium alanate ($LiMg(AlH_4)_3$) goes back to a work of Bulychev et al. [18], who prepared the compound from MgCl₂, LiAlH₄ and NaAlH₄ in ether.

As shown in the following, $LiMg(AlH_4)_3$ in mixture with LiCl can be prepared by ball milling of MgCl₂ with LiAlH₄ in a molar ratio of 1:3 (Scheme 3). Separation of $LiMg(AlH_4)_3$ from the mixture with LiCl was carried out according to the procedure given in Ref. [18].

The X-ray diffraction lines of LiMg(AlH₄)₃ in mixture with LiCl (Fig. 10(a)) and of the neat compound Fig. 10(b) are in agreement with each other and with those from Ref. [18] (or PDF-2 data base no. 34-926). The X-ray patterns (Fig. 10(a and b)) show that after dissolution of the main crystalline component LiCl, the powder pattern of the remaining sample (Fig. 10(b)) shows a very high amorphous background and reflections with very low intensities. This indicates that after dissolution of the salt only a very small amount of crystalline LiMg(AlH₄)₃ is present.



Fig. 10. X-ray powder patterns of: (a) $LiMg(AlH_4)_3 + 2LiCl$ mixture and (b) $LiMg(AlH_4)_3$ after separation from LiCl (thin lines, PDF-2 data base no. 34-926).



Fig. 11. Thermovolumetric course of the thermal dissociation of the $LiMg(AlH_4)_3 + 2LiCl$ mixture; (---) temperature in °C.

Thermolysis of the LiMg(AlH₄)₃ + 2LiCl mixture (Fig. 11) proceeds in two steps, the first step being completed at 100 and the second at 150 °C, the molar ratio of hydrogen released in the two steps being 2:1. According to Fig. 12(a), the thermolysis products of the mixture are MgH₂, Al and LiCl. On the basis of the thermolysis products, we assume that the thermolysis of the LiMg(AlH₄)₃ + 2LiCl mixture proceeds according to Scheme 3, although diffraction lines of the expected product LiH could not be identified in the X-ray powder pattern.

The 2:1 molar ratio of hydrogen released in the twostep dissociation of $LiMg(AlH_4)_3$ (Fig. 11) reminds of the two-step thermal (or catalyzed) dissociation of alkali metal alanates [1,28,29], which takes place according to Eq. (9).

$$3MAlH_4 \rightarrow M_3AlH_6 + 2Al + 3H_2$$

$$\rightarrow 3MH + 3Al + 1.5H_2, \quad M = Li, Na, K$$
(9)

It can therefore be assumed that the two-step thermal dissociation of $LiMg(AlH_4)_3$ proceeds according to Eqs. (10) and



Fig. 12. X-ray powder pattern of the thermal dissociation products of: (a) $LiMg(AlH_4)_3 + 2LiCl mixture and (b) MgCl_2/3 LiAlH_4/2 mol% Ti[*] mixture after ball milling.$

(11), with LiMgAlH $_6$ as an intermediate.

$$\operatorname{LiMg}(\operatorname{AlH}_4)_3 \xrightarrow{100^{\circ}\mathrm{C}} \operatorname{LiMgAlH}_6 + 2\operatorname{Al} + 3\operatorname{H}_2$$
(10)

$$\text{LiMgAlH}_6 + 2\text{Al} \xrightarrow{150^{\circ}\text{C}} \text{MgH}_2 + (\text{LiH}) + 3\text{Al} + 1.5\text{H}_2 \quad (11)$$

Upon ball milling of MgCl₂ with LiAlH₄ (molar ratio 1:3) in the presence of 2 mol% of Ti^{*} (Scheme 3), the X-ray powder pattern of the product (Fig. 12(b)) is in accordance with that of the LiMg(AlH₄)₃ + 2LiCl mixture (Fig. 12(a)) heated to 150 °C (except that the amount of amorphous material is higher than in Fig. 12(a)). This indicates a Ti^{*}-catalyzed dissociation of the in situ formed LiMg(AlH₄)₃ (Scheme 3).

3.4. Determination of dissociation enthalpies of Mg(AlH₄)₂, Ca(AlH₄)₂ and LiMg(AlH₄)₃ by means of DSC

A decisive factor for the application of metal hydrides for the reversible hydrogen storage is the enthalpy change associated with hydrogen release or uptake. A dissociation pressure of a hydride of 1–10 bar at 0–100 °C, suitable for many practical applications, corresponds to an enthalpy change of between 15 and 24 kJ mol_H⁻¹ [2]. DSC measurements were applied as a suitable and quick method for determination of dissociation reaction enthalpies [30].

DSC measurements were carried out on 1-4 mg samples of mechanochemically prepared $Mg(AlH_4)_2 + 2NaCl$ mixtures at heating rates of 2, 5, 10 K/min, which gave identical results with respect to the heat of reaction. A chart of the DSC measurement of the mixture at 5 K/min is shown in Fig. 13(a). The DSC curve shows three endothermal peaks with maxima at 137, 273 and 449 °C, of which the first two peaks on the basis of XRD (Fig. 4), can be assigned to the two-step thermal dissociation of $Mg(AlH_4)_2$ (Scheme 1). The third (sharp) peak is due to the melting of the Mg–Al alloy (Ref. [31]; 453 °C). Evaluation of peak areas of three independent DSC measurement (heating rate 2, 5 and 10 K/min) gave enthalpy values of 1.7 kJ/mol for the first decomposition step (endothermic) and 48.8 kJ/mol for the second step (endothermic), respectively. For the reverse of the second step dissociation, hydrogenation of the Mg₃Al₂ alloy with formation of MgH₂ and Al, an enthalpy value of 63.4 kJ/mol is reported in literature [32,33], which in view of different Mg/Al ratios in both cases is a satisfactory agreement.

The DSC chart of the thermal dissociation of the Ca(AlH₄)₂ + 2NaCl mixture is given in Fig. 13(b). The DSC curve shows that the dissociation proceeds in several steps, of which the first step (127 °C), being weakly exothermic, and the second one (250 °C), an endothermic one, can probably be assigned to dissociation of Ca(AlH₄)₂ according to Eqs. (4) and (5). This assignment is supported by the results of thermovolumetric and XRD measurements (Section 3.2). Higher temperature endothermic peaks, which are also associated with H₂ losses, arise possibly from formation of Ca–Al alloys from CaH₂ and Al. Evaluation of peak areas of the first



Fig. 13. Charts of DSC measurements on: (a) Mg(AlH₄)₂ + 2NaCl; (b) Ca(AlH₄)₂ + 2NaCl; (c) LiMg(AlH₄)₃ + 2LiCl.

two peaks of three independent measurements (heating rates 2, 5 and 10 K/min) gave values of -7.4, -7.4, -7.6 kJ/mol for the first step (exothermic) and 31.1, 31.6 and 32.3 kJ/mol for the second decomposition step (endothermic) (CaAlH₅).

The DSC curve of LiMg(AlH₄)₃ dissociation (Fig. 13(c)) shows, as in the case of Ca(AlH₄)₂, a first exothermic (154 °C) and a second endothermic peak (185 °C), followed by two further endothermic peaks. From the peak areas of two independent measurements (heating rates 5 and 10 K/min), assigned to Eqs. (9) and (10), enthalpy values of 14.9, 15.1 kJ/mol for the first decomposition step (exothermic) and 13.1, 13.0 kJ/mol for the second step (endothermic) are calculated.

4. Summary and conclusion

Ball milling of MgCl₂ and CaCl₂ with NaAlH₄ or LiAlH₄ proved to be a simple and efficient method for the preparation of magnesium, calcium and lithium–magnesium alanates, although in mixture with NaCl or LiCl (Schemes 1–3). Using wet chemical separation methods, it was possible to obtain these alanates in nearly pure state.

The investigated alkaline earth metal alanates were characterized by X-ray diffractometry, solid-state ²⁷Al NMR and IR spectroscopy and thermovolumetric and DSC measurements. The thermal dissociation products of the alanates resulting from TV measurements were identified via X-ray diffractometry. Mg(AlH₄)₂ (in mixture or neat) dissociates at 150–170 °C in one step to MgH₂, Al and hydrogen (Scheme 1 and Eq. (2)); at a higher temperature (310–320 °C), MgH₂ and Al react with hydrogen evolution to give a Mg–Al alloy.

Unlike Mg(AlH₄)₂, the thermal dissociation of Ca(AlH₄)₂ to CaH₂ and Al (Scheme 2 and Eq. (5)) proceeds in two steps, with roughly equal amounts of hydrogen released in each of the steps (Figs. 8(a and b) and 13(b)). This leads, as proposed by Dymova and co-workers [9], to CaAlH₅ (Eqs. (4), (5)) as a possible intermediate.

On the other hand, the two-step dissociation of $LiMg(AlH_4)_3$ to LiH, MgH₂, Al and hydrogen (Scheme 3) takes place presumably via LiMgAlH₆ as an intermediate (Eqs. (10) and (11)), resulting in the observed (Fig. 11) 2:1 ratio of hydrogen liberated in the two consecutive steps.

Of interest is the finding that upon attempted preparation of the three alanates via ball milling of MgCl₂ or CaCl₂ with NaAlH₄ in the presence of Ti catalysts (Ti^{*} or TiCl₃) only the respective thermal dissociation products of alanates (Schemes 1–3) are obtained. Release of hydrogen during ball milling [16] could be experimentally proven (Figs. 3(c) and 8(c)). These results suggest that a Ti-catalyzed dissociation, resp. a Ti-catalyzed hydrogen release of the investigated alanates takes place.

Thermodynamic properties of the alanates in question were assessed by means of DSC measurements. Accordingly, the dissociation of Mg(AlH₄)₂ to MgH₂, Al and hydrogen is accompanied by a heat uptake of (only) \sim 1.7 kJ/mol. The thermodynamic stability of Mg(AlH₄)₂ is thus far below that suitable for the reversible hydrogen storage (15–24 kJ mol_H⁻¹ [2]).

With respect to the dissociation of the first two steps of calcium and lithium-magnesium alanates, in both cases the DSC measurements (Fig. 13(b and c)) proved the first step to be weakly exothermic and the second to be endothermic. Determination of ΔH values for the second, endothermic step of calcium and lithium-magnesium alanate dissociation gave values of ~31.6 and ~13.1 kJ/mol, respectively. Based on the found dissociation enthalpy of 31.6 kJ/mol for the dissociation of CaAlH₅ (Eq. (5)), an attempt was made to calculate the dissociation pressure using van't Hoff isochore (in $p_{\text{H}_2} = -\Delta S/R + \Delta H/RT$ [34]), which corresponds to a dissociation pressure at 20 °C of 8.4 bar (1 bar at -21 °C) and at 60 °C of 40.0 bar. Further work will concentrate on the possible reversible properties of CaAlH₅ for hydrogen storage.

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