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Pressure–composition isotherms and thermodynamic properties of TiF₃-enhanced Na₂LiAlH₆

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Abstract

The mixed alanate Na₂LiAlH₆ was prepared by ball-milling and subsequent heat-treatment under H₂ pressure. After the synthesis, 2 mol% TiF₃ was added by ball-milling. Pressure–composition isotherms were measured for the Ti-enhanced material in the temperature range of 170–250 °C. A van't Hoff plot was constructed using the equilibrium desorption plateau pressures. From this plot, a dissociation enthalpy of 56.4 ± 0.4 kJ/mol H₂ and a corresponding entropy of 137.9 ± 0.7 J/K mol H₂ was found for Na₂LiAlH₆. © 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; Alanates; Ball-milling; Pressure-composition isotherms; Thermodynamic properties

1. Introduction

The reversibility and hydrogen storage properties of NaAlH₄ with Ti-based additives has been thoroughly investigated, e.g. in Refs. [1–9], since the initial report by Bogdanovic and Schwickardi in 1997 [10]. Theoretically, NaAlH₄ can reversibly store 5.6 wt.% H₂ under practical temperature and pressure conditions. The theoretical capacity has proved difficult to obtain experimentally, however a hydrogen storage capacity of 3.5 wt.% has been maintained up to 100 hydrogenation/dehydrogenation cycles for Ti-catalyzed NaAlH₄ (hydrogenation: 150–120 °C, ~115 bar for 12 h; dehydrogenation: 160 °C, against 1 bar for 3 h) [11].

Despite the high theoretical hydrogen storage capacity, NaAlH₄ with its two decomposition steps is at a disadvantage relative to the simpler, one-plateau Na₃AlH₆, even though the latter has a theoretical storage capacity of only 3.0 wt.% H₂. The dissociation of Ti-enhanced NaAlH₄ to Na₃AlH₆ and Al occurs at very high pressures, so that rehydrogenation pressures above 100 bar are needed [1] for this step at an operating temperature of e.g. 170 °C. Rehydrogenation in the Na₃AlH₆ system (with Ti-based additive) can however be

accomplished at much lower hydrogen pressures (absorption plateau pressure <12 bar at 170 °C) [1]. On the other hand, the relatively low plateau pressures of Na₃AlH₆ at low temperatures may represent a problem with regard to potential applications. To use Na₃AlH₆ as a hydrogen storage material, temperatures above 170 °C may be required to obtain a sufficient plateau pressure.

The LiAlH₄ (8.0 wt.%) and Li₃AlH₆ (5.6 wt.%) systems have higher theoretical hydrogen storage capacities than NaAlH₄. While some reports exist regarding the desorption reaction of catalyzed LiAlH₄ and Li₃AlH₆ [12–15], reversibility in these two systems has not yet been realized. The mixed alanate Na₂LiAlH₆ (3.5 wt.% H₂) is however known to be reversible with a Ti-based additive, and has a lower plateau pressure than Na₃AlH₆ [10] and Li₃AlH₆ [16] (both with addition of a Ti species).

Claudy et al. [17] synthesized Na₂LiAlH₆ by reaction of LiAlH₄ with 2 NaH either in toluene or by a solid-state reaction at elevated temperatures and high H₂ pressure. In the absence of a solvent, pressures > 30 kbar and temperatures > 300 °C were needed in order for formation of small amounts of Na₂LiAlH₆ to occur. A cubic unit-cell of 7.405 Å was obtained for Na₂LiAlH₆ from PXD data. Synthesis of Na₂LiAlH₆ without a solvent is facilitated by ball-milling, as demonstrated by Huot et al. [18] who obtained Na₂LiAlH₆

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by ball-milling a mixture of NaH, LiH and NaAlH₄ for 40 h. Brinks et al. [19] later synthesized Na₂LiAlD₆ by ball-milling LiAlD₄ and 2 NaAlD₄, followed by annealing under 30 bar D₂ pressure at 180 °C. Na₂LiAlD₆ was found by combined PXD and PND measurements to have an ordered perovskitetype structure (space group $Fm\bar{3}m$) with unit-cell dimension a = 7.38484(5) Å.

Pressure versus composition isotherm (PCT) measurements of alanates are scarce in literature and focus mainly on the NaAlH₄ system [1,8,10,20–23]. Only two of these reports concern PCT characteristics of Li-substituted Na₃AlH₆. In the study by Bogdanovic and Schwickardi [10], a PCT curve was measured at 211 °C for a Na₂LiAlH₆ material with 2 mol% of a Ti-based additive. In that measurement, the middle of the desorption plateau was found at approximately 13 bar. Zaluski et al. [23] investigated a more Li-rich material, Na_{1.7}Li_{1.3}AlH₆, and found a desorption plateau pressure at 220 °C of approximately 9 bar, confirming the trend that Li-substitution increases the stability of the alanate relative to the parent Na₃AlH₆.

The aim of this study is to synthesize Na_2LiAlH_6 by ballmilling and obtain PCT characteristics and thermodynamic information for this mixed alanate with addition of 2 mol% TiF₃.

2. Experimental

Na₂LiAlH₆ was synthesized by ball-milling (Pulverisette 7) a 2:1 molar mixture of NaAlH₄ (techn. >90%, Sigma Aldrich) and LiH (Sigma Aldrich) for 3 h at a speed of 700 rpm. The milling vial and milling balls were made of stainless steel, and the weight ratio of balls to powder was 20:1. An initial hydrogen pressure of 80 bar was then applied to the milled powder in a constant-volume system and the sample was allowed to equilibrate overnight at 180 °C. The annealed powder was further ball milled with 2 mol% of TiF₃ (Alfa Aesar) for 20 min at 350 rpm. All operations were performed under argon with <1 ppm of O₂ and H₂O.

Powder X-ray diffraction (PXD) data at 295 K was collected at the Swiss-Norwegian beam line (station BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Measurements were performed after addition of TiF₃ to the annealed powder (termed the as-prepared sample) and after cycling in the PCT experiments (termed the cycled sample). The latter had been desorbed stepwise at 250 °C and then reabsorbed in one step at 170 °C under 58 bar of H₂. The samples were contained in rotating 0.5 mm boron–silica–glass capillaries. Data was collected between $2\theta = 6.0^{\circ}$ and 30.0° in steps of $\Delta(2\theta) = 0.003^{\circ}$ or 0.005°. The wavelength was 0.51979 Å, obtained from a channel-cut Si(1 1 1) monochromator.

Rietveld refinements were carried out with the program Fullprof (version 2.50) [24]. The X-ray form factor coefficients were taken from the Fullprof library. Pseudo-Voigt profile parameters were used and background modelling was performed by linear interpolation between manually selected points.

PCT characteristics were measured by an in-house built, fully automated Sieverts instrument that can be operated up to 100 bar and 600 °C. The pressure in the reference volume is monitored by a MKS120 pressure transducer (accuracy 0.08% of reading, supplier's calibration) below 28 bar and by a Presens sensor (accuracy ± 4 mbar up to 200 bar, calibration against a dead-weight tester) based on silicon piezoresistivity above 28 bar. The volume containing the MKS120 sensor is closed above its usable pressure range, thereby reducing the system volume from 50 to 33 ml. The sample is kept in an autoclave and the sample temperature can be kept constant within ± 0.2 °C. Apart from a volume of 4 ml heated to the sample temperature, the remaining volume is kept at 40.00 °C in two heating cabinets with temperature stabilities of ± 0.02 and ± 0.05 °C. The stability criterion during the PCT measurements was set at a pressure change with time of 8 (at 170, 200, 230 and 250 °C) or 15 mbar/h (at 210 °C), corresponding to a change in the hydrogen content per formula unit of Na₂LiAlH₆ (H/f.u.) of 0.007 and 0.013 per hour, respectively. The H₂ compressibilities of Hemmes et al. [25] were used.

3. Results and discussion

PXD confirmed formation of Na_2LiAlH_6 and Al in the as-prepared sample, corresponding to the expected reaction:

$$2 \operatorname{NaAlH}_4 + \operatorname{LiH} \rightarrow \operatorname{Na}_2 \operatorname{LiAlH}_6 + \operatorname{Al} + (3/2) \operatorname{H}_2$$
(R1)

In addition, 0.7 mol% of Na₃AlH₆ was observed. In the cycled sample, the Na₃AlH₆ phase had completely disappeared. No evidence of Ti- or F-containing phases could be found prior to cycling. The measured unit-cell parameter of Na₂LiAlH₆, a = 7.40654(15) Å agrees well with the 7.405 Å measured by Claudy et al. [17] and is, as expected, larger than that found for Na₂LiAlD₆ (a = 7.38484 Å) [19]. The fit from the Rietveld refinement of the as-prepared sample is shown in Fig. 1.

Assuming that Ti^{3+} from the TiF_3 additive is reduced to zerovalent by reaction with Na_2LiAlH_6 during the ball-milling, some reversible storage capacity is lost. This capacity loss can occur in several ways, depending on whether formation of LiF is preferred over formation of NaF, as would be thermodynamically favorable in a simpler system, or not. Assuming no solid solubility between Na_2LiAlH_6 and Na_3AlH_6 , the reactions with minimum and maximum decomposition of Na_2LiAlH_6 can be represented, respectively, as



Fig. 1. PXD pattern for Na_2LiAlH_6 at 295 K showing observed (circles), calculated (upper line) and difference (bottom line) plots. The positions of the Bragg reflections are shown for Al (upper), Na_2LiAlH_6 (middle) and Na_3AlH_6 (lower).

and

 $Na_2LiAlH_6 + 0.02 TiF_3$

$$\rightarrow 0.94 \text{ Na}_2 \text{LiAlH}_6 + 0.04 \text{ Na}_3 \text{AlH}_6 + 0.06 \text{ LiF} + 0.02 \text{ Al} + 0.02 \text{ Ti} + 0.06 \text{ H}_2$$
(R3)

Crystalline NaF or LiF were not detected by PXD in the asprepared or cycled samples. Any Bragg reflections from LiF, however, would overlap strongly with the reflections from Al due to similar crystal structures and unit-cell parameters, and presence of LiF can thus not be excluded. The presence of Na₃AlH₆ in the as-prepared sample could suggest that (R3) occurs during the reaction with TiF₃, however the disappearance of Na₃AlH₆ after cycling is counterindicative. Furthermore, Na₃AlD₆ was also observed upon preparation of Na₂LiAlD₆ without additives [19]. As the presence of NaF in an X-ray amorphous state cannot be ruled out, (R2) is thus considered to be more likely than (R3). The assumption of constant composition Na2LiAlH6 is however an oversimplification. Taking into account that the Na:Li ratio in the mixed alanate has been observed to be variable [17,23], a variation on (R3) is also possible, wherein Li is leached from the alanate to form LiF and thus shifting the alanate composition according to

$$\begin{split} \text{Na}_2 \text{LiAlH}_6 + 0.02 \text{ TiF}_3 \\ & \rightarrow \ 0.98 \, \text{Na}_{2.04} \text{Li}_{0.96} \text{AlH}_6 + 0.06 \, \text{LiF} \, + \, 0.02 \text{Al} \\ & + \, 0.02 \, \text{Ti} \, + \, 0.06 \, \text{H}_2 \end{split} \tag{R4}$$

Further studies are needed to unequivocally determine the reaction path for reduction of the TiF_3 additive. In the following, all calculations are performed assuming additive-induced decomposition of Na₂LiAlH₆ according to (R2).

Pressure–composition isotherms of Na_2LiAlH_6 with 2 mol% TiF₃ additive are shown in Fig. 2. The PCT diagrams



Fig. 2. Pressure–composition isotherms for Na_2LiAlH_6 with addition of 2 mol% TiF₃. The term H/f.u. equals the number of hydrogen atoms per formula unit of Na_2LiAlH_6 . Filled and open symbols represent absorption and desorption measurements, respectively.

show only one plateau, in accordance with the reversible reaction:

$$Na_2LiAlH_6 \leftrightarrow 2NaH + LiH + Al + (3/2)H_2$$
 (R5)

Upon drawing the PCT curves, completion of (R5) is assumed in the desorption measurements, i.e. H/f.u. = 3 at the end of the desorption and start of the absorption measurements. Furthermore, H/f.u. corresponding to the amount of Na₂LiAlH₆ remaining after reaction with TiF₃ (R2) is given.

The PCT curves were measured in the following order: 210, 200, 170, 230 °C (full desorption and absorption cycle) and finally 250 °C (desorption only). The desorption plateau pressures, defined at the center of the plateau, were determined to be (in order of increasing temperature) 2.95, 9.35, 12.75, 22.15 and 36.95 bar. The plateau pressure at 210 °C is in excellent agreement with the ~13 bar found by Bog-danovic and Schwickardi [10] at 211 °C.

The plateau in the absorption isotherms is not as well defined as in the desorption measurements. The onset of the plateau was abrupt, and in some cases an overpressure of more than 1 bar was needed in order to nucleate the Na₂LiAlH₆ phase. On the high-pressure side, the end of the plateau was more gradual, extending over a relatively wide pressure–composition region. The difference between the absorption and desorption plateau was 2.8, 3.4, 7.8 and 4.0 bar at 170, 200, 210 and 230 °C, respectively.

At 200 °C, the measured width of the plateau corresponds to 2.8 wt.% H₂. This is slightly lower than the theoretical capacity (3.5 wt.%), even after correction for reaction with the TiF₃ additive during ball-milling. The reason why the hydrogen storage capacity is lower than the theoretical value is not clear. The width of the plateau in the desorption isotherms appears to increase with increasing temperature. The largest increase in width occurs between 210 and 230 °C. This apparent increase in capacity with temperature may be a result of repeated cycling rather than originating from the material properties of Na₂LiAlH₆.

The PCT curves below the plateau appear, both in absorption and desorption mode, to be nearly vertical, whereas in the high-pressure section of the isotherms, particularly above 200 °C, the slope is lower. The change of slope in the isotherm above the plateau pressure from ≤ 200 to > 200 °C is likely to originate from intrinsic material properties. The plateau pressure of Na₃AlH₆ (and Li₃AlH₆) is higher than for Na₂LiAlH₆ and neither Na nor Li hexa-alanates should therefore be formed in these PCT measurements. Even the final reabsorption at 170 °C and 58 bar, which is much above the plateau pressure of Na₃AlH₆ [1], does not result in formation of Na₃AlH₆. The initial Na₃AlH₆ impurity could therefore only affect the isotherm at 210 °C, as this was measured first. However, the impurity phase should be fully desorbed prior to the start of the measurement series (the sample was allowed to equilibrate at 27 bar and 210 °C), since the plateau pressure of Ti-enhanced Na₃AlH₆ is higher than 30 bar at this temperature [10].

The equilibrium desorption pressures, taken from the middle of the plateau, are shown as a van't Hoff plot in Fig. 3. The thermodynamic properties for the desorption of Na₂LiAlH₆ (R5) are extracted using the van't Hoff equation. A dissociation enthalpy of 60.7 ± 0.9 kJ/mol H₂ and a corresponding entropy of 146.5 ± 1.9 J/K mol H₂ is found for Na₂LiAlH₆ using data for all five measured temperatures. However, a better fit to the data is found by excluding the data point measured at 170 °C, which lies significantly below a linear fit to the four points measured at 200-250 °C. This gives a dissociation enthalpy of 56.4 ± 0.4 kJ/mol H₂ and a corresponding entropy of 137.9 ± 0.7 J/K mol H₂. The dissociation enthalpy is lower than the 62.8 kJ/mol measured by Claudy et al. [17] by DSC, but is slightly more positive than the 47 kJ/mol H₂ reported for Na₃AlH₆ [1], in accordance with the higher stability of Na₂LiAlH₆ relative to Na₃AlH₆.



Fig. 3. van't Hoff plot showing equilibrium desorption pressures as a function of temperature for 2 mol% TiF₃-catalyzed Na₂LiAlH₆.



Fig. 4. Time required to cross the desorption plateau of Na_2LiAlH_6 as a function of temperature.

It is also worth mentioning that measurements of pressure-composition isotherms at near equilibrium conditions are much more time-consuming than cycling with a large chemical driving force. As an example, almost complete rehydrogenation of Na₂LiAlH₆ could be achieved within 1–2 h when a large overpressure was used, whereas typically 40 h would be required to reach equilibrium for each point at the plateau when measuring the PCT curve. The time needed to cross the Na₂LiAlH₆ desorption plateau, defined as the total time spent waiting for the equilibrium criterion to be fulfilled, is given as a function of sample temperature in Fig. 4. The figure clearly shows that reduction of the temperature leads to a significant increase in the required measurement time. Only a small amount of time is gained by increasing the temperature from 230 to 250 °C. The measurement at 210 °C was carried out with a less restrictive equilibrium condition (15 mbar/h instead of 8 mbar/h), hence the point for this temperature lies significantly below the trend from the other measurements. These results show that even with the strict equilibrium criterion of 8 mbar/h (0.007 H/f.u. per hour), the low curvature of P(t) at the plateau leads to underestimation of the plateau pressures. Note also that even with addition of a Ti catalyst, total measurement times for a complete desorption-absorption measurement can reach 3 weeks or more at low temperatures, whereas approximately 2 weeks are needed at higher temperatures.

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