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PII: S0925-8388(19)31060-6

DOI: https://doi.org/10.1016/j.jallcom.2019.03.234

Reference: JALCOM 49998

To appear in: Journal of Alloys and Compounds

Received Date: 30 January 2019

Revised Date: 14 March 2019

Accepted Date: 15 March 2019

Please cite this article as: Y.S. Chua, Z. Xiong, G. Wu, P. Chen, Ternary amide-hydride system: A study on LiAI(NH₂)₄-LiAIH₄ interaction, *Journal of Alloys and Compounds* (2019), doi: https://doi.org/10.1016/j.jallcom.2019.03.234.

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Ternary Amide-Hydride System: A Study on LiAl(NH₂)₄-LiAlH₄ Interaction

Yong Shen Chua,^{1*} Zhitao Xiong,^{2*} Guotao Wu² and Ping Chen²

¹School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Pulau Pinang, Malaysia.
²Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, 116023, Dalian, P. R. China.

Abstract

LiAl(NH₂)₄ is a ternary amide that readily decomposes to release ammonia at temperatures as low as ~ 90 °C. Owing to such instability as compared to binary amides, we hypothesize that the dehydrogenation mechanism involving ternary amide-hydride interaction would be significantly different from those of binary metal amide-hydride interaction. Therefore, in this study, interaction of LiAl(NH₂)₄ and LiAlH₄ has been investigated by means of mechanical milling and thermal method. It was found that dehydrogenation occurred spontaneously during the milling process and the rate of dehydrogenation increased with increasing amount of LiAlH₄, suggesting an ion migration mediated dehydrogenation. As reaction progressed, the formation of Li₃AlH₆ as an intermediate was detected and a total of 8 equiv. of H₂ (7.5 wt%) can be released, forming LiH and AlN as the final product. In contrast, heating the homogenously ground LiAl(NH₂)₄ and LiAlH₄ sample resulted in the release of NH₃ at low temperatures, indicating that NH₃ mediation would take place in case of dehydrogenation. Further increase in temperature resulted in a rapid release of hydrogen from the interaction of the LiAl(NH)₂ and LiAlH₄. It was also found that hydride with higher basicity is required to trigger amide-hydride interaction for dehydrogenation at low temperatures.

Keywords

Amide-hydride interaction; Dehydrogenation; Ion migration mechanism; NH₃ mediation mechanism;

Hydrogen storage

1.0 Introduction

Rapid development in fuel cell technologies arouses a breakthrough in the field of hydrogen storage. Conventional storage methods, including compressed hydrogen, liquefied hydrogen and metal hydride, do not meet the volumetric and gravimetric densities requirements as described in 2020 DOE target [1]. Research efforts were presently moved to borohydrides [2, 3], metal organic frameworks [4], alanates [3] and metal-N-H systems [5, 6]. In particular, the discovery of reversible hydrogen storage on LiNH₂-LiH system in 2002 triggered intensive investigations on amide-hydride systems [7]. Metal hydrides, MH as reported, is known to play an important role in destablizing metal amides, including binary [8-10] and ternary [11-14] amides, to allow dehydrogenation to occur at much reduced temperatures with negligible emission of NH₃. Over the past 10 years, it has been debated whether dehydrogenation process in amide-hydride system is governed by ion migration mechanism or NH₃ mediated mechanism. Chen et al. [15] suggested that the remarkable improvement in the dehydrogenation properties of MNH2-MH system is due to the ion migration as results of the high combination potential of the two oppositely charged $H^{\delta+} \cdots H^{\delta-}$ situating respectively in amide and hydride. Ichikawa et al. [16] on the other hand suggested that the improvement is ascribed to the lowered MNH₂ decomposition temperature as results of the introduction of metal hydride, releasing NH₃ that reacts spontaneously with MH. However, recent research showed that both mechanisms are valid and the mechanism involved is mainly governed by the ions mobility [17]. In Li₂NH₂Br [18], the LiNH₂ moiety is constrained by the cage of Br anions. Due to the limited mobility of LiNH₂ moiety, the hydrogen desorption from Li₂NH₂Br-2LiH system appears to follow NH₃ mediated mechanism. In contrast, Li^+ (from LiH) and H⁺ (from LiNH₂) ions migration at the interface play important roles leading to hydrogen formation when LiNH₂ and LiH are intimately in contact.

Unlike LiNH₂-LiH system, the interaction of LiAlH₄ (or NaAlH₄) and LiNH₂ (or NaNH₂) proceed spontaneously. Eventhough the decomposition of NaNH₂ and LiNH₂ require high temperatures of ca. 210 °C [20] and 350 °C [17], respectively, in the presence of LiAlH₄, the reaction thermodynamic changes significantly, releasing most of the hydrogen during the mechanical milling process [8, 9, 19, 20]. This result manifests that dehydrogenation via ion migration is more favorable than NH_3 mediated mechanism. Different from binary amides, $LiAl(NH_2)_4$ is a ternary amide which decomposes to release NH_3 at much lower temperatures (95 °C) as compared to $LiNH_2$ and $NaNH_2$, requiring lesser energy for its decomposition. Therefore, when $LiAl(NH_2)_2$ is used as an amide source in amide-hydride reaction, the dehydrogenation mechanism may be different from that of binary amide-hydride system. In 2007, Janot et al. [21] first investigated the interaction of ternary amide-hydride system focusing on $LiAl(NH_2)_4$ -LiH (1:4). In their study, they found that the post milled $LiAl(NH_2)_4$ -LiH began to dehydrogenate even at room temperature. Such improvement was attributed to the catalytic role of LiH as results of the dihydrogen interaction between amide and hydride. Despite the author suggested NH_3 mediation as the dehydrogenation mechanism, there is no clear evidence showing the preference of NH_3 mediated mechanism over the ion migration mechanism in the dehydrogenation process.

More recently, the interactions of ternary amides and borohydrides were investigated out by Hauback et al. [12]. It was found that milling equimolar of LiAl(ND₂)₄ and LiBH₄ resulted in the formation of new compound, $Li_2Al(ND_2)_4BH_4$. This compound decomposed in a stepwise manner, releasing ND₃ from the Al(ND₂)₄⁻ unit and H₂ from BH₄⁻ unit in Li₂Al(ND₂)₄BH₄, separately. Neither the ND₂⁺ nor ND₃ interacts with the [BH₄]⁻ unit to induce dehydrogenation at low temperatures. Similar results were observed in Li(NH₃)_nBH₄, n = 1, 2, 3, 4 which desorbs NH₃ reversibly rather than interact with [BH₄]⁻ to form H₂ [22].

As $LiAlH_4$ represents an important source of hydride in amide-hydride interactions and its interaction with ternary amide remains unclear, therefore it is essential to study the interaction of $LiAl(NH_2)_4$ - $LiAlH_4$ under different conditions and understand the dehydrogenation mechanism and pathway involved. The influence of hydrides of different basicity towards the interaction with $LiAl(NH_2)_4$ are also discussed in this study.

2.0 Experimental

LiAlH₄ (Fluka, 97%) was used as received. LiAl(NH₂)₄ was on-site synthesized by mechanical milling LiAlH₄ in purified ammonia gas atmosphere at room temperature. Detailed description of the synthesis can be

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found elsewhere [23]. Hydrogen was detected at the end of reaction and the weight gain of the solid suggested the occurrence of following reaction (R1):

(1)

 $LiAlH_4 + 4NH_3 \rightarrow LiAl(NH_2)_4 + 4H_2$

LiAl(NH₂)₄-LiAlH₄ in molar ratios of 1:1, 1:2 and 1:3 were mechanically milled using a Retsch PM400 planetary mill. The rotation speed was regulated at 120 rpm and the ball-to-sample ratio was about 30. As milling progressed, pressure increase inside the milling vessel was observed, signaling a spontaneous reaction to form gaseous product has occurred. Time dependence of hydrogen pressure reading in the milling processes were recorded by connecting the milling vessel to a pressure gauge. Therefore, the amount of desorbed hydrogen can be calculated by applying ideal gas state of equation. One of the concerns on amide-hydride system is the production of ammonia. To precisely detect the presence of ammonia gas, gas in milling vessel was also connected to pink cobalt (II) nitrate solution to observe color change. In the event when small amount of NH₃ was presented in the gaseous product, green precipitate of $Co(OH)_2(H_2O)_4$ shall be detected. In fact, in all three post-milled samples, no color change was observed.

Structure identifications were conducted on a Bruker D8-advance X-Ray Diffractometer (XRD) using a XRD cell with Pt base. N-H stretches in the reactant and post milled samples were monitored by a Perkin Elmer FT-IR-3000 in DRIFT mode. Alterations of chemical environment of ⁷Li and ²⁷Al nuclei in the milling process were monitored by a DRX 400 magic angle spinning (MAS) solid state NMR. Lithium chloride and aluminum nitrate solution were used as references.

The decomposition behavior of the samples were investigated by using a custom made temperatureprogrammed-desorption coupled with a mass spectrometer and the corresponding heat effects were measured on a DSC 204HP unit. A dynamic flow mode was employed with purified argon gas as carrier gas and the heating was set at 2 °C/min. All sample handlings were carried out in an Argon filled MBRAUN glovebox to prevent oxygen and moisture contaminations.

3.0 Result and Discussion

3.1 Interaction of LiAl(NH₂)₄-LiAlH₄ (1:1, 1:2, 1:3) via mechanical milling

One of the kinetic barriers in solid-solid interaction is mass transition and generally, intimate contact of the reactants in solid mixture is demanded to overcome this barrier. Therefore, the samples were mechanically milled to reduce their particle size to enhance the interactions between the starting materials. To avoid additional heat from milling machine building up inside the milling vessel a low milling speed of 120 rpm was chosen. In addition, solid interaction between LiAl(NH₂)₄ and LiAlH₄ was not violent but somewhat controllable at this milling speed, allowing operations such as pressure monitoring and intermediate collection at different intervals of interaction. Figure 1 shows the pressure variations inside the milling vessel as a function of time. 3.7 equiv. H₂, 7.6 equiv. H₂ and 8 equiv. of H₂ (or 5.4 wt%, 8.7 wt% and 7.5 wt% of H₂) can be released upon extensively milling LiAl(NH₂)₄-LiAlH₄ mixture in molar ratios of 1:1, 1:2 and 1:3, respectively. Up to 70% of hydrogen (5.7 wt%) can be released from 1:3 sample within 2 hours of milling. For comparison, LiAlH₄ and LiAl(NH₂)₄ were individually milled under the same conditions. LiAlH₄ was stable against mechanical milling at 120 rpm as no pressure build up was detected, in agreement with the previous reports [8]. As for LiAl(NH_2)₄, no gaseous product was found in the first 3 hours but detectable amount of ammonia was evolved only after milling for 22 h. These results suggest that the rapid hydrogen desorption from LiAl(NH₂)₄-LiAlH₄ can only be resulted from the interaction of the two starting precursors. Furthermore, the increasing rate of dehydrogenation (dH/dt) with increasing amount of LiAlH₄ (Figure 1, inset) clearly manifests ion migration mechanism in the dehydrogenation process. If NH₃ mediation dehydrogenation were to take place, the amount of LiAlH₄ should have no big effect on the rate of dehydrogenation.



Figure 1. Time dependence hydrogen desorption at ambient temperature and at a milling speed of 120 rpm. The inset shows the dehydrogenations occur at the early stage of mechanical milling.

3.2 Dehydrogenation pathway of LiAl(NH₂)₄-LiAlH₄ (1:3)

To understand the dehydrogenation pathway, $LiAl(NH_2)_4$ -LiAlH₄ in a molar ratio of 1:3 was further investigated in detail by collecting the samples at different milling intervals and further characterized by FTIR, XRD and NMR. As shown in FTIR spectra (Figure 2), self-made LiAl(NH₂)₄ presented five distinct -NH₂ bands at 3406, 3397, 3357, 3337 and 3297 cm⁻¹. As milling progressed, these five bands gradually disappeared, suggesting the consumption of NH₂ group in the milling process and the post milled samples are of -NH₂ free structure. XRD analyses (Figure 3) also revealed the diminishing diffraction patterns of LiAlH₄ and LiAl(NH₂)₄ with milling time and finally these patterns disappeared. Interestingly, diffraction pattern of Li₃AlH₆ was detected when 5 equiv. H₂ were evolved, suggesting its existence as an intermediate species in the interaction of LiAl(NH₂)₄-LiAlH₄. However, the amorphous nature of the post milled samples impedes the structural analysis on the final product formed. In order to achieve a better crystallinity, the final product was annealed at 400 °C and the resulting XRD pattern evidenced the presence of AlN and LiH in the sample.

Magic angle spinning solid state NMR (MAS NMR) was also employed to investigate the chemical

environment of ²⁷Al and ⁷Li. Figure 4(A) shows the ²⁷Al NMR spectra of the post milled LiAl(NH₂)₄-LiAlH₄ (1:3) collected at different milling intervals. It can be seen that the ground LiAl(NH₂)₄-LiAlH₄ (1:3) mixture displayed two overlapping peaks which are resulted from the superposition of the starting materials, LiAl(NH₂)₄ and LiAlH₄ at 91.9 and 120.7 ppm, respectively. Prolonging mechanical milling treatment the resonances of the starting materials became weaker and finally disappeared. The LiAl(NH₂)₄-LiAlH₄ (1:3) sample evolving 4 and 5 equiv. H₂ demonstrated a small peak centered at -36.1 ppm which can be assigned to Al in six-coordinated $[AlH_6]^{3-}$ sites of Li₃AlH₆, agreeing with the XRD results. When 5 equiv. H₂ were evolved from LiAl(NH₂)₄-LiAlH₄ (1:3), no LiAl(NH₂)₄ resonance can be observed. Instead, a broad and asymmetry resonance centered at 105.7 ppm was detected. Since the resonance falls between Al in LiAlH₄ (93 ppm) and Al in AlN (114 ppm), the formation of intermediate compounds with $(AlH_{4,x}N_x)$ coordination sphere is thus highly possible. A similar observation was also reported by Xiong et al. [24] in the interaction of LiAlH₄-2LiNH₂. At the end of mechanical milling, the broad asymmetric resonance shifted downfield to 112.7 ppm, closer to the chemical shift of four coordinated AlN_4 environment in AlN (114 ppm). The asymmetry of the peak may be due to the remaining of (AlH_{4-x}N_x) in the sample. Figure 4(B) shows that ground sample possessed LiAl(NH₂)₄-like ⁷Li environment at 2.0 ppm, which also overlapped with the ⁷Li resonance in LiAlH₄. As the mechanical milling progressed, the peak centered at 2.0 ppm shifted upfield towards a LiH-like environment. In conjunction with the FTIR, XRD and NMR analyses, the complete reaction pathway can be realized by following equation (R2):

 $LiAl(NH_2)_4 + 3LiAlH_4 \rightarrow 4LiH + 4AlN + 8H_2(7.5 \text{ wt\% } H_2)$

(2)



Figure 2. FTIR spectra of self-made $LiAl(NH_2)_4$ (a), milled $LiAl(NH_2)_4$ - $LiAlH_4$ (1:3) with 4 equiv. H₂ evolved

(b), 5 equiv. H_2 evolved (c) and 8 equiv. H_2 evolved (d).



Figure 3. XRD patterns of the ground LiAl(NH₂)₄-LiAlH₄ (1:3) (a), milled LiAl(NH₂)₄-LiAlH₄ (1:3) with 4 equiv. H₂ evolved (b), 5 equiv. H₂ evolved (c), 8 equiv. H₂ evolved (d) and further annealed at 400 °C (e). Peaks correspond to platinum (Pt) base are marked with asterisks.



Figure 4. ²⁷Al (A) and ⁷Li (B) MAS solid state NMR spectra of LiAl(NH₂)₄-LiAlH₄ (1:3) ground sample (a), milled with 4 equiv. H₂ evolved (b), 5 equiv. H₂ evolved (c), 8 equiv. H₂ evolved (d), self-made LiAl(NH₂)₄ (e), LiH (f), AlN (g) and LiAlH₄ (h). Asterisks denote the spinning sidebands.

3.3 Interaction of LiAl(NH₂)₄-LiAlH₄ (1:3) via thermal method

In order to compare the influence of the sample preparation (mechanical milling vs thermal method) towards the dehydrogenation mechanism, in a separate experiment, $LiAl(NH_2)_4$ and $LiAlH_4$ mixture in the molar ratio of 1:3 was ground gently using mortar and pester to minimize their interactions and the decomposition was investigated by using TPD-MS and DSC. XRD characterization of the ground sample (Figure 3) clearly demonstrated a diffraction pattern which resembles to the combined patterns of LiAlH₄ and $LiAl(NH_2)_4$, indicating a physical mixture of the two starting materials. Figure 5 shows the TPD-MS results of the ground $LiAl(NH_2)_4$ -LiAlH₄ (1:3). As can be seen, only NH₃ can be detected at ca. 100 °C which is attributed to the decomposition of $LiAl(NH_2)_4$ (R3). DSC analysis shown in Figure 6 further confirms the existence of only endothermic NH₃ release at ~110 °C. Surprisingly, the release of NH₃ did not trigger the secondary reaction with $LiAlH_4$ to release H₂. This result is in contrary with the Luo's work which suggested a rapid interaction between NH₃ and $LiAlH_4$ to release H₂ on demand [25]. This difference could be attributed to

the fact that the experiments reported by Luo et al. were carried out by dosing NH_3 into a LiAlH₄ filled container, while the current TPD-MS was carried out in an open flow mode whereby the NH_3 released from LiAl(NH_2)₄ diffused through LiAlH₄ rapidly as the sample was directly exposed to the flowing inert gas. In their experiments, NH_3 has a longer contact time with LiAlH₄ in the container, thus trapping all the NH_3 completely and producing H_2 . In contrast, a relatively shorter contact time is expected under an open flow mode, inhibiting the interaction between NH_3 and LiAlH₄.

Further increasing temperature resulted in the dehydrogenation which dehydrogenation pattern has changed slightly as compared to that observed in the decomposition of pristine LiAlH₄ [26]. A rapid release of hydrogen at 158 °C can be clearly observed near the shoulder of the first dehydrogenation step of LiAlH₄. It corresponds to a strong exothermic process in DSC analysis which evidences an interaction between the decomposed residue LiAl(NH)₂ and LiAlH₄ to release H₂. Due to the fact that LiAl(NH)₂ is metastable and it exothermically transforms into LiNH₂ and AlN (R4) [11], thus, it is plausible to attribute the rapid release of H₂ to the interaction of LiNH₂ and LiAlH₄. This assumption is further supported by the observation of a similar phenomenon in the interaction of NaNH₂ and LiAlH₄ [9].

| $LiAl(NH_2)_4 \rightarrow LiAl(NH)_2 + 2NH_3$ | (3) |
|---|-----|
| $LiAl(NH)_2 \rightarrow LiNH_2 + AlN$ | (4) |

The remaining of the process matches well with the characteristic decomposition of $LiAlH_4$ which involves endothermic phase transition at ~160 °C, exothermic dehydrogenation of $LiAlH_4$ to Li_3AlH_6 , LiH and Al at 175 °C and endothermic dehydrogenation of Li_3AlH_6 to LiH and Al at 220 °C.



Figure 5. TPD-MS curves of ground LiAl(NH₂)₄-LiAlH₄(1:3) (top) and self-made LiAl(NH₂)₄ (bottom).



Figure 6. DSC measurement of ground LiAl(NH₂)₄-LiAlH₄ (1:3) and self-made LiAl(NH₂)₄.

3.4 Comparison of LiH, LiBH₄ and LiAlH₄ in the interaction with LiAl(NH_2)₄

LiH essentially shows ionic interaction between Li and H with finite charge transfer from Li to H. LiBH₄

and LiAlH₄, on the other hand, consist of ionic interaction between Li⁺ and XH₄⁻ (X = B, Al) and covalent interaction between X and H. Hydrogen in MH₄⁻ is covalently bonded to central X in tetrahedral geometry with relatively smaller amount of charge transfer to H than that in LiH. The amount of charge transfer to H further varies with the Pauling electronegativity of the X element. For instances, the Pauling electronegativity of Al is lower than B (1.61 vs 2.04), thus the amount of charge transfer to H is more from Al in AlH₄⁻ than that from B in BH₄⁻, making the hydride in LiAlH₄ a stronger base. In LiBH₄, a lower electron density on H^{δ} resulted in Li₂Al(ND₂)₄BH₄ rather than dehydrogenation when LiAl(ND₂)₄⁻ unit and H₂ from BH₄⁻ unit in Li₂Al(ND₂)₄BH₄, separately. In contrast, when a higher basicity hydride such as LiAlH₄ or LiH [21] was employed, it reacted with LiAl(NH₂)₄ to release H₂ at much lower temperatures. In current study, due to the presence of the oppositely charged atoms in LiAl(NH₂)₄-LiAlH₄ system, it is plausible to ascribe the strong electrostatic attractions of H^{δ +...}H^{δ} as the driving forces for the dehydrogenation to occur at low temperatures. On the other hand, we cannot rule out the driving force from strong donor-acceptor attraction between Al in LiAlH₄ and N in ternary amide.

4.0 Conclusion

In this study, we have investigated the interaction of LiAl(NH₂)₄-LiAlH₄ via mechanical milling and thermal method. The results indicate that interaction of LiAl(NH₂)₄ and LiAlH₄ is an energy viable process at ambient condition, releasing 70 % of the hydrogen (6 equiv. of H₂ or 5.7 wt% H₂) within 2 hours of mechanical milling. During the mechanical milling, the rate of dehydrogenation increased with increasing amount of LiAl(H₄, indicating that the dehydrogenation mechanism is prone to ion migration over NH₃ mediation. In the ground LiAl(NH₂)₄-LiAlH₄ (1:3) when the starting materials are not in intimate contact, NH₃ mediated dehydrogenation is prone to occur. However, in the current study, the NH₃ released from LiAl(NH₂)₄ did not trigger the interaction with LiAlH₄. Instead, the decomposed residue, LiAl(NH)₂ reacted with LiAlH₄ and resulted in rapid release of hydrogen. It is also important to note that hydride with higher basicity is required to trigger amide-hydride interaction to achieve dehydrogenation at low temperatures.

Acknowledgement

Y.S. Chua would like to acknowledge the financial support from USM Short Term Grant (304/PKIMIA/6313210). G. Wu and P. Chen also thank the Project of National Science Funds for Distinguish Young Scholars (51801197) and Sino-Japanese Research Cooperative Program of Ministry of Science and Technology (2016YFE0118300) for financial support.

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Highlights

- Large amount of H_2 can be released from LiAl(NH_2)₄-LiAlH₄ system upon milling
- H₂ release is prone to ion migration mechanism in mechanical milling
- NH₃ mediated H₂ release would occur in homogenously ground sample during heating
- Hydride with higher basicity is required to induce H₂ release at low temperatures

Chillip Marker