

Short communication

Investigation on chemical reaction between LiAlH_4 and LiNH_2

Zhitao Xiong, Guotao Wu, Jianjiang Hu, Ping Chen*

Physics Department, National University of Singapore, 10 Kent Ridge Crescent, Singapore 117542, Singapore

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Abstract

Although the transformation of the tetrahedral $[\text{AlH}_4]^-$ to the octahedral $[\text{AlH}_6]^{3-}$ occurs at high temperature, it was realized by ball milling (BM) of LiAlH_4 at ambient temperature in the presence of LiNH_2 . Instead of a catalytical role, we found that LiNH_2 may react with LiAlH_4 to form an intermediate with a 1:1 stoichiometry. Our results show that a total amount of about 8 wt% H_2 can be detached from the mixture of LiAlH_4 – LiNH_2 which is potential for an effective hydrogen storage system. Calculations combined with DSC measurements result in a very low enthalpy effect of the H_2 release reaction, further implying a possible reversibility in hydrogen storage.

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1. Introduction

The demand for high efficient hydrogen storage system for the hydrogen fuel cell vehicles motivates intensive research activities [1–4]. In the past 3 years, considerable efforts have been given to metal–N–H compounds [5–12], which cover from binary nitrides and imides to ternary complexes. Lithium imide (Li_2NH) could reversibly take up 7.0 wt% of hydrogen [5]. However, temperatures for hydrogen desorption at 1.0 bar equilibrium pressure are above 250 °C. Continuous efforts in optimizing Li_2NH lead to the attempts of changing chemical composition to alter the thermodynamic parameters [6–9]. Ternary systems, such as Li–Mg–N–H and Li–Ca–N–H, have been developed successfully via reacting lithium amide with hydrides of Mg and Ca, respectively [6]. Importantly, these newly developed ternary compounds possess distinct properties in the hydrogen absorption and desorption compared with that of Li_2NH . $\text{Li}_2\text{MgN}_2\text{H}_2$, as an example, could reversibly store more than 5.5 wt% of hydrogen at 180 °C with the equilibrium desorption pressure higher than 20 bar [6,7]. More recently, efforts have been given to Mg–Na–N–H and Li–B–N–H systems, both of them are formed by reacting amides and hydrides of corresponding metals or metalloids [10,11], evidencing the universality of the amides–hydrides interaction. It was suggested that one of the chemical driving forces lying behind of such an

interaction could probably be the high potential of combining $\text{H}^{\delta+}$ in amides and $\text{H}^{\delta-}$ in ionic (or partially ionic) hydrides into H_2 molecule [12]. Theoretically, a variety of metal–N–H compounds or complexes can be synthesized following the same scheme, which could also lead to the generation of new hydrogen storage materials. In this paper, interaction between LiAlH_4 and LiNH_2 is investigated. A chemical reaction, which leads to ~8 wt% of hydrogen desorption, was identified.

2. Experimental

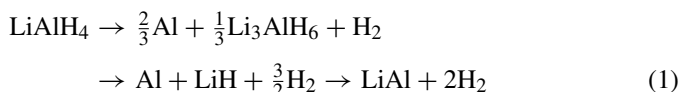
The ball milling (BM) was conducted in a planetary mill at 200 rpm with ball to sample weight ratio of 30/1. The home-made mill vessels were equipped with two gas valves. After certain period of ball milling, one of the valves was open and connected to a pressure gauge to measure the pressure inside the mill vessel. Thereafter, the gaseous products were analyzed by mass spectrometer. Details of temperature-programmed-desorption (TPD) system can be found elsewhere [5]. Approximately 100 mg of sample was used each time. Temperature was increased from room temperature to about 500 °C at 2 °C min^{-1} . The volumetric soak and release measurements with ~500 mg sample were performed in a Gas Reactor Controller provided by Advanced Materials Co. The hydrogen absorption and desorption values have been re-calculated by taking account of purities of the starting materials (95% for LiNH_2 and 95% for LiAlH_4). All the sample loadings were conducted in a MBRAUN glove box. A Bruker D8-advance X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation and equipped with an in situ cell was used to iden-

* Corresponding author. Tel.: +65 68742982; fax: +65 67776126.
E-mail address: phychenp@nus.edu.sg (P. Chen).

tify structural/compositional changes. The vibrations of N–H bond in the post-milled and post-TPD samples were monitored by a Perkin-Elementer FTIR-3000. Thermodynamic measurements were conducted in a DSC 204HP provided by Netzsch.

3. Results and discussion

LiAlH₄ has been explored for hydrogen storage over the past few years [13–16]. Four H atoms can be detached from one LiAlH₄ molecule via a three-step reaction, i.e.



As can be seen in the temperature-programmed-desorption curve (Fig. 1a), three peaks assignable to the stepped H₂ desorption are observed at 149, 195 and 402 °C, respectively. Although the overall enthalpy of the first step is a mild endothermic process [13], relatively higher temperature is needed by LiAlH₄ to overcome the kinetic barrier in the transformation from tetrahedral [AlH₄][−] to octahedral [AlH₆]^{3−}. Such a kinetic barrier is hard to be removed by ball milling [14]. Our experimental result also shows that, even if LiAlH₄ has been milled at 200 rpm for 36 h, negligible hydrogen can be detected in the ball milling vessel (Table 1). However, by mixing LiAlH₄ and LiNH₂ with hydride-to-amide molar ratio of 1/1, hydrogen gas was accumulated gradually in the milling vessel with the milling time. As can be seen in Table 1, ~10 psi hydrogen was released after 0.5 h milling, which is equivalent to ~0.26 H atom per LiNH₂–LiAlH₄ (i.e. one LiNH₂ molecule plus one LiAlH₄ molecule). 0.44, 1.2, 1.9, 3.0 and 3.8 H atoms were released after 1, 2, 3, 5 and 10 h of ball milling, respectively.

XRD characterization shows that after 1 h ball milling, the solid residue consists of LiAlH₄, Li₃AlH₆, LiNH₂ and Al (Fig. 4a). After 3 h ball milling LiAlH₄ disappeared and Li₃AlH₆, Al and LiNH₂ phases persisted (Fig. 4b). Taking into account of the previously released 1.9 H atoms, one could deduce that the decomposition of LiAlH₄ to Li₃AlH₆ has been carried out within the 3 h ball milling. It further evidences that the kinetic barrier in the solid-state transformation of tetrahedral [AlH₄][−] to octahedral [AlH₆]^{3−} is largely reduced by the presence of LiNH₂. However, unlike the Ti-doped LiAlH₄ system [15,16], LiNH₂ may not simply work as catalyst. We reduced the LiNH₂/LiAlH₄ molar ratio from 1/1 to 1/10 and repeated the

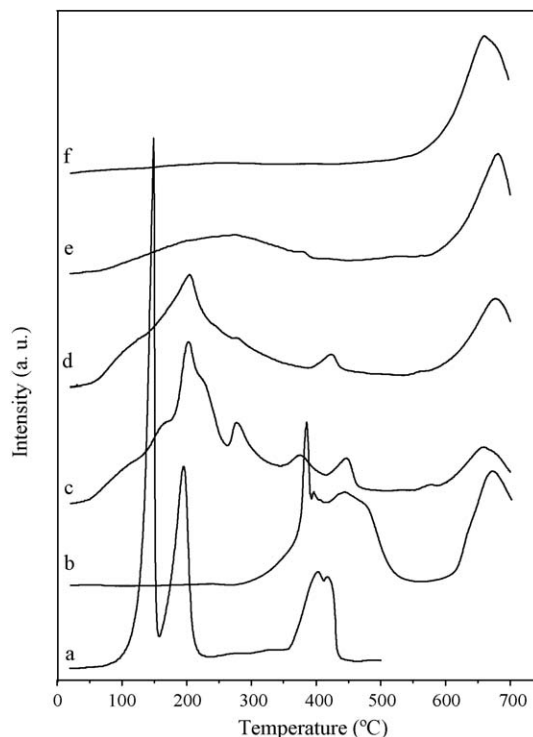


Fig. 1. Temperature-programmed-desorption of: (a) LiAlH₄; (b) LiNH₂; (c) post-3 h-milled LiAlH₄–LiNH₂ sample; (d) post-5 h-milled sample; (e) post-10 h-milled sample; (f) Li₂NH–Al sample after 10 h ball milling.

ball milling treatment. Only 13 psi of H₂ was released after 10 h of ball milling (Table 1). A stoichiometric interaction between LiNH₂ and LiAlH₄ may exist, which reduces the stabilization effect of Li⁺ on [AlH₄][−], and consequently, facilitates the transformation of [AlH₄][−] to [AlH₆]^{3−}. The following up TPD measurement showed the largely depressed characteristic peak of decomposing LiAlH₄ to Li₃AlH₆ (Fig. 1c). The main H signal peaked at around 200 °C is broadened and incorporates with multi-side peaks. No ammonia can be detected in the whole testing process. Also, a weak exothermic behavior in the temperature range of 50–170 °C and two weak endothermic peaks at 210 and 240 °C were observed by DSC, respectively (Fig. 2c). Clearly, LiNH₂ is involved in the subsequent decomposition of Li₃AlH₆, and therefore, changes the chemical nature. ~2.9 H atoms were released from the mixture as temperature reaches 400 °C (Fig. 3a). Thus, the total number of H atoms detached

Table 1
Summary of number of hydrogen atoms detached from LiAlH₄–LiNH₂ mixture during ball milling and TPD

Sample	BM time (h)	H ₂ pressure (psi)	No. H-BM ^a	No. H-TPD ^a	Total no. H
LiAlH ₄ –LiNH ₂ (1/1)	0.5	10	0.26	–	–
	1	17	0.44	–	–
	2	46	1.2	–	–
	3	73	1.9	2.9	4.8
	5	117	3.0	2.0	5.0
	10	146	3.8	1.1	4.9
LiAlH ₄ –LiNH ₂ (1/10)	10	13	0.35	–	–
LiAlH ₄	36	6	–	4	4

^a Number of hydrogen atoms detached from one LiAlH₄ plus one LiNH₂.

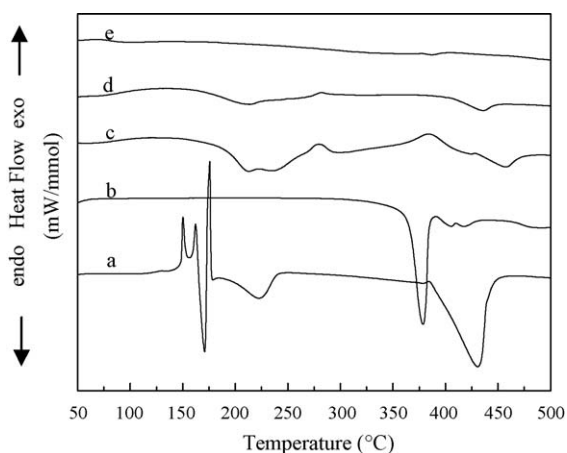


Fig. 2. Differential scanning calorimeter measurement of: (a) LiAlH_4 ; (b) LiNH_2 ; (c) post-3 h-milled LiAlH_4 - LiNH_2 sample; (d) post-5 h-milled sample; (e) post-10 h-milled sample.

from the LiAlH_4 - LiNH_2 (1/1) mixture approaches five, which is greater than the 4 H atoms that can be released from pure LiAlH_4 .

More hydrogen was released from the LiNH_2 - LiAlH_4 (1/1) mixture when milling time was extended. After 5 and 10 h ball milling ~ 3 and 3.8 H atoms were released, respectively. Noted that the last step in the decomposition of LiAlH_4 , i.e. $\text{LiH} + \text{Al} \rightarrow \text{LiAl} + \text{H}$, is highly endothermic that could not be carried out under the mild milling condition, a kind of reaction among Li_3AlH_6 , LiNH_2 and perhaps Al should take place during the ball milling, which is supported by the sequential drop in the H_2 desorption intensity at ~ 200 and 420°C . Additional 2.0 and 1.1 H atoms were released from the post-5 h and 10 h-milled samples when temperature reached 400°C (Fig. 3), which make up ~ 5 H atoms detached per LiAlH_4 - LiNH_2 mixture (Table 1). Attenuated Li_3AlH_6 and LiNH_2 phases in the post-milled samples were observed by XRD (Fig. 4c and d). However, Al phase was also weakened monotonically with the milling time. No distinct new structure can be detected. In addition, uprising in the

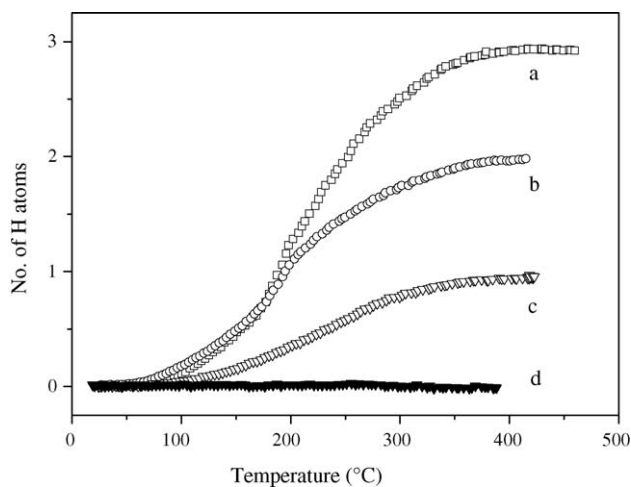


Fig. 3. Volumetric release of: (a) post-3 h-milled LiAlH_4 - LiNH_2 sample; (b) post-5 h-milled sample; (c) post-10 h-milled sample; (d) volumetric soak on post-TPD LiAlH_4 - LiNH_2 sample.

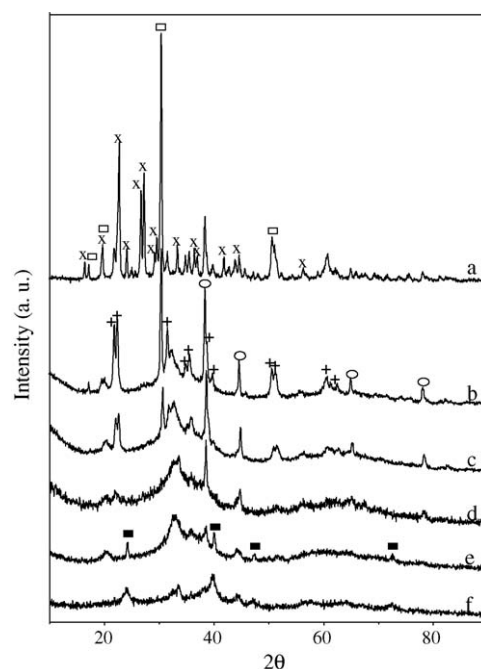
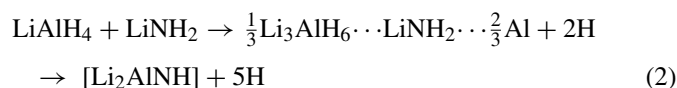


Fig. 4. X-ray diffraction patterns of: (a) post-1 h-milled LiAlH_4 - LiNH_2 sample; (b) post-3 h-milled sample; (c) post-5 h-milled sample; (d) post-10 h-milled sample; (e) post-TPD LiAlH_4 - LiNH_2 sample; (f) post-10 h-milled Li_2NH -Al sample. (x) represents LiAlH_4 , (+) Li_3AlH_6 , (○) Al, (□) LiNH_2 , (■) LiAl . Broad peaks at $\sim 20^\circ$, $32-33^\circ$ and 56° belong to LiOH , Li_2O .

XRD baselines of the post-milled samples was observed, which reveals the existence of amorphous structure. The post-TPD sample presented further weakened Al phase and weak LiAl phase. Again, no new structure can be detected. We ball milled pure Al and AlN for 10 h under the same milling conditions and noticed the persistence of distinct diffraction peaks of these compounds. Little uprising in baselines was observed. Therefore, it is reasonable to deduce that the amorphous product(s) may not be in the pure form of either Al or AlN. FTIR characterization on the post-milled and post-TPD samples only showed the weakened or disappeared N-H stretching in LiNH_2 . No new N-H vibration was detected. By summarizing the information obtained from ball milling, TPD and XRD measurements, a chemical process describing the LiAlH_4 - LiNH_2 interaction can be written as:



Previous analysis and thermodynamic calculations indicate that Al and AlN are unlikely to be the final products (a strong exothermic nature with Al and AlN produced was not observed by DSC measurement). Noted that the TPD features of LiNH_2 at temperature higher than 550°C (where LiNH_2 has converted to Li_2NH) resemble those of the post-milled LiAlH_4 - LiNH_2 samples (Fig. 1), Li_2NH may somehow be involved in the unknown solid product. To confirm this assumption, mixture of Li_2NH and Al with molar ratio of 1/1 was milled for 10 h and collected for XRD and FTIR characterizations. As can be seen in Fig. 4f, Al phase is almost undetectable; no distinct diffraction peaks (except weak LiAl phase) can be observed and the baseline

is upraised, which are similar to the post-TPD $\text{LiAlH}_4\text{--LiNH}_2$ sample. The characteristic N–H stretching in Li_2NH at around 3160 cm^{-1} was also undetectable, indicating the formation of a new structure consisting of Al, Li, N and H. In this context, we would refer to the Al imide complexes. Due to the Lewis acidity of Al and the electron lone pair at N, dative bonding may be established between Al and –NH group [17,18]. NMR is, therefore, highly useful to identify the newly developed structure. It is worth mentioning that the chemistry between Al and N is rather complicated. There could be competing or subsequent reaction pathways leading to the formation of LiAl alloy. Similar reaction between LiAlH_4 and primary amines (RNH_2 , R is an organic substitution) was observed by Finholt et al. [19]. However, no structural information was given to the solid residues.

Calculation shows that $\sim 8.0\text{ wt}\%$ of hydrogen is released from reaction (2), making $\text{LiAlH}_4\text{--LiNH}_2$ (1/1) an attractive system for hydrogen storage. Provided that the final products are Li_2NH and Al the overall reaction heat is $\sim 67\text{ kJ mol}^{-1}$ LiAlH_4 or $\sim 27\text{ kJ mol}^{-1}$ H_2 . By incorporating the heat of formation of $[\text{Li}_2\text{AlNH}]$ the actual enthalpy should be even lower. We tried to integrate the area of endothermic peaks for H_2 desorption in the post-5 h-milled sample (Fig. 2d); it comes with the heat of desorption of just around 7 kJ mol^{-1} H_2 . Such a weak endothermic nature indicates that either high pressure or lower temperature is needed to re-charge H_2 into the post-milled or post-TPD samples. Our attempt in charging 80 bar of hydrogen gas into the post-10 h-milled sample at room temperature was unsuccessful. However, the ongoing research shows that changing the chemical composition within Li–Al–N–H leads to the reversible hydrogen storage in the temperature range of $50\text{--}350\text{ }^\circ\text{C}$. We will discuss the chemical composition effect in the following up publication.

4. Conclusion

Kinetic barrier in the transformation from tetrahedral $[\text{AlH}_4]^-$ in LiAlH_4 to octahedral $[\text{AlH}_6]^{3-}$ was easily overcome by mixing LiAlH_4 with LiNH_2 with hydride-to-amide molar ratio of 1/1. Each $\text{LiNH}_2\text{--LiAlH}_4$ molecule will release 3.8 H atoms after ball milling 10 h of their mixture. XRD clearly identified the appearance of Li_3AlH_6 and Al in milling process. Heating post-milled sample to certain temperature resulted more hydrogen released and at last total 5 H atoms or $\sim 8\text{ wt}\%$ of

hydrogen were released. $[\text{Li}_2\text{AlNH}]$, predicted experimentally as the final product, is tough to be characterized. Other measurement, i.e. NMR is highly recommended to identify those newly developed structures.

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