



Dehydrogenation properties of the $\text{LiNH}_2\text{BH}_3/\text{MgH}_2$ and $\text{LiNH}_2\text{BH}_3/\text{LiBH}_4$ bi-component hydride systems for hydrogen storage applications

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Abstract

Lithium amidoborane (LiAB) is known as an efficient hydrogen storage material. The dehydrogenation reaction of LiAB was studied employing temperature-programmed desorption methods at varying temperature and H_2 pressure. As the dehydrogenation products are in amorphous form, the XRD technique is not useful for their identification. The two-step decomposition temperatures (74 and 118 °C) were found to hardly change in the 1–80 bar pressure range. This is related either to kinetic effects or to thermal dependence of the reaction enthalpy. Further, the possible joint decomposition of LiNH_2BH_3 with LiBH_4 or MgH_2 was investigated. Indeed LiBH_4 proved to destabilize LiAB, producing a 10 °C decrease of the first-step decomposition temperature, whereas no significant effect was observed by the addition of MgH_2 . The $5\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ assemblage shows improved hydrogen storage properties with respect to pure lithium amidoborane.

Keywords Lithium amidoborane · Hydrogen storage · Destabilization · Lithium borohydride · Magnesium hydride

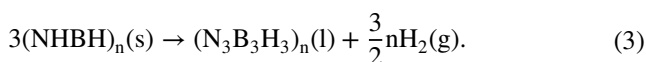
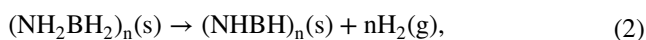
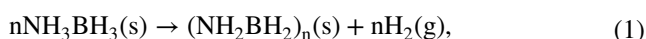
Introduction

Energy is one of the most significant factors which is discussed in the economic literature. Today, all economic and industrial activities are strongly affected by energy consumption and use efficiency. Energy production from fossil fuels is one of the important causes of greenhouse gas emissions and climate change. Further, due to the limited resources of oil, coal, and natural gas, alternative solutions should be envisaged to support more sustainable demands. In other words, shortage of fossil fuel reserves and the negative effects of greenhouse gas emission on the climate indicate the necessity of increasing the contribution of renewable and sustainable sources to energy consumption. In this scenario, hydrogen is known to be an energy carrier with a

great potential interest [1, 2], and the step of its storage in the industrial cycle has a crucial importance.

Various types of solid materials have shown the capability for hydrogen storage in a specific working condition [3, 4]. High pressure and low temperature is required to store hydrogen in metal–organic frameworks (MOF) [5, 6], while other types of materials such as metal hydrides or complex hydrides [7–12], and in some cases a mixture of these compounds [13–15], can be applied as storage materials at ambient conditions.

Ammonia borane NH_3BH_3 , synthesized first in 1955 [16], is a solid compound at room temperature with 19.6 wt% (H) hydrogen capacity. The endothermic dehydrogenation reaction of this compound occurs in three steps [17]:



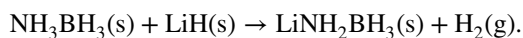
Reaction (1) takes place in the temperature range 70–112 °C, while the reactions (2) and (3) occur between 110 and 200 °C. The borazine produced during reaction (3) can be harmful for the fuel cell catalysts. A number

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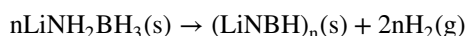
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of investigations have focused on the dehydrogenation properties of NH_3BH_3 [18–23]. In previous studies, one protonic hydrogen of ammonia borane was substituted by alkali or alkaline-earth elements to achieve a chemically modified compound with acceptable hydrogenation/dehydrogenation behaviour [24–26]. Xiong et al. [24] synthesized lithium amidoborane, LiNH_2BH_3 (LiAB), during a direct reaction of LiH with NH_3BH_3 during the ball milling process, reporting the following reaction:



LiNH_2BH_3 was reported to release hydrogen at around 92 °C without any trace of borazine or other byproducts, while the dehydrogenation temperature of NH_3BH_3 is about 108–154 °C along with a small release of borazine. In addition, LiNH_2BH_3 is quite stable as a solid powder in air at ambient pressure and temperature.

The gravimetric capacity of this compound is 10.9%, which can be yielded within 1 h according to the reaction:



Consequently, this compound was emphasized as one of the promising storage material for hydrogen in the annual progress report of DOE hydrogen program in 2008 [26]. To apply this material as an energy carrier for vehicular applications, the kinetics of hydrogen release, the reversibility, and the temperature of dehydrogenation reaction have to be optimized. The first report on the destabilization of hydrides was given by Reilly and Wiswall [27]. The basic idea was to let the hydride react with some appropriate compound so as to lower the dehydrogenation enthalpy and consequently, the reaction temperature. This required that the formed mixed dehydrogenated product was much more stable than the simple product of the original reaction [28].

The present study was first undertaken to investigate the thermodynamic or kinetic barriers in the dehydrogenation reaction of LiNH_2BH_3 by monitoring the effect of H_2 pressure in dynamic conditions. The second aim of this research was to detect possible destabilization effects of additive hydrides such as MgH_2 and LiBH_4 on lithium amidoborane, to further lower its dehydrogenation temperature. These additives were selected because (a) they are themselves well-known and characterized for hydrogen storage properties, with large H_2 capacity and satisfactory kinetic performance, and (b) they have already proved to work as destabilizers with each other [29] and with other systems [28, 30].

Experimental methods and synthesis of materials

Lithium hydride and NH_3BH_3 were employed in the synthesis of LiNH_2BH_3 [31]. Commercial LiH and amidoborane in 1:1 molar ratio were loaded into a stainless-steel vial containing 1 cm diameter balls, with ball-to-powder weight ratio equal to 30. The milling was performed in an argon atmosphere at 400 rounds min^{-1} for 24 h by a Retsch planetary mill apparatus. X-ray diffraction (Bruker D8 Advance X-ray powder diffractometer) with Cu $\text{K}\alpha$ radiation was employed to analyze the produced powder; owing to air sensitivity, this was kept in a special sample holder under argon atmosphere during measurements. It was found that a mostly pure orthorhombic α phase of lithium amidoborane [31] had been obtained, with a trace of post-decomposed product of $\text{LiNH}_2\text{BH}_3 \cdot \text{NH}_3\text{BH}_3$ (Fig. 1a).

On mixing commercial LiBH_4 or MgH_2 (Sigma-Aldrich) with the synthesized LiNH_2BH_3 powder, and grinding them in an agate mortar, the $\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ and $\text{LiBH}_4 + \text{MgH}_2$ composites were prepared. Every handling step was performed in a glove box filled with recirculated argon atmosphere.

A Sievert-type equipment (Advanced Materials Corporation) was employed to measure the progress of decomposition reaction vs. temperature and hydrogen pressure in dynamic conditions. 0.6 g of the selected sample was loaded in a small stainless-steel crucible connected to the pressure manifold and inserted in a furnace. At room temperature, after three proper washing cycles, hydrogen gas (99.9995%) was introduced into the sample holder to reach the desired

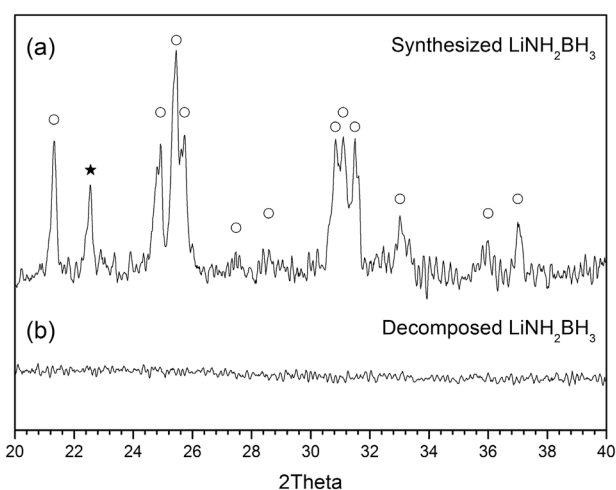


Fig. 1 X-ray diffraction patterns of: **a** as-synthesized LiNH_2BH_3 , with marked peaks (open circle) for α - LiNH_2BH_3 and (filled asterisk) for the post-decomposed product of $\text{LiNH}_2\text{BH}_3 \cdot \text{NH}_3\text{BH}_3$ [31]; **b** amorphous final decomposition product of LiNH_2BH_3

pressure. The dehydrogenation experiments were performed by increasing the sample temperature from 25 to 180 °C with 1 °C min⁻¹ rate at constant pressure; different pressure values were selected in the 1–80 bar (at room temperature) range. During temperature-programmed desorption (TPD) dynamic runs, the amount of released hydrogen is determined from the pressure change in the sample container.

Results and discussion

Dehydrogenation of pure LiNH₂BH₃

Four TPD measurements were performed on LiAB in the Sievert's apparatus, under 1, 10, 20, and 80 bar of hydrogen pressure. The results are shown in Fig. 2.

Each curve shows two inflexion points, suggesting that two different reactions (A, B) occur during decomposition. The first step is quite sharp, and it is responsible for about 40% of the total hydrogen release; at step B, instead, the curve is much less steep and the process covers a wide thermal range. The corresponding *T* values have been obtained from minima in the derivative curve of TPD data, and they are reported in Table 1. Considering the accuracy of the built-in pressure transducer and thermocouple, the position of the furnace heating zone in each sample loading experiment and the human error in the homogeneity of sample preparation a certain level of temperature tolerance is expected. As a result, the dependency of reaction temperature and the applied pressure is not statistically significant, except perhaps a slight tendency to increase with *p* for the A case.

The X-ray diffraction pattern of decomposed LiAB (Fig. 1b) shows that the products are fully amorphous, so it

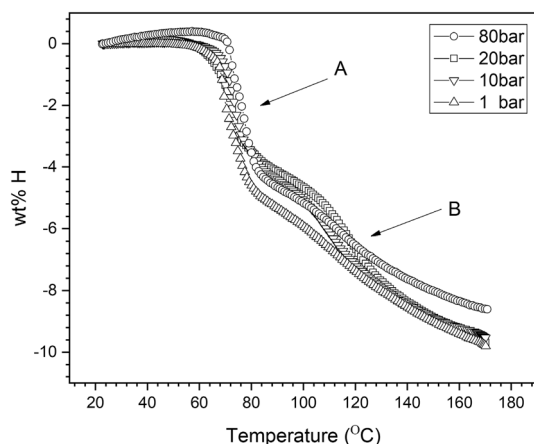


Fig. 2 Dynamic thermal decomposition of LiNH₂BH₃ at different hydrogen pressures (heating rate 1 °C min⁻¹ in Sievert apparatus). The A and B steps of dehydrogenation are emphasized

Table 1 Temperatures of inflexion points of TPD curves of LiNH₂BH₃ at different pressures (Fig. 2)

Pressure (bar)	Reaction temperatures (°C)	
	A	B
1	74	118
10	74	110
20	74	117
80	76	113

is not possible to define the dehydrogenation reaction by this technique. This observation is in agreement with the results given by Wu et al. [26].

Xiong et al. [24] reported a reaction enthalpy $\Delta_r H$ of -3 to -5 kJ mol⁻¹ (H₂) (measured by DSC method in Ar flow at room pressure) for the slightly exothermic A process. Therefore, in conditions of ideal thermodynamic equilibrium, an increase of pressure should lead to a decrease of decomposition temperature, according to the van't Hoff equation:

$$\ln \frac{p}{p_0} = -\frac{\Delta_r H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (4)$$

where $p_0 = 1$ bar, $T_0 = T(1 \text{ bar})$, and the reaction enthalpy is referred to T_0 .

On using the $\Delta_r H = -5$ kJ mol⁻¹ literature value, one would obtain the decomposition temperatures reported in Table 2. These contrast sharply with the experimental result that the dehydrogenation temperature is practically insensitive to a pressure increase (Table 1). A similar difference between theoretical and actual temperature was also observed in the case of NH₃BH₃ by Baitalov et al. [32]. Such phenomena are usually explained by assuming that, close to room temperature and in dynamic conditions such as those of the TPD experiment, the reaction may be controlled by kinetic rather than ideal thermodynamic barriers, so as to make predictions based on the van't Hoff equation wrong. However, in addition to these arguments, purely thermodynamic reasons can also account for the failure of formula (4), when the reaction enthalpy is very small in absolute value. Let us recall that Eq. (4) relies upon the zeroth order approximation that reaction enthalpy and entropy are independent

Table 2 Expected decomposition temperatures of LiAB calculated by the van't Hoff equation on the basis of $\Delta_r H = -5$ kJ mol⁻¹ [24]

<i>p</i> (H ₂) (bar)	A reaction temperature (°C)	
1	74	Fixed
10	-124	Calculated
20	-146	
80	-175	

of temperature; on upgrading instead to first-order dependence, an additional term should be introduced according to:

$$\ln \frac{p}{p_0} = -\frac{\Delta_r H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{\Delta_r C_p (T - T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (5)$$

where $\Delta_r C_p$ is the heat capacity change of reaction at T_0 . Now, for significant values of $|\Delta_r H|$ (of the order of tens of kJ mol^{-1}), the second term in the sum is usually negligible with respect to the first one, and the van't Hoff equation in form (4) is quite adequate for all purposes. If, on the other hand, $|\Delta_r H|$ amounts to only few kJ mol^{-1} , then the second term becomes important and on neglecting it, large errors can be introduced in the calculation of the decomposition temperature T as a function of p . We believe that this applies to the present case.

Combined reaction of LiAB with MgH_2 and LiBH_4

The results of TPD measurements on the $\text{LiAB} + \text{MgH}_2$ and $\text{LiAB} + \text{LiBH}_4$ composites are shown and compared with those of LiAB in Fig. 3, and the corresponding temperatures of the first-observed dehydrogenation process (A) are listed in Table 3.

The presence of MgH_2 appears to hardly affect the LiAB decomposition process, as the $\text{LiAB} + \text{MgH}_2$ curve is almost overlapped with that of pure LiAB . On the other hand, significant changes ensue with the addition of LiBH_4 to LiAB . First, the decomposition temperature for the A process decreases by about 10°C . Second, a much larger release of hydrogen follows quickly, reaching full dehydrogenation at 100°C well below the temperature observed for pure LiAB . Just after the A reaction, a weak shoulder appears, followed by a sharp inflexion point at about 70°C ; this might

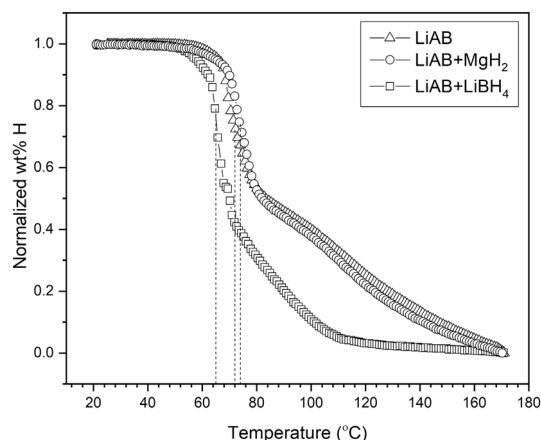
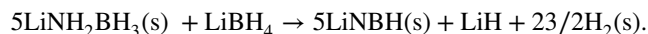


Fig. 3 Dynamic thermal decomposition of $\text{LiNH}_2\text{BH}_3 + \text{MgH}_2$ (open circle), $\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ (open square), and pure LiNH_2BH_3 (open triangle) under 1 bar hydrogen pressure (heating rate 1°C min^{-1} in Sievert apparatus)

correspond to the B process at a much lower temperature, or it could be a different reaction. Curves are normalized in Fig. 3 for better comparison; indeed, the absolute hydrogen loss of 7.2 wt% (H) for the $\text{LiAB} + \text{LiBH}_4$ composite (Table 4) shows that slightly more than 2H_2 molecules are released as for pure LiAB , so that it could be questioned whether LiBH_4 is really involved in the reaction (cf. its decomposition temperature of 300°C at 1 bar in pure form). However, the substantial decrease of reaction temperature (from 74 to 64°C), indicating an enthalpy reduction, supports clearly the joint decomposition of the two hydrides. This can only be made consistent with the small hydrogen loss of 7.2% on assuming a different reaction stoichiometry.

To investigate this hypothesis, TPD runs were done on samples with different compositions, keeping all other conditions identical. The result for $5\text{LiAB} + \text{LiBH}_4$ is plotted in Fig. 4, together with the curves of $\text{LiAB} + \text{LiBH}_4$ and of pure LiAB for comparison. A very similar or even slightly lower A reaction temperature is observed, with respect to the $\text{LiAB} + \text{LiBH}_4$ case, but the ensuing part of the curve resembles more that of pure LiAB . However, the total amount of released hydrogen is larger than expected in that instance (Table 4). We observe an excess of about 3 H atoms with reference to the 20 expected (4 H per LiAB formula unit), which fits with the assumption that LiBH_4 is jointly decomposed together with 5LiAB according to the following reaction scheme:



This result suggests that joint dehydrogenation of LiBH_4 with LiAB is actually observed only in ratios less than 1:1, whereas for larger amounts of LiBH_4 a fraction of lithium borohydride does not react and then the hydrogen yield is less than expected.

Table 3 The first dehydrogenation temperature (A process) of the three different LiNH_2BH_3 composites (TPD with heating rate 1°C min^{-1} under 1 bar H_2 pressure)

First dehydrogenation temperature ($^\circ\text{C}$)	Composition
74	LiAB
72	$\text{LiAB} + \text{MgH}_2$
64	$\text{LiAB} + \text{LiBH}_4$

Table 4 Amount of hydrogen release from different compositions of the $\text{LiNH}_2\text{BH}_3/\text{LiBH}_4$ assemblage

Composition	Experimental wt% (H)
LiAB	9.8
$\text{LiAB} + \text{LiBH}_4$	7.2
$5\text{LiAB} + \text{LiBH}_4$	10.9

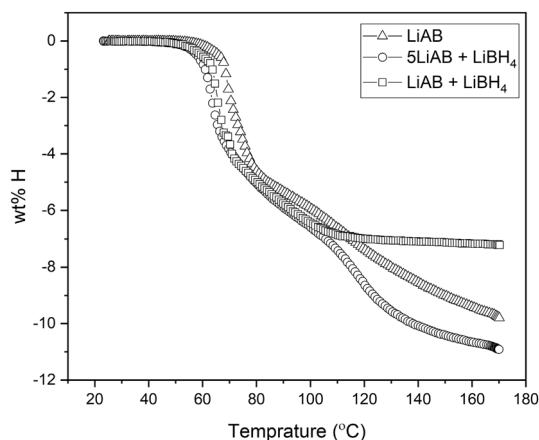


Fig. 4 Dynamic thermal decomposition of $5\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ (open circle), $\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ (open square) and pure LiNH_2BH_3 (open triangle) under 1 bar hydrogen pressure (heating rate $1\text{ }^\circ\text{C min}^{-1}$ in Sievert apparatus)

Conclusions

The dehydrogenation reaction of lithium amidoborane was shown to be scarcely affected by increasing the $p(\text{H}_2)$ pressure up to 80 bar. This contrasts with the expected decrease of the reaction temperature, according to the small negative reaction enthalpy reported in the literature. However, it was shown that the predictions supported by the simple van't Hoff equations may not be reliable in case the reaction enthalpy is small in absolute value, as neglecting the temperature dependence of the reaction enthalpy may not be justified in this case.

On investigating the decomposition of $\text{LiAB} + \text{MgH}_2$ and $\text{LiAB} + \text{LiBH}_4$ composites, it was found that the first additive has no effect on the LiAB properties. On the other hand, the second one lowers significantly the reaction temperature from 74 to 64 $^\circ\text{C}$, so as to support a real joint decomposition of the two hydrides by decreasing the dehydrogenation enthalpy. While pure LiNH_2BH_3 releases approximately 9.8 wt% (H) upon heating to 180 $^\circ\text{C}$, $\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ and $5\text{LiNH}_2\text{BH}_3 + \text{LiBH}_4$ yield about 7.2 and 10.9 wt% (H) under the same conditions, respectively. Thus, LiBH_4 is proved to react with LiAB in the 1:5 rather than 1:1 stoichiometric ratio, according to the suggested reaction $5\text{LiNH}_2\text{BH}_3(\text{s}) + \text{LiBH}_4 \rightarrow 5\text{LiNBH}(\text{s}) + \text{LiH} + 23/2\text{H}_2(\text{g})$. The $5\text{LiAB} + \text{LiBH}_4$ composite is therefore a promising material for hydrogen storage applications.

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