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# Exploring the potential of ammonia alane $\text{AlH}_3\text{NH}_3$ as hydrogen carrier

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## Abstract

Ammonia alane  $\text{AlH}_3\text{NH}_3$  (AA) exhibits a high gravimetric hydrogen storage capacity, with 12.86 wt% H, positioning it as a potential solid hydrogen carrier. It has nevertheless received limited attention, with only few computational studies exploring its capabilities, and it has been overshadowed by its boron analog ammonia borane  $\text{BH}_3\text{NH}_3$  (AB). The lower focus on AA can be attributed to its instability at temperatures above  $-80$  °C. However, the dehydrogenation of AA has been predicted to be endothermic, and this is an attractive feature for achieving reversible hydrogen storage. AA holds thus potential as a hydrogen carrier even though its implementation is likely to pose challenges. This is the guiding principle of this article. It aims to (i) comprehensively review existing work on AA, (ii) compare the current understanding of the potential of AA as a hydrogen carrier to that of AB, (iii) address the limitations and challenges that must be overcome for effective use of AA as a solid hydrogen carrier, and (iv) discuss perspectives.

## Keywords

Alane-ammonia complex; Ammonia alane; Ammonia borane; Hydrogen carrier; Hydrogen storage.

## Introduction

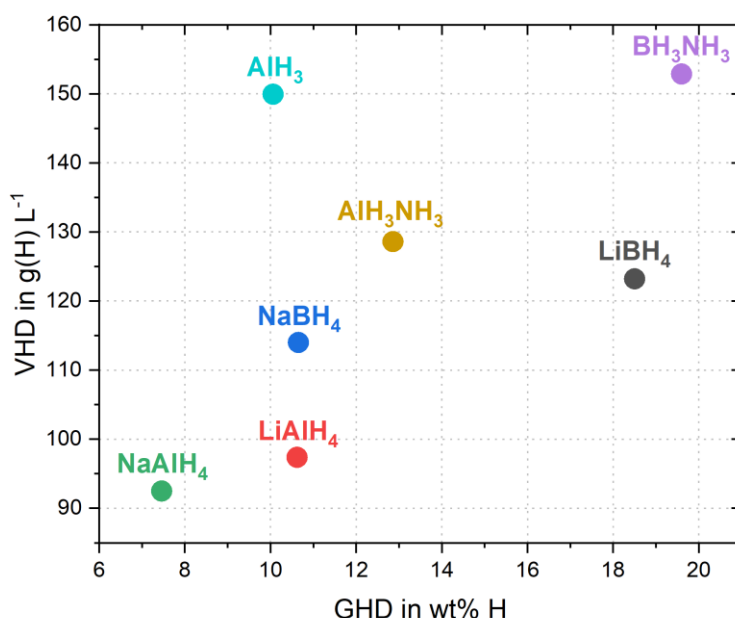
One of the primary challenges that must be addressed for the hydrogen economy to thrive fully is its storage. The solutions can be categorized into three main types: physical storage through compressed H<sub>2</sub> (>700 bar) or liquefied H<sub>2</sub> (–253 °C) [1,2]; liquid hydrogen carriers (such as LOHCs, i.e. liquid organic hydrogen carriers, and ammonia NH<sub>3</sub> at >7.5 bar and 20°C); and storage utilizing solid-state materials [3-5]. As for the last category, it can be subdivided into two main types: highly porous materials that store H<sub>2</sub> under cryogenic conditions (typically –196 °C for most) [6], and materials of a metallic, complex, or chemical nature, where H is bound to a less electronegative element (such as magnesium, boron, or aluminum) [7,8]. With respect to complex and chemical hydrides, they are also referred to as solid hydrogen carriers.

Complex and chemical hydrides composed of hydrogen and light elements (2s, 2p, 3s and 3p like boron and aluminum, respectively) provide high hydrogen densities [9-11]. Examples are lithium alanate LiAlH<sub>4</sub> (10.62 wt% H, 97.38 g(H) L<sup>-1</sup>), sodium borohydride NaBH<sub>4</sub> (10.65 wt% H, 113.99 g(H) L<sup>-1</sup>), magnesium borohydride Mg(BH<sub>4</sub>)<sub>2</sub> (14.93 wt% H, 120.92 g(H) L<sup>-1</sup> with respect to the orthorhombic structure with space group *P2c-c*), ammonia borane BH<sub>3</sub>NH<sub>3</sub> (19.6 wt% H, 152.87 g(H) L<sup>-1</sup>; also called borazane or borane-ammonia complex, and denoted AB hereafter) and alane AlH<sub>3</sub> (10.06 wt% H, 149.94 g(H) L<sup>-1</sup> for the  $\alpha$  phase). The challenge lies in decomposing these hydrides to release only H<sub>2</sub>. For instance, LiAlH<sub>4</sub> releases 5.3 wt% of H<sub>2</sub> when heated at 150-175 °C and 2.6 wt% of H<sub>2</sub> at 180-220 °C; this translates to an effective gravimetric hydrogen storage capacity of 7.9 wt%. However, the dehydrogenation temperatures remain relatively high and the dehydrogenation kinetics are too slow for practical applications; these prompted many studies involving the addition of catalysts, for example [12-14]. Another widely studied hydride is NaBH<sub>4</sub>. It releases H<sub>2</sub> when heated, but the process requires temperatures above 470 °C [15]. Otherwise, it undergoes slow hydrolysis at ambient conditions, and the release of H<sub>2</sub> can be regulated by using a suitable metal-based catalyst [16,17]. Due to these characteristics, NaBH<sub>4</sub> has been extensively investigated in hydrolytic conditions rather than in thermolytic ones [18]. Another noteworthy example is AB. Under heating, AB can release approximately 13 wt% of H<sub>2</sub> up to 200

°C [19]. However, side reactions occur during thermolysis, leading to decomposition into unwanted gases such as  $\text{NH}_3$  and borazine  $\text{B}_3\text{N}_3\text{H}_6$  [20]. Neat AB is actually not suitable for hydrogen storage, and numerous efforts have been directed towards its destabilization using strategies such as doping, solubilization coupled with homogeneous catalysis, nanoconfinement, and chemical modification [21,22].

Boron and aluminum belong to group 13 elements (Figure 1). As mentioned above, both have anionic hydrides in the form of ionic salts  $\text{MBH}_4$  and  $\text{MAIH}_4$  (borohydrides and alanates respectively, with  $\text{M} = \text{Li}, \text{Na}$  for example) that have been considered as hydrogen carriers [11]. On the one hand,  $\text{MBH}_4$  and  $\text{MAIH}_4$  readily hydrolyze upon contact with water and release  $\text{H}_2$ , and on the other hand, they dehydrogenate when heated (above 150 °C for  $\text{LiAlH}_4$  [23] and 400 °C for  $\text{LiBH}_4$  [24] for example). Both boron and aluminum have also neutral hydrides. With respect to aluminum, the neutral hydride is  $\text{AlH}_3$ . It has garnered particular attention as hydrogen carrier as its  $\alpha$  polymorph releases all of its hydrogen when heated above 150 °C [9,25]. The boron analog  $\text{BH}_3$  only exists in its dimeric form, i.e. diborane  $\text{B}_2\text{H}_6$  that is a gas (m.p. -165.5 °C, b.p. -92 °C).  $\text{B}_2\text{H}_6$  has played a crucial role in boron chemistry but it is difficult to use due to its flammability and toxicity [26]; consequently, it has never been considered as a potential hydrogen carrier. Returning to the entity  $\text{BH}_3$ , it nevertheless plays a role as hydrogen carrier, since this Lewis acid readily combines with a Lewis base (e.g.  $\text{NH}_3$  and amines) to produce the aforementioned complex AB and more widely amine-borane adducts [27]. In comparison, the aluminum analogue, ammonia alane  $\text{AlH}_3\text{NH}_3$  (also called alazane or alane-ammonia complex, and denoted AA hereafter) has been studied very little, and its potential as hydrogen carrier has never been explored experimentally, while it has a theoretical gravimetric hydrogen density of 12.86 wt%. However, a number of other amine-alane adducts have been synthesized and studied [28], either as intermediates (e.g. triethylamine-alane  $\text{AlH}_3\text{N}(\text{C}_2\text{H}_5)_3$ ) to produce  $\text{AlH}_3$  from aluminum [29] or to propose derivatives of  $\text{AlH}_3$  (e.g. triethylenediamine-alane  $\text{AlH}_3\text{N}_2(\text{C}_2\text{H}_4)_3$ ) offering reversible hydrogen storage [30]. In summary, the exploration of boron hydrides and aluminum hydrides as hydrogen carriers has proceeded in a comparable parallel manner, with notable exceptions in the cases of AB and AA, and particularly of AA. This is the topic under discussion here.

We recently initiated systematic work to experimentally explore the properties and potential of AA. In this context, the present review article aims to address two key questions: why so few experimental studies have been devoted to AA, and whether AA could offer prospects for use as a hydrogen carrier. Where relevant, we provide brief feedback on our experience of AA syntheses and analyses. The article is structured around three main sections. The first section provides a comprehensive summary of existing work, encompassing syntheses, predicted physicochemical properties, chemical stability, and hydrogen storage properties of AA. This section also addresses the species (polymers and resulting nitrides) that form due to AA instability above 0 °C, providing the reader with a comprehensive understanding of the challenges associated with AA synthesis. The second section presents an analysis comparing the current understanding of the potential of AA as a hydrogen carrier to that of AB. In the third and final section, preceding the conclusion, the article contextualizes the first two sections, addressing the limitations and challenges that need to be overcome for AA to be effectively used as a hydrogen carrier.



**Figure 1.** Theoretical gravimetric and volumetric hydrogen densities (GHD and VHD, respectively) of boron- and aluminum-based hydrides studied as solid hydrogen carriers. With respect to AA ( $\text{AlH}_3\text{NH}_3$ ), its VHD was calculated assuming a density of  $1 \text{ g cm}^{-3}$  (since the experimental density is unavailable), and has to be considered with an error, likely to be of 20-25%.

# Ammonia alane

## Synthesis

The initial attempts to synthesize AA date from the 1950s. Wiberg and May [31] reported the reaction of one equivalent of  $\text{AlH}_3$  in diethyl ether with an equal amount of  $\text{NH}_3$  at  $-80\text{ }^\circ\text{C}$ , resulting in AA in the form of a white precipitate. Under these conditions, no  $\text{H}_2$  evolution was observed, aligning with the expected Lewis acid-base reaction between  $\text{AlH}_3$  and  $\text{NH}_3$ :



At temperatures exceeding  $-80\text{ }^\circ\text{C}$ , AA was found to be unstable (Figure 2). AA (left in diethyl ether) began to dehydrogenate when the temperature rose above  $-45\text{ }^\circ\text{C}$ . Notably, the release of one equivalent of  $\text{H}_2$  occurred when the temperature was maintained between  $-40$  and  $-30\text{ }^\circ\text{C}$ :



Intermolecular dehydrogenation, also known as dehydrocoupling, occurred leading to the formation of a polymer (polyaminoalane denoted PAA or polyalazene) with the structural unit  $\text{AlH}_2\text{NH}_2$  (aminoalane or alazene). At room temperature, a subsequent dehydrogenation occurred, and the second equivalent of  $\text{H}_2$  was released:



A polymer (polyiminoalane denoted PIA) with the structural unit  $\text{AlHNNH}$  (iminoalane) formed. The gradual release of the third equivalent of  $\text{H}_2$  occurred at temperatures exceeding  $100\text{ }^\circ\text{C}$ , leading to the progressive formation of aluminum nitride  $\text{AlN}$ . For instance,  $\text{AlH}_{0.23}\text{NH}_{0.23}$  formed after a heating process at  $150\text{ }^\circ\text{C}$  for 1 h.

Wiberg and May gleaned two key insights from the aforementioned study: (i) AA exhibits instability above  $-80\text{ }^\circ\text{C}$ , and (ii)  $\text{AlN}$  begins to form above  $100\text{ }^\circ\text{C}$ . Subsequently, they delved into the synthesis of various AA derivatives with the aim of employing them as precursors for  $\text{AlN}$ . They successfully synthesized  $\text{AlH}_2(\text{NH}_2)(\text{NH}_3)$  by reacting one equivalent of  $\text{AlH}_3$  with an excess of  $\text{NH}_3$  (four equivalents) at  $-196\text{ }^\circ\text{C}$ , followed by  $-80\text{ }^\circ\text{C}$ . Further rise in temperature up to  $-50\text{ }^\circ\text{C}$ , led to the synthesis of  $\text{AlH}(\text{NH}_2)_2$  [32]:

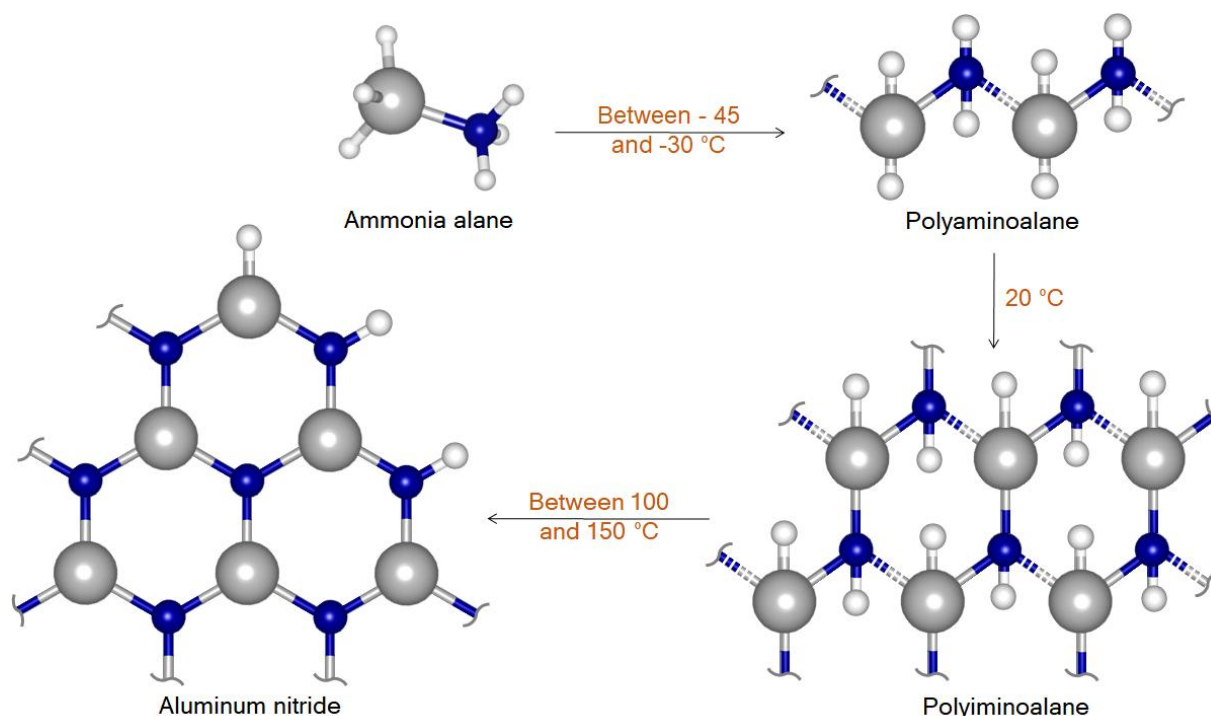




They also produced  $\text{Al}(\text{NH}_2)_3$  by reaction of  $\text{AlH}(\text{NH}_2)_2$  with  $\text{NH}_3$  at  $-80\text{ }^\circ\text{C}$ , then  $-50\text{ }^\circ\text{C}$  and finally  $-30\text{ }^\circ\text{C}$ :



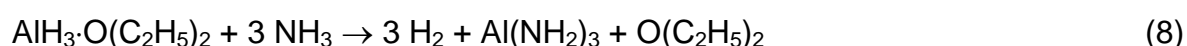
$\text{Al}(\text{NH}_2)_3$  proved to be a highly effective precursor for AlN, yielding the nitride with an atomic ratio Al:N of 1:1.16 after pyrolysis at  $430\text{ }^\circ\text{C}$  for 4 h. Notably, Wiberg and May synthesized other carbon-containing derivatives such as methylamine alane  $\text{AlH}_3\text{NH}_2\text{CH}_3$  [33] and tertiary amine alanes  $\text{AlH}_3\text{NR}_3$  with R as  $\text{CH}_3$  or  $\text{C}_5\text{H}_6$  [34-36], among others [37]. Subsequent studies delved into various amine alanes [38-40], including cases involving substitution of the alane (e.g.  $\text{Al}(\text{C}_6\text{H}_5)_3$  instead of  $\text{AlH}_3$ ) [41,42]. These investigations explored diverse applications such as using them as reducing agents in organic synthesis [43], to produce polymers with Al-N backbones [44], and to examine intermediates in aluminum hydrogenation and  $\text{AlH}_3$  production ( $\text{AlH}_3$  being exploited as hydrogen carrier) [30,45-47].



**Figure 2.** From ammonia alane to aluminum nitride, via polyaminoalane and polyiminoalane, as reported by Wiberg and May [31]. The Al, N and H atoms are shown by the grey, blue and white spheres, respectively.

Three decades after the seminal work summarized above, Ochi et al. [48] adopted the protocols established by Wiberg and May to synthesize  $\text{Al}(\text{NH})\text{NH}_2$ . The

synthesis involved the reaction of  $\text{AlH}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{NH}_3$  at subzero temperature conditions, followed by a temperature increase up to 140 °C.  $\text{Al}(\text{NH})\text{NH}_2$  served as a precursor for AlN, which was obtained through pyrolysis at temperatures ranging from 900 to 1100 °C. Pursuing the same objective, Maya [49] utilized  $\text{Al}(\text{NH}_2)_3$  as a precursor for AlN. This compound was tentatively synthesized through a two-step process: initially,  $\text{LiAlH}_4$  reacted with aluminum chloride  $\text{AlCl}_3$  in diethyl ether at room temperature to produce  $\text{AlH}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ , and subsequently, ammonolysis of the as-obtained product was carried out at -50 °C to form  $\text{Al}(\text{NH}_2)_3$ :



However,  $\text{Al}(\text{NH}_2)_3$  was found to be unstable at room temperature, undergoing a loss of  $\text{NH}_3$  to form a polymeric amide-imide with cross-linking, represented by the formula  $[\text{Al}(\text{NH}_2)_{0.864}\text{NH}_{0.069}]_n$ . The latter, however, yielded AlN when heated above 600 °C. Notably, at 1200 °C, thermogravimetric analysis revealed a weight loss of 28.2%, favorably comparing the 27.9 wt% of hydrogen of the original polymeric precursor.

With a slightly different approach from that of Wiberg and May, Janik and Paine [50] directly aimed for PIA by reacting  $\text{LiAlH}_4$  with ammonium bromide  $\text{NH}_4\text{Br}$  in diethyl ether at -78 °C and then -23 °C:



The produced PIA was not entirely pure, containing 5-10 wt% of diethyl ether, which persisted even after vacuum drying at 100 °C. It is noteworthy reporting that, upon repeating the aforementioned synthesis, we also observed the release of diethyl ether by mass spectrometry when the polymer was heated above 100 °C. Janik and Paine finally opted for diethyl ether (b.p. 35 °C) over dimethoxyethane (b.p. 85 °C) and tetrahydrofuran (b.p. 66 °C). Indeed, high percentages of dimethoxyethane were found in the PIA, and tetrahydrofuran degraded, which led to heavily carbon-contaminated AlN. Janik and Paine also observed that using  $\text{NH}_4\text{Br}$  instead of ammonium chloride  $\text{NH}_4\text{Cl}$  was preferable because  $\text{LiBr}$ , unlike  $\text{LiCl}$ , is soluble in diethyl ether, facilitating its separation from the PIA, and because the reaction proceeded smoothly with the bromide salt. The PIA underwent pyrolysis and thermogravimetric analysis up to 1000 °C revealed three weight losses associated



with solvent loss and dehydrogenation resulting in a total weight loss of 13-15 wt%. The ceramic yield was calculated to be 85-87%. By infrared spectroscopy, it was observed that the N–H and Al–H stretching bands (at 3400-3200 and 1800-1600  $\text{cm}^{-1}$ , respectively) disappeared entirely at 950 °C, leaving a single broad band centered at approximately 700  $\text{cm}^{-1}$  due to Al–N stretching.

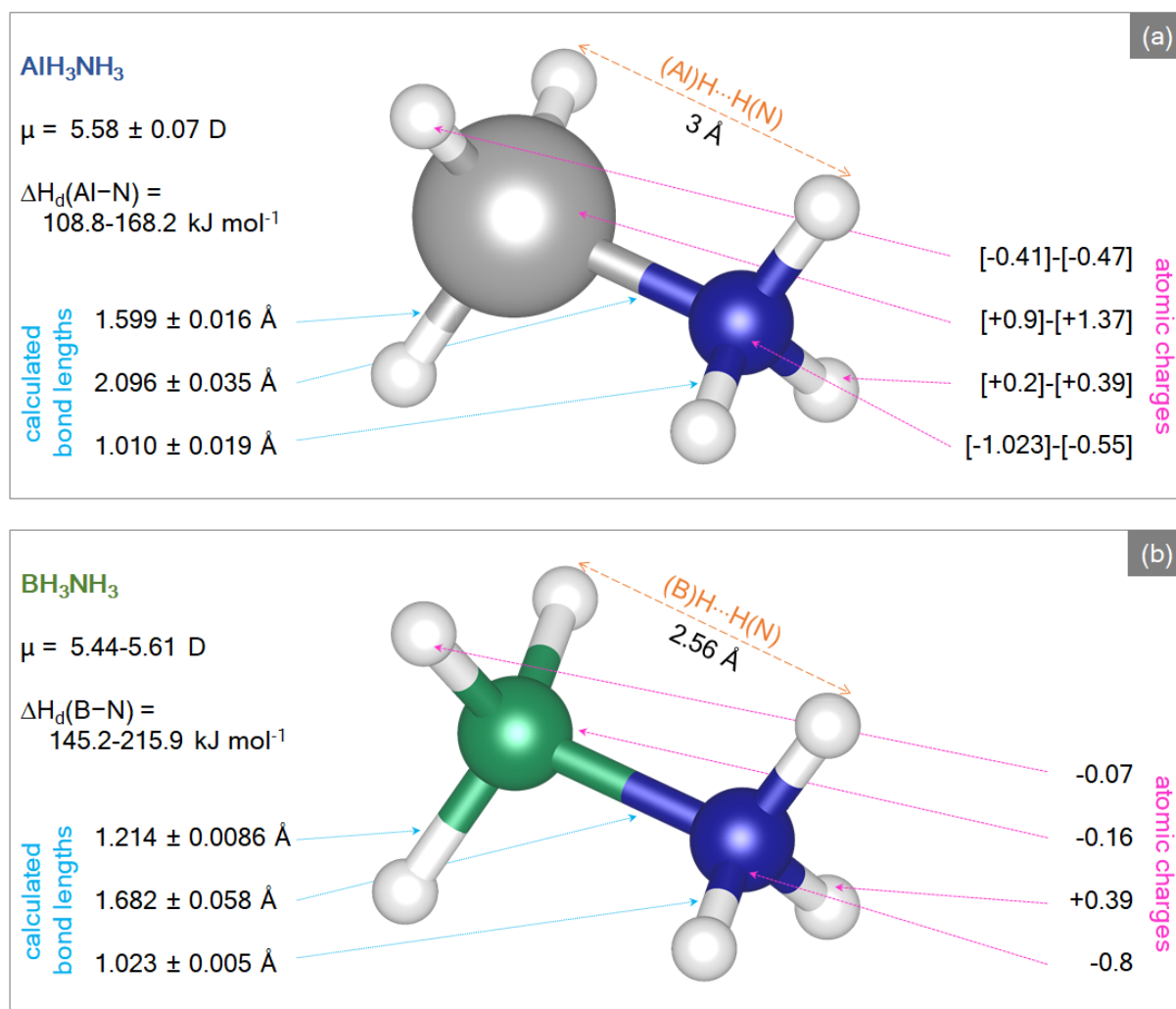
Janik and Paine's approach (Eq. 9) has inspired other research groups to explore the  $\text{MAIH}_4\text{-NH}_4\text{X}$  systems ( $\text{M} = \text{Li, Na}$ ;  $\text{X} = \text{F, Cl, Br}$ ) as hydrogen carriers. Zhang et al. [51] observed that the solid reaction between one equivalent of  $\text{MAIH}_4$  and one equivalent of  $\text{NH}_4\text{Cl}$  released three equivalents of  $\text{H}_2$  (as in Eq. 9) when the system was heated up to 170 °C. This resulted in an effective gravimetric hydrogen storage capacity of 6.6 wt% for the  $\text{LiAlH}_4\text{-NH}_4\text{Cl}$  system, for example. Zheng et al. [52] also investigated the  $\text{LiAlH}_4\text{-NH}_4\text{Cl}$  system and found that doping it with ceria (e.g. 1 mol%) enabled faster hydrogen production rates and shorter induction times. By incorporating a solvent like diethyl ether to the system, Wang et al. [53,54] enabled  $\text{H}_2$  release at temperatures as low as 25 °C. The enthalpy of the dehydrogenation reaction for  $\text{LiAlH}_4\text{-NH}_4\text{Cl}$  in diethyl ether was determined to be approximately  $+41 \text{ kJ mol}(\text{H}_2)^{-1}$ . Regardless of the dehydrogenation conditions, the  $\text{MAIH}_4\text{-NH}_4\text{X}$  systems consistently resulted in the formation of  $\text{MX}$  and  $\text{PIA}$  (as in Eq. 9), and the presence of residual solvent (often coordinated to  $\text{PIA}$ ) was noticed. The as-obtained  $\text{PIA}$  transformed into  $\text{AlN}$  when heated above 800 °C [51,53].

In summary,  $\text{AA}$  has never been isolated or could be isolated, which has prevented its analysis. Following the Wiberg and May preliminary attempt, research has mainly focused on the synthesis of molecular (e.g.  $\text{Al}(\text{NH}_2)_3$ ) and polymeric (e.g.  $\text{PIA}$ ) precursors for the production of  $\text{AlN}$  by pyrolysis at high temperature.

## Predicted properties

Ab initio and quantum chemical calculations have provided valuable insights into  $\text{AA}$  at the molecular scale. For detailed information on the various theories and calculation methods employed, the reader is encouraged to refer to the cited references for an explanation of the data intervals presented below.

The AA molecule has a total energy of  $300 \pm 1$  Hartrees and a dipole moment of  $5.58 \pm 0.07$  D [55-58]. The calculated bond lengths are (Figure 3): N-H  $1.010 \pm 0.019$  Å; Al-H  $1.599 \pm 0.016$  Å; Al-N  $2.096 \pm 0.035$  Å [55,57,59,60]. The Al-N bond dissociation energy was predicted to be between 108.8 and 168.2 kJ mol<sup>-1</sup> [55,57,59-61]. The distance between H of AlH<sub>3</sub> and H of NH<sub>3</sub> is approximately 3 Å, which is more than twice the van der Waals radius for H (1.2 Å) [59].



**Figure 3.** The (a) AA and (b) AB molecules, with indications about the calculated energies (Al-N and B-N bond dissociation energy  $\Delta H_d$ ), dipole moments  $\mu$ , bond lengths, atomic charges and distance between H of AlH<sub>3</sub> or BH<sub>3</sub> and H of NH<sub>3</sub>. The references for the given data are provided throughout the text.

The atomic charges of Al, N, H(Al), and H(N) were calculated within the ranges [+0.9]-[+1.37], [-1.023]-[-0.55], [-0.41]-[-0.47], and [+0.2]-[+0.39], respectively (Figure 3) [55,56,59,60,62], which is in agreement with the lower electronegativity of Al ( $\chi$  1.61) versus that of N ( $\chi$  3.04), and the intermediate electronegativity of H ( $\chi$

2.2). Based on such data, Czerw et al. [59] concluded that the bonding of AlH<sub>3</sub> with NH<sub>3</sub> in AA is predominantly electrostatic.

The vibrational frequencies for AA were also predicted [55-57,61,63], providing a valuable database for the analysis of IR spectra. The available data is listed in Table 1.

**Table 1.** Vibrational frequencies in cm<sup>-1</sup> for AA as predicted in references [55-57,61,63].

	[55]	[56]	[57]	[61]	[63] <sup>a</sup>
NH <sub>3</sub> sym str	3690-3588	3511	3588-3397	3355	3303
AlH <sub>3</sub> sym str	1986-1935	1957	1986-1811	1827	1780
NH <sub>3</sub> sym bend (def)	1383-1342	1329	1342-1173	1263	1183
AlH <sub>3</sub> sym bend (def)	844-829	811	829-712	791	748
Al-N str	418-408	414	439-354	422	380
NH <sub>3</sub> asym str	3814-3712	3639	3712-3531	3483	3440
AlH <sub>3</sub> asym str	1966-1898	1945	1966-1816	1827	
NH <sub>3</sub> asym bend (def)	1785-1711	1684	1711-1579	1665	1556
AlH <sub>3</sub> asym bend (def)	865-845	839	853-732	800	
Asym combined NH <sub>3</sub> ,AlH <sub>3</sub> bend (def)	756-741	730	741-674	709	659
Asym NH <sub>3</sub> ,AlH <sub>3</sub> bend (def)	416-395	386	395-342	373	

<sup>a</sup> As determined from the spectra proposed by the authors of the cited reference.

## As hydrogen carrier

Since the research conducted by Wiberg and May [31], AA has not been experimentally isolated for an in-depth study as a hydrogen carrier. This can be explained by the fact that AA is unstable above -80°C. With this challenge acknowledged, there is thus a significant experimental hurdle to overcome. However, as reported below, theoretical studies (utilizing ab initio molecular orbital theory, for example) have revealed attractive properties.

Grant and Dixon [61] predicted that the intramolecular dehydrogenation of AA into AlH<sub>2</sub>NH<sub>2</sub> is slightly endothermic:



The enthalpy was calculated as +14.6 and +20.9 kJ mol<sup>-1</sup> at -273 and 25 °C respectively, and this aligns well with the value of +16.7 kJ mol<sup>-1</sup> predicted by Davy and Jaffrey [56] and Nguyen et al. [64]. According to Davy and Jaffrey's calculations

[56], the total energy of  $\text{AlH}_2\text{NH}_2$  (with a double bond between Al and N) is between  $-298.725692$  and  $-299.176246$  Hartrees (depending on the ab initio molecular electronic structure method used). Compared to the bond lengths in AA (see above), the Al=N bond of  $\text{AlH}_2\text{NH}_2$  is shorter at  $1.779 \pm 0.007 \text{ \AA}$ , the Al-H bond is slightly shorter, e.g.,  $1.576 \text{ \AA}$ , and the N-H bond is negligibly shortened at  $1.002 \pm 0.003 \text{ \AA}$ .

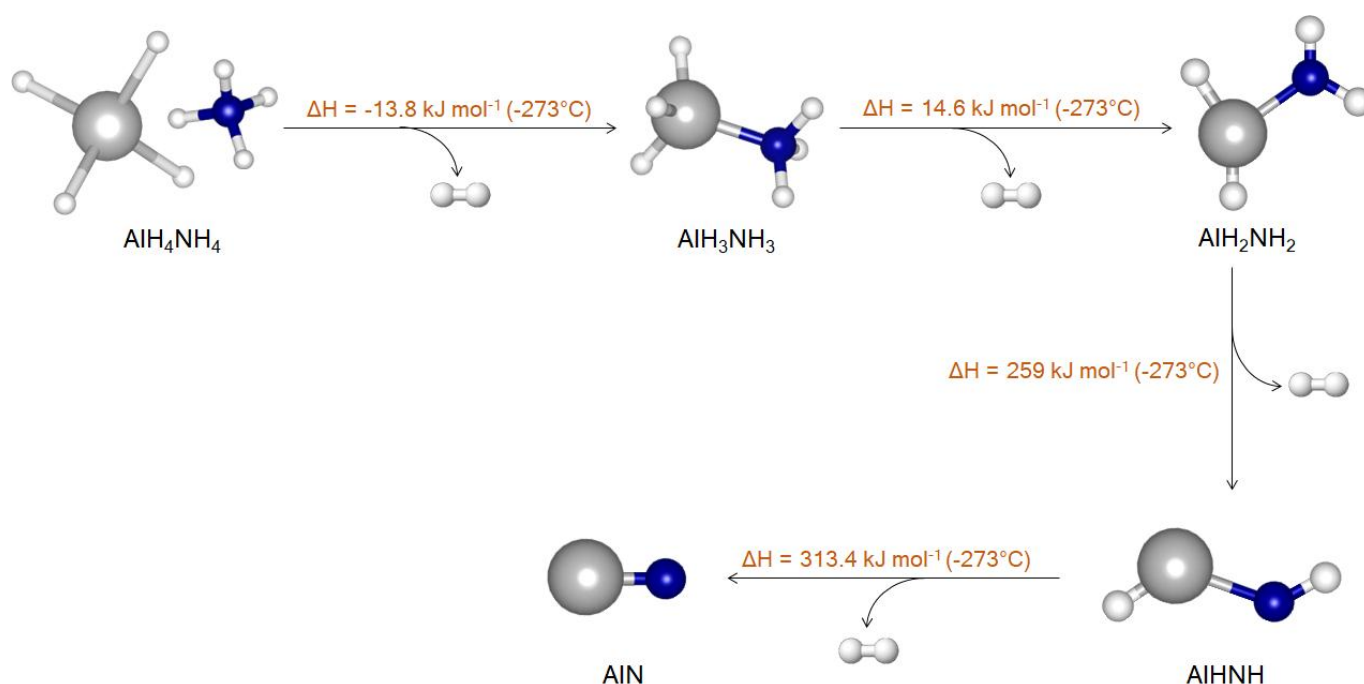
In fact, Grant and Dixon [61] focused on the sequential release of  $\text{H}_2$  from the ammonium alanate salt  $\text{AlH}_4\text{NH}_4$  (Figure 4), where the first step involves the dehydrogenation of  $\text{AlH}_4\text{NH}_4$  into AA:



The enthalpy was calculated as  $-13.8 \text{ kJ mol}^{-1}$  at  $-273 \text{ }^\circ\text{C}$ . The second step involves the dehydrogenation of AA (as mentioned above) with an enthalpy of  $+14.6 \text{ kJ mol}^{-1}$  at  $-273 \text{ }^\circ\text{C}$  (Eq. 10). Subsequently, the as-formed  $\text{AlH}_2\text{NH}_2$  undergoes dehydrogenation in a third step, with an enthalpy of  $+259 \text{ kJ mol}^{-1}$  at  $-273 \text{ }^\circ\text{C}$ :



The third and last step is the dehydrogenation of  $\text{AlHNNH}$  into  $\text{AlN}$ , with an enthalpy of  $+313.4 \text{ kJ mol}^{-1}$  at  $-273 \text{ }^\circ\text{C}$ :

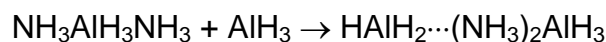


**Figure 4.** Sequential release of  $\text{H}_2$  from the ammonium alanate salt  $\text{AlH}_4\text{NH}_4$ , as predicted by Grant and Dixon [61].

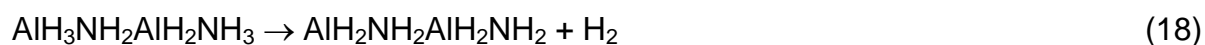
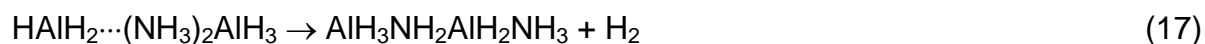
According to Nguyen et al. calculations [64], the decomposition of AA via cleavage of the Al–N bond is slightly more favorable. The resulting AlH<sub>3</sub> then plays a catalytic role in dehydrogenating another AA molecule:



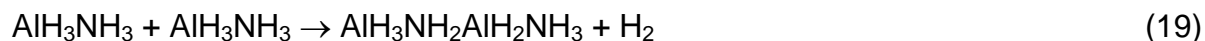
Nguyen et al. [63] proposed another possible pathway occurring upon the decomposition of AA (Eq. 14). It involves the condensation of NH<sub>3</sub> and an AA molecule to form a stable linear species (NH<sub>3</sub>AlH<sub>3</sub>NH<sub>3</sub>). This is followed by the combination of the latter with AlH<sub>3</sub> to produce a cyclic species where two H of AlH<sub>3</sub> form dihydrogen bonds with one H from each NH<sub>3</sub> of NH<sub>3</sub>AlH<sub>3</sub>NH<sub>3</sub>:



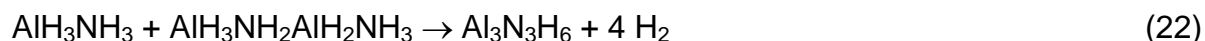
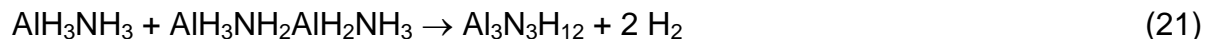
From the aforementioned bicyclic species, hydrogen elimination is predicted to be a facile process:



A last pathway proposed by Nguyen et al. [63] is the intermolecular dehydrogenation (dehydrocoupling):



The dimer AlH<sub>3</sub>NH<sub>2</sub>AlH<sub>2</sub>NH<sub>3</sub> is capable of reacting with another AA. This occurs through a multistep dehydrogenation process that includes the following reactions [65]:



Triaminoalane, cyclotriazane and/or alazine, respectively, are then produced (Figure 5).

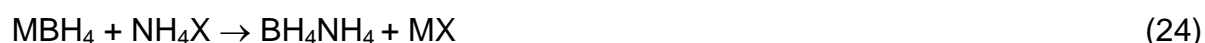
## Comparing ammonia alane to ammonia borane

### Syntheses

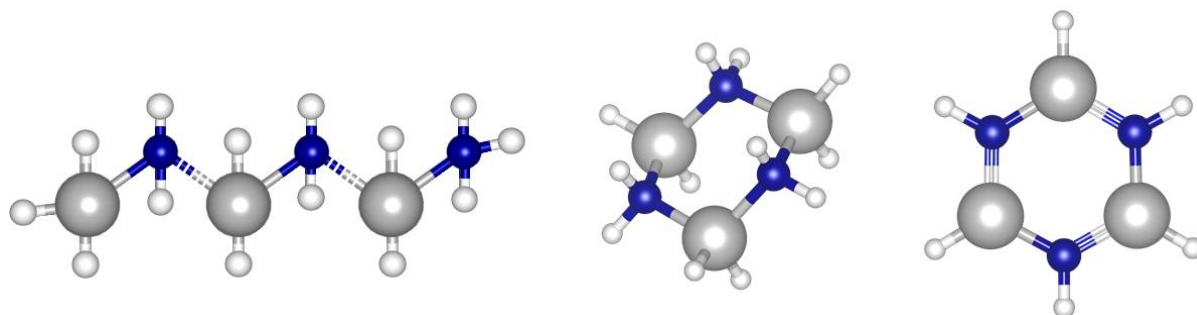
Only the Lewis acid-based reaction between  $\text{AlH}_3$  and  $\text{NH}_3$  (Eq. 1) has been explored as a synthetic route to produce AA, whereas AB can be produced by two different paths. The first one is as the one of AA, where diborane  $\text{B}_2\text{H}_6$ , a Lewis acid, is reacted with  $\text{NH}_3$  in diethyl ether at  $-44\text{ }^\circ\text{C}$  for example [66]:



The second pathway involves a metathesis reaction between a borohydride salt ( $\text{MBH}_4$ ) and an ammonium salt ( $\text{NH}_4\text{X}$  with  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , or  $(\text{NH}_4)_2\text{Y}$  with  $\text{Y} = \text{SO}_4, \text{CO}_3$ ). This reaction occurs in, for example, diethyl ether at  $30\text{ }^\circ\text{C}$ . Finally, there is a spontaneous dehydrogenation of the resulting ammonium borohydride  $\text{NH}_4\text{BH}_4$  [67]:



To isolate  $\text{BH}_4\text{NH}_4$  and to avoid the reaction shown in Eq. 27, the synthesis must be performed at, low temperature, i.e.  $-78\text{ }^\circ\text{C}$ . Indeed,  $\text{BH}_4\text{NH}_4$  is unstable above  $-40\text{ }^\circ\text{C}$  [68]. Otherwise, AB dissolved in diethyl ether is directly produced. After the solvent removal, AB is recovered in the form of a white solid that is crystalline (orthorhombic structure with space group  $Pmn2_1$  below  $-48\text{ }^\circ\text{C}$ , and tetragonal structure with space group  $I4mm$  at higher temperatures [69]). On the contrary, the crystal structure of AA is still unknown.



**Figure 5.** Triaminoalane, cyclotriazane and alazine, respectively.

As  $\text{MAIH}_4$  is analogous to  $\text{MBH}_4$ , another potential path to produce AA could involve the reaction of  $\text{MAIH}_4$  with an ammonium salt, like for AB:



As discussed earlier, the reaction between  $\text{MAIH}_4$  and  $\text{NH}_4\text{X}$  has been explored and reported elsewhere; however, the goal was not to produce AA [51-54].  $\text{MAIH}_4$  and

$\text{NH}_4\text{X}$ , both in solid state, react at 170 °C to release  $\text{H}_2$ , and form PIA and MX (Eq. 9). When a solvent, such as diethyl ether, is introduced to solubilize one of the two reactants, the reaction between  $\text{MAI}\text{H}_4$  and  $\text{NH}_4\text{X}$  takes place at 25 °C and even at lower temperatures, such as –40 °C, yielding the same products. However, to isolate AA, it is necessary to operate at temperatures lower than –80 °C [31]. Such low temperatures can influence the kinetics and potentially the yields, depending on the reaction times. This also necessitates using a solvent that remains liquid below –80 °C and can solubilize AA (crucial for its separation from MX) or MX (if a suitable solvent for AA cannot be found). For instance, Janik and Paine [50] showed that diethyl ether (m.p. –116 °C) is a suitable solvent for dissolving LiBr, which is formed upon reaction of  $\text{LiAlH}_4$  and  $\text{NH}_4\text{Br}$ . Diethyl ether, as initially reported by Wiberg and May [31], does not solubilize AA (that precipitates). Based on our recent experiments, diethyl ether remains the solvent of choice.

It is worth mentioning that Gutowsk and Autrey [70] computationally predicted the crystal structure of  $\text{BH}_4\text{NH}_4$  (Eq. 24) and  $\text{AlH}_4\text{NH}_4$  (Eq. 26), both being potential hydrogen carriers at subzero temperature conditions (as discussed hereafter). The former one would have a stable zinc blende ZnS structure while the latter a wurtzite one.

### Thermal and chemical stability

As a precipitate in diethyl ether, AA is unstable and undergoes dehydrogenation above –80°C (Figure 6). The three equivalents of  $\text{H}_2$  are released one after the other, respectively at about –30 °C, room temperature, and above 100 °C. This leads to the formation of PAA, PIA, and AIN respectively [31]. The thermal stability of AA differs significantly from that of AB (Figure 6). In the solid state, temperatures above 80 °C are required to initiate the intermolecular dehydrogenation of AB, which proceeds stepwise up to approximately 200 °C for the release of the first two equivalents of  $\text{H}_2$  [19]. The third equivalent is released above 200 °C [71]. The difference in behavior between AA and AB is fundamental, especially in the context of their potential use as hydrogen carrier, with the latter being extensively studied. This is analyzed hereafter.

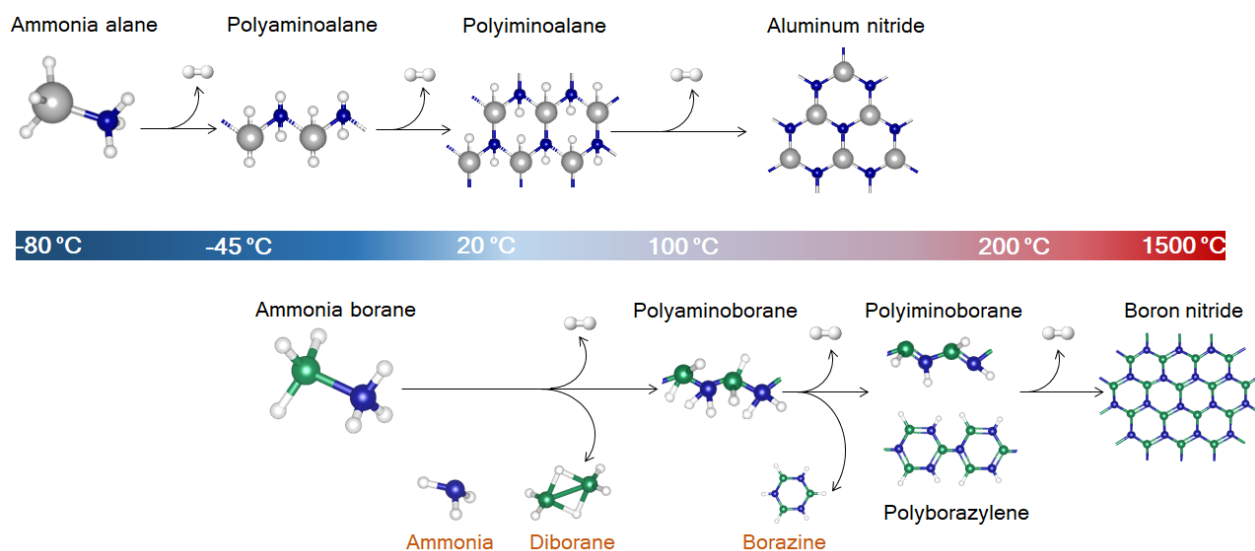
AA, PAA and PIA (Eq. 2 and 3, and denoted  $\text{AlNH}_x$  for brevity in Eq. 29 below) are unstable against a Brønsted acid (e.g. HCl) attack [31]. They mineralize such as:



Both AA and AB are thus unstable in the presence of protons. In the case of the latter, this has garnered significant attention to produce  $\text{H}_2$  at low temperatures, both in the presence [72] and absence [73] of water. A typical example is the  $\text{H}^+$ -catalyzed hydrolysis of AB [72]:



The hydrolysis of AB to produce  $\text{H}_2$  at 20-30 °C has been deeply investigated within the last two decades, thanks to the simplicity of the reaction and a theoretical gravimetric hydrogen storage capacity of 7.1 wt% (taking into account the weight of water) [74]. In contrast, the hydrolysis of AA to produce  $\text{H}_2$  does not seem realistic and relevant. This is primarily due to its instability above -80 °C, and because the fact that AA does not offer any advantages over AB. In any case, the hydrolysis of both AA and AB is not practical when compared to other candidates, such as  $\text{NaBH}_4$ .



**Figure 6.** Ammonia alane versus ammonia borane: temperature range of stability, and species forming upon dehydrogenation up to the formation of the aluminum and boron nitrides at high temperature.

## Properties of the molecules

Quoting Marsh et al. [55], “the resemblance of AA to the related compound AB is quite strong” (Figure 3). Leboeuf et al. [57] predicted comparable dipole moments



with 5.51-5.53 D for AA and 5.44-5.61 D for AB. The calculated N–H bond lengths are also comparable, with N–H  $1.010 \pm 0.019$  Å for AA [55,57,59,60] and  $1.023 \pm 0.005$  Å for AB [57,59,60]. With respect to the other bonds, they are predicted to be longer in the case of AA, which agrees with the bigger size of the aluminum element versus boron: Al–H  $1.599 \pm 0.016$  Å [55,57,59,60] and B–H  $1.214 \pm 0.008$  Å [57,59,60]; Al–N  $2.096 \pm 0.035$  Å [55,57,59,60] and B–N  $1.682 \pm 0.058$  Å [57,59,60]. Accordingly, the distance of approximately 3 Å between H of AlH<sub>3</sub> and H of NH<sub>3</sub> in AA is longer than the distance of 2.56 Å between H of BH<sub>3</sub> and H of NH<sub>3</sub> in AB [59].

When the predicted atomic charges for AA and AB are compared, both similarities and differences emerge [59]. For instance, the charges of N and N(H) are quite similar: N is –1.02 for AA and –0.80 for AB, and H(N) is 0.39 for both molecules. The charges of H(Al) and H(B) are both negative, with values of –0.41 and –0.07 respectively, but H(Al) is more hydridic. The charges of Al and B differ, with Al being positive at 1.06 and B slightly negative at –0.16 (considering that B ( $\chi$  2.04) is less electronegative than Al ( $\chi$  1.61)). Combining these findings, Czerw et al. [59] concluded that the bonding of AlH<sub>3</sub> with NH<sub>3</sub> in AA is predominantly electrostatic and that the geometric/steric effect are insignificant. In contrast, the bonding of BH<sub>3</sub> with NH<sub>3</sub> in AB exhibits a much greater dative character and a higher covalent nature. This corroborates a slightly higher dissociation energy of the N–B bond for AB. For instance, Leboeuf et al. [57], using a Gaussian density functional method, calculated dissociation energies of 145.2-215.9 kJ mol<sup>–1</sup> for AB and 126.4-167.4 kJ mol<sup>–1</sup> for AA.

Another consequence of the more hydridic character of hydrogens in AA is that the H(Al) exhibit higher reactivity than H(B) in AB and are more prone to react with H(N) [75]. This aligns with the lower thermal stability of AA.

### **As hydrogen carriers**

There is limited experimental data supporting the potential use of AA as a hydrogen carrier, with the only available data published by Wiberg and May [31]. Nevertheless, theoretical studies offer avenues for analysis.

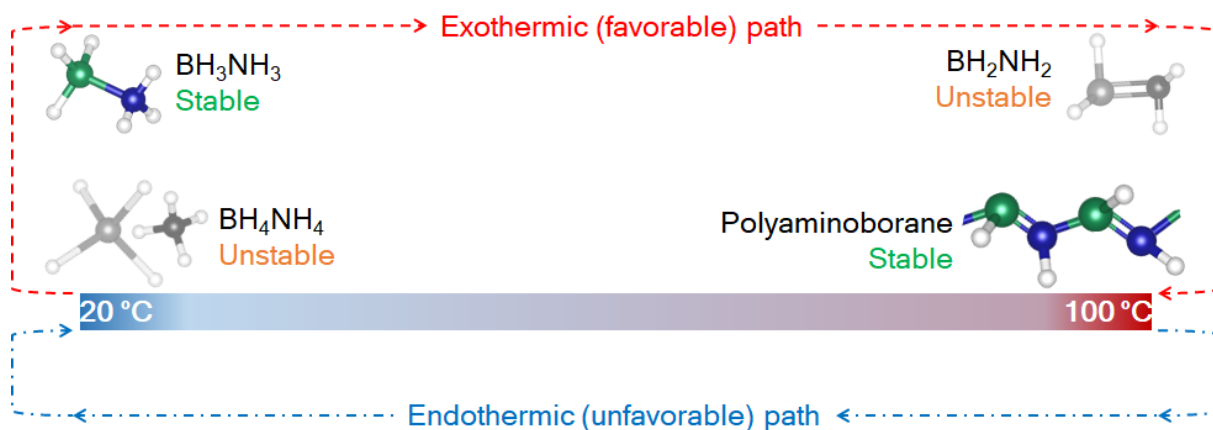
At first glance, the instability of AA above  $-80\text{ }^{\circ}\text{C}$  appears problematic. However, this instability provides an advantage in terms of thermodynamics to rehydrogenate its dehydrogenated forms. As mentioned earlier, the predicted enthalpy of hydrogenation of  $\text{AlH}_2\text{NH}_2$  is negative ( $-16.7\text{ kJ mol}^{-1}$ ) [56]. In other words, the release of  $\text{H}_2$  from AA, particularly the first equivalent of  $\text{H}_2$ , is reversible. In contrast with AB, the calculated enthalpy of hydrogenation of  $\text{BH}_2\text{NH}_2$  is positive, ranging between  $20.9$  and  $33.1\text{ kJ mol}^{-1}$  [56]. The release of the first equivalent of  $\text{H}_2$  from AB is exothermic as measured experimentally, confirming the irreversibility of the dehydrogenation reaction [20]. More broadly, the rehydrogenation of the polymers stemming from AB dehydrogenation by using only  $\text{H}_2$  has not been demonstrated yet. However, the AB polymers (mainly polyborazylene) can be recycled (i.e. chemically transformed) to regenerate AB; this can be done via chemical processes involving acid digestion or hydrazine reduction [76]. It is also worth mentioning that boron nitride has been reported to be hydrogenated under  $\text{H}_2$  pressure [77] or by reaction with lithium hydride [78].

When heated above  $80\text{ }^{\circ}\text{C}$ , neat AB decomposes rather than undergoing dehydrogenation (Figure 6). Unwanted gases such as  $\text{NH}_3$  and  $\text{B}_3\text{N}_3\text{H}_6$  (along with  $\text{H}_2$ ) are produced [20], which represent a major limitation to the development of neat AB as a hydrogen carrier. With respect to AA, PAA and PIA [31,50], they do not produce any byproduct at lower temperatures. Our recent experiments confirm this observation for temperatures up to  $300\text{ }^{\circ}\text{C}$ . Indeed, we observed the release of  $\text{NH}_3$  when PAA and PIA were heated above  $300^{\circ}\text{C}$ . In summary, AA and its polymers release pure  $\text{H}_2$  below  $200\text{ }^{\circ}\text{C}$ . Semenenko et al. [75], who surveyed the study of Wiberg and May cited above, stressed on this point. They pointed out that aluminum is less inclined to form double bonds due to its specific electronic configuration with incomplete 3p orbitals. This element is expected to form three covalent bonds and thus an Al-N network, as seen in PAA and PIA (Figure 2). This means that decomposition products with double bonds would not form. In other words, the only reaction occurring by heating AA above  $-80\text{ }^{\circ}\text{C}$  would be intermolecular dehydrogenation, resulting in the release of pure  $\text{H}_2$ . This is a significant advantage over AB.

As things stand, it would be inappropriate to not consider the possibility of other reactions such as those predicted by Nguyen et al. [63,65] that lead to linear and cyclic trimers of AA (Eq. 14 to 22; Figure 5). In this scenario, AA would encounter the same issues as neat AB (as discussed above).

Grant and Dixon [61] predicted that  $\text{AlH}_4\text{NH}_4$  is a potential hydrogen carrier. It dehydrogenates in AA (Eq. 11), which then dehydrogenates in  $\text{AlH}_2\text{NH}_2$  (Eq. 10), and both steps are predicted to be almost thermoneutral. This is an attractive feature for hydrogen carriers, knowing besides that  $\text{AlH}_4\text{NH}_4$  has theoretical gravimetric and volumetric hydrogen densities of 16.4 wt% H and  $108.7 \text{ g(H) L}^{-1}$  (the latter value being calculated using the density of  $0.663 \text{ g cm}^{-3}$  as predicted elsewhere [70]). By extrapolation, one could expect, at the material level, hydrogen storage capacities of about 8.2 wt% and  $54.4 \text{ g(H) L}^{-1}$  for the sequence  $\text{AlH}_4\text{NH}_4 \leftrightarrow \text{AlH}_3\text{NH}_3 \leftrightarrow \text{AlH}_2\text{NH}_2$ ; furthermore, each step would be potentially reversible owing to the predicted favorable thermodynamics (Figure 4). This would require, however, operating at temperatures below  $-80^\circ\text{C}$  for both  $\text{AlH}_4\text{NH}_4$  and  $\text{AlH}_3\text{NH}_3$ .

$\text{AlH}_4\text{NH}_4$  has never been synthesized, and the question of its thermal stability arises (considering that AA is only stable below  $-80^\circ\text{C}$ ). Another uncertainty concerning  $\text{AlH}_2\text{NH}_2$  is that its formation (Eq. 10) is hypothetical. It has never been isolated. In contrast, Wiberg and May [31] isolated PAA (Eq. 2) after the release of the first equivalent of  $\text{H}_2$  from AA. Hydrogenation of this polymer is most likely tricky, i.e., is thermodynamically less favorable than that of the monomer  $\text{AlH}_2\text{NH}_2$ . We can draw a parallel with AB (Figure 7):  $\text{BH}_4\text{NH}_4$  has been little or not considered as a hydrogen carrier due to its instability above  $-40^\circ\text{C}$  [68];  $\text{BH}_2\text{NH}_2$  is unstable, thereby spontaneously polymerizing into polyaminoborane [79]; and the uptake of  $\text{H}_2$  by polyaminoborane is endothermic and thus unfavorable [20].



**Figure 7.** From ammonium borohydride, unstable at 20 °C, to polyaminoborane, via the formation of ammonia borane, stable below 80 °C, and the unstable aminoborane.

## Discussion

We thus have AA and AB, two materials that have distinct advantages and constraints (**Figures 4** and **6**). (i) AA is stable below  $-80$  °C and must be kept at these temperatures, while AB is stable up to  $80$  °C. (ii) AA is synthesized under restrictive conditions, at temperatures lower than  $-80$  °C, while AB is synthesized at  $20$ - $30$  °C. (iii) AA releases its first equivalent of  $H_2$  between  $-80$  and  $-30$  °C, and the reaction is predicted to be slightly endothermic, while AB releases its first equivalent of  $H_2$  between  $80$  and  $120$  °C, and the reaction is exothermic. (iv)  $AlH_2NH_2$  could be hydrogenated as the reaction is predicted to be slightly exothermic whereas hydrogen storage is irreversible with AB. (v) AA releases pure  $H_2$ , while AB decomposes into  $H_2$  and unwanted gaseous products. In other words, there is a dilemma with AA and AB: the former is unstable above  $-80$  °C but it could allow a reversible hydrogen storage, and the latter is stable but its thermodynamics are against reversible hydrogen storage.

Conducting additional experimental studies with AA is essential for gaining a deeper understanding of its properties and potential. This forms the core of our current focus and recent experimental initiatives. We aim to address the following key questions: Is there one or more ways to stabilize AA above  $-80$  °C? Does  $AlH_2NH_2$  form? What is the enthalpy of each dehydrogenation step measured by calorimetry? Are PAA and

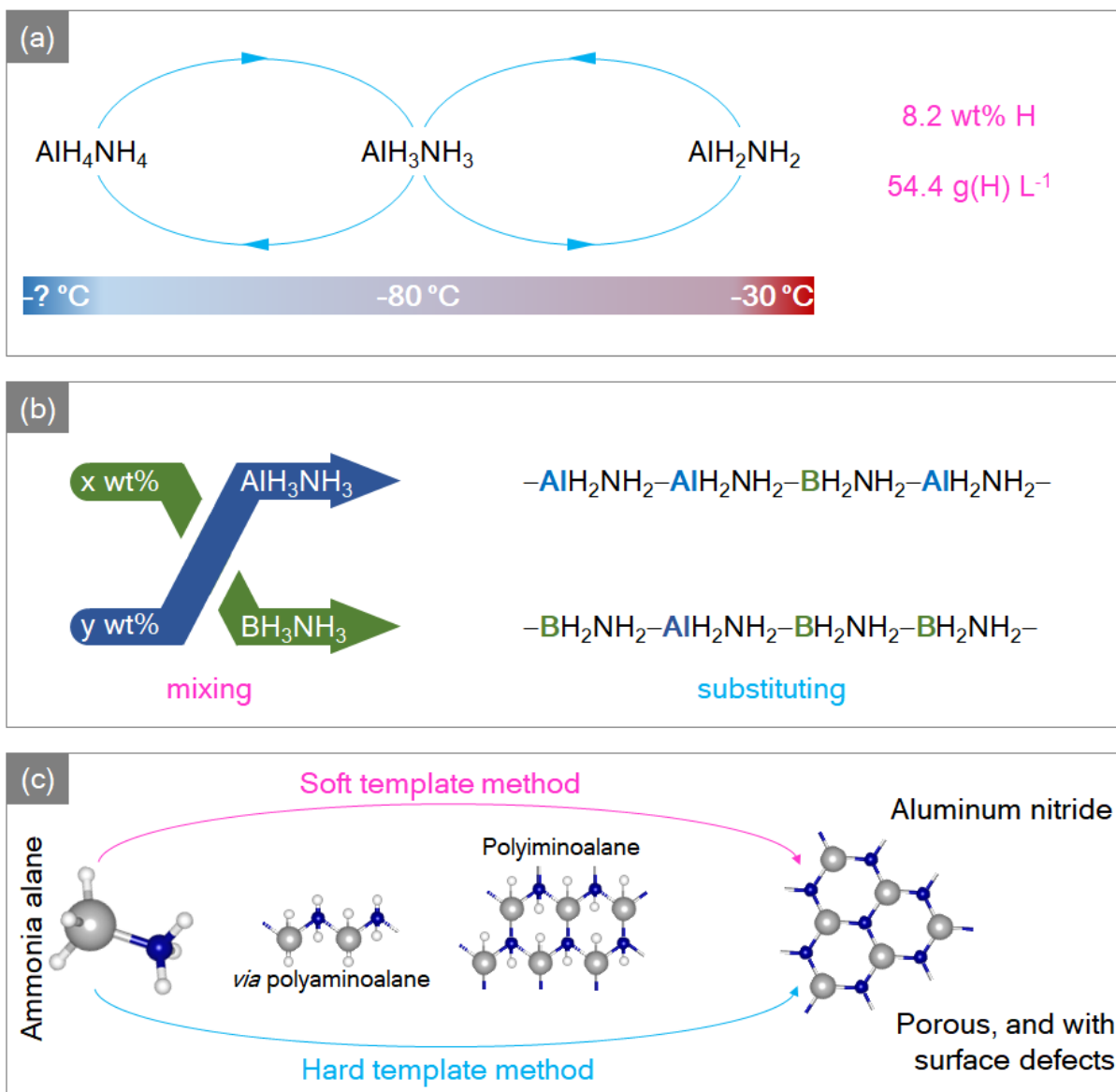
PIA hydrogenated under H<sub>2</sub> pressure, making hydrogen storage with AA (partially or entirely) reversible?

It would be also interesting to attempt the synthesis and isolation of AlH<sub>4</sub>NH<sub>4</sub>, in order to gain a better understanding of AA through the dehydrogenation of AlH<sub>4</sub>NH<sub>4</sub>, and then explore the potential of the sequence AlH<sub>4</sub>NH<sub>4</sub>↔AlH<sub>3</sub>NH<sub>3</sub>↔AlH<sub>2</sub>NH<sub>2</sub> occurring at subzero conditions (**Figure 4**). Today, cryogenics is an option for storing H<sub>2</sub>, either liquefied (−253 °C) [2] or cryoadsorbed on the surface of highly porous materials (−196 °C for most) [6], and tomorrow cryogenics could be an option for reversibly storing hydrogen at effective capacities of 8.2 wt% H and 54.4 g(H) L<sup>−1</sup> via the AlH<sub>4</sub>NH<sub>4</sub>↔AlH<sub>3</sub>NH<sub>3</sub>↔AlH<sub>2</sub>NH<sub>2</sub> sequence (**Figure 8a**). A first step towards an AA-based system for hydrogen storage is to find a practical synthetic route to obtain a pure compound. If the dehydrogenation reaction is truly reversible, this would facilitate the management and storage of the product. This could make sense, regardless the complexity of implementation.

Considering the points (i) to (v) mentioned above, an alternative solution might involve a material that combines the advantages of both AA and AB. This approach might offer new perspectives. Perhaps an initial step would be to mix AB and AA at various contents and analyze their thermal stability, and a second step would be to substitute a fraction of boron in an AB-based oligomer with aluminum or a fraction of aluminum of an AA-based oligomer with boron (**Figure 8b**). We could also consider the case to stabilizing AA by modifying its structure. For instance, the purpose of the chemical modification of AB is to destabilize it. However, the magnesium derivative of AB (and of hydrazine borane as well) exhibits a higher thermal stability than the parent borane [80,81]. This is likely due to the large Pauling electronegativity of the Mg atom. Would it be possible to stabilize the molecule by synthesizing a virtual magnesium derivative of AA?

There may be another way of using AA. On the one hand, Wiberg and May [32] demonstrated that AA is a precursor for AlN synthesis upon pyrolysis at elevated temperatures. Janik and Paine [50] confirmed this, even though the precursor they used was PIA. On the other hand, computational calculations focusing on AlN

nanostructures (e.g. nanowires, nanosheets, nanocages, etc.) predicted that AlN have the potential to be used as medium for the reversible storage of H<sub>2</sub>. AlN would offer unsaturated aluminum sites that are capable of binding one H<sub>2</sub> molecule [82], and/or nitrogen sites that can adsorb two H<sub>2</sub> molecules [83]. To our knowledge, no experimental study on AlN nanostructures has been published to date. The only study available involves a systematic examination of dense nitrides, including AlN (commercial, with a purity of 99.9%). The nitrides were ball-milled (at 400 rpm) for 20 h under H<sub>2</sub> (10 bar) at 23 °C [84]. AlN (for which textural properties were not determined) adsorbed 0.4 wt% H<sub>2</sub>. The presence of N–H bonds was confirmed by infrared spectroscopy, indicating hydrogenation of the nitrogen sites with possible formation of imides, according to the authors. This study, while interesting, is limited to dense ball-milled AlN. It, nevertheless, suggests encouraging prospects for (highly) porous AlN with surface defects (Figure 8c). These AlN-based structures could be synthesized using AA, PAA and/or PIA as a precursor and by using the soft or hard templating method.



**Figure 8.** Research perspectives offered by ammonia alane for developing alternative solutions for hydrogen storage: (a) the sequence  $\text{AlH}_4\text{NH}_4 \leftrightarrow \text{AlH}_3\text{NH}_3 \leftrightarrow \text{AlH}_2\text{NH}_2$  at subzero conditions; (b) mixing ammonia alane and ammonia borane, towards the substitution of aluminum by boron in an AlNH oligomer; (c) ammonia alane as precursor of porous aluminum nitride.

## Conclusion

Both ammonia alane  $\text{AlH}_3\text{NH}_3$  (AA, with 12.86 wt% H) and ammonia borane  $\text{BH}_3\text{NH}_3$  (AB, with 19.6 wt% H) are potential hydrogen carriers. However, there is a dilemma with AA and AB: AA is unstable above  $-80\text{ }^\circ\text{C}$  but could potentially allow for reversible hydrogen storage, whereas AB is stable at room temperature, but its thermodynamics are against reversible hydrogen storage. Conducting additional experimental studies with AA is thus essential for gaining a deeper understanding of

its properties as hydrogen carrier. Otherwise, the computational studies conducted to date suggest exploring the pathway leading to ammonium alanate  $\text{AlH}_4\text{NH}_4$ , specifically the sequence  $\text{AlH}_4\text{NH}_4 \leftrightarrow \text{AlH}_3\text{NH}_3 \leftrightarrow \text{AlH}_2\text{NH}_2$  associated to the reversible release and uptake of two equivalents of  $\text{H}_2$  (i.e. 8.2 wt% H) at subzero conditions. Additionally, we propose two other avenues to explore: focusing on a material that combines the advantages of both AA and AB such as an AA-based oligomer where some aluminum is substituted by boron; and, using AA as a precursor of AlN (porous and with surface defects) to be considered as a sorbent for  $\text{H}_2$  storage.

Our group is currently conducting experimental work, which has enabled us to include above, information related to our growing experience with AA and related materials. In this context, another objective of this review article is to pique the interest of other research groups to explore AA and discover new derivatives, thereby expanding our collective knowledge of these materials.

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## References

- [1] Elberry AM, Thakur J, Santasalo-Aarnia A, Larmi M. Large-scale compressed hydrogen storage as part of renewable electricity storage systems. *Int J Hydrogen Energy* 2021;46:15671-90. <https://doi.org/10.1016/j.ijhydene.2021.02.080>
- [2] Faye O, Szpunar J, Eduok U. A critical review on the current technologies for the generation, storage, and transportation of hydrogen. *Int J Hydrogen Energy* 2022;47:13771-802. <https://doi.org/10.1016/j.ijhydene.2022.02.112>
- [3] Tawalbeh M, Murtaza SZM, Al-Othman A, Alami AH, Singh K, Olabi AG. Ammonia: A versatile candidate for the use in energy storage systems. *Renew Energy* 2022;194:955-77. <https://doi.org/10.1016/j.renene.2022.06.015>
- [4] Sathe RY, Kumar TJD, Ahuja R. Furtherance of the material-based hydrogen storage based on theory and experiments. *Int J Hydrogen Energy* 2023;48:12767-95. <https://doi.org/10.1016/j.ijhydene.2022.11.306>
- [5] D'Ambra F, Gébel G. Literature review: state-of-the-art hydrogen storage technologies and Liquid Organic Hydrogen Carrier (LOHC) development. *Sci Technol Energy Transit* 2023;78:32. <https://doi.org/10.2516/stet/2023029>
- [6] Ramirez-Vidal P, Sdanghi G, Celzard A, Fierro V. High hydrogen release by cryo-adsorption and compression on porous materials. *Int J Hydrogen Energy* 2022;47:8892-8915. <https://doi.org/10.1016/j.ijhydene.2021.12.235>
- [7] Lai Q, Sun Y, Wang T, Modi P, Cazorla C, Demirci UB, Ares Fernandez JR, et al. How to design hydrogen storage materials? Fundamentals, synthesis, and storage tanks. *Adv Sust Syst* 2019;3:1900043. <https://doi.org/10.1002/adsu.201900043>
- [8] Hirscher M, Yartys VA, Baricco, von Colbe JB, Blanchard D, Bowman Jr RC, Broom DP, et al. Materials for hydrogen-based energy storage – past, recent

progress and future outlook. *J Alloys Compd* 2020;827:153548. <https://doi.org/10.1016/j.jallcom.2019.153548>

[9] Graetz J, Reilly JJ, Yartys VA, Maehlen JP, Bulychev BM, Antonov VE, Tarasov BP, Gabis IE. Aluminum hydride as a hydrogen and energy storage material: Past, present and future. *J Alloys Compd* 2011;509:5517-28. <https://doi.org/10.1016/j.jallcom.2010.11.115>

[10] Kumar R, Karkamkar A, Bowden M, Autrey T. Solid-state hydrogen rich boron–nitrogen compounds for energy storage. *Chem Soc Rev* 2019;48:5350-80. <https://doi.org/10.1039/C9CS00442D>

[11] Milanese C, Jensen TR, Hauback BC, Pistidda C, Dornheim M, Yang H, Lombardo L, et al. Complex hydrides for hydrogen storage. *Int J Hydrogen Energy* 2019;44:7860-74. <https://doi.org/10.1016/j.ijhydene.2018.11.208>

[12] Milanese C, Garroni S, Gennari F, Marini A, Klassen T, Dornheim M, Pistidda C. Solid state hydrogen storage in alanates and alanate-based compounds: A review. *Metals* 2018;8:567. <https://doi.org/10.3390/met8080567>

[13] Suarez-Alcantara K, Tena-Garcia JR, Guerrero-Ortiz R. Alanates, a comprehensive review. *Materials* 2019;12:2724. <https://doi.org/10.3390/ma12172724>

[14] Zhao L, Xu F, Zhang C, Wang Z, Ju H, Gao X, Zhang X, et al. Enhanced hydrogen storage of alanates: Recent progress and future perspectives. *Int J Hydrogen Energy* 2021;31:165-79. <https://doi.org/10.1016/j.pnsc.2021.01.007>

[15] Yang H, Lombardo L, Luo W, Kim W, Züttel A. Hydrogen storage properties of various carbon supported NaBH<sub>4</sub> prepared via metathesis. *Int J Hydrogen Energy* 2018;43:7108-16. <https://doi.org/10.1016/j.ijhydene.2018.02.142>

[16] Abdelhamid HN. A review on hydrogen generation from the hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2021;46:726-65. <https://doi.org/10.1016/j.ijhydene.2020.09.186>

[17] Demirci UB. Exploring the technological maturity of hydrogen production by hydrolysis of sodium borohydride. *Int J Hydrogen Energy* 2023;48:29682-98. <https://doi.org/10.1016/j.ijhydene.2023.04.176>

[18] Singh R. Reversible chemical hydrogen storage in borohydrides via thermolysis and hydrolysis: Recent advances, challenges, and perspectives. *Int J Hydrogen Energy* 2022;47:26549-73. <https://doi.org/10.1016/j.ijhydene.2021.10.022>

[19] Petit JF, Miele P, Demirci UB. Ammonia borane  $H_3N-BH_3$  for solid-state chemical hydrogen storage: different samples with different thermal behaviors. *Int J Hydrogen Energy* 2016;41:15462-70. <https://doi.org/10.1016/j.ijhydene.2016.06.097>

[20] Baitalow F, Baumann J, Wolf G, Jaenicke-Rössler K, Leitner G. Thermal decomposition of B-N-H compounds investigated by using combined thermoanalytical methods. *Thermochim Acta* 2002;391:159-68. [https://doi.org/10.1016/S0040-6031\(02\)00173-9](https://doi.org/10.1016/S0040-6031(02)00173-9)

[21] Demirci UB. Ammonia borane, a material with exceptional properties for chemical hydrogen storage. *Int J Hydrogen Energy* 2017;42:9978-10013. <https://doi.org/10.1016/j.ijhydene.2017.01.154>

[22] Li H, Yan Y, Feng S, Chen Y, Fan H. Ammonia borane and its applications in the advanced energy technology. *J Energy Resour Technol* 2021;143:110801. <https://doi.org/10.1115/1.4049929>

[23] Liu SS, Zhang Y, Sun LX, Zhang J, Zhao JN, Xu F, Huang FL. The dehydrogenation performance and reaction mechanisms of  $Li_3AlH_6$  with  $TiF_3$  additive. *Int J Hydrogen Energy* 2010;35:4554-61. <https://doi.org/10.1016/j.ijhydene.2009.12.108>

[24] Ding Z, Li S, Zhou Y, Chen Z, Yang W, Ma W, Shaw L.  $LiBH_4$  for hydrogen storage – New perspectives. *Nano Mater Sci* 2020;2:109-19. <https://doi.org/10.1016/j.nanoms.2019.09.003>

[25] Jiang W, Wang H, Zhu M.  $\text{AlH}_3$  as a hydrogen storage material: Recent advances, prospects and challenges. *Rare Met* 2021;40:3337-3356. <https://doi.org/10.1007/s12598-021-01769-2>

[26] Schlesinger HI, Burg AB. Recent developments in the chemistry of the boron hydrides. *Chem Rev* 1942;31:1-41. <https://doi.org/10.1021/cr60098a001>

[27] Staubitz A, Robertson APM, Sloan ME, Manners I. Amine- and phosphane-borane adducts: New interest in old molecules. *Chem Rev* 2010;110:4023-78. <https://doi.org/10.1021/cr100105a>

[28] Liu H, Zhang L, Ma H, Lu C, Luo H, Wang X, Huang X, et al. Aluminum hydride for solid-state hydrogen storage: Structure, synthesis, thermodynamics, kinetics, and regeneration. *J Energy Chem* 2021;52:428-40. <https://doi.org/10.1016/j.jechem.2020.02.008>

[29] Lacina D, Wegrzyn J, Reilly J, Celebi Y and Graetz J. Regeneration of aluminium hydride using dimethylethylamine, *Energy Environ. Sci.* 2010;3:1099-1105. <https://doi.org/10.1039/c002064h>

[30] Graetz J, Chaudhuri S, Wegrzyn J, Celebi Y, Johnson JR, Zhou W, Reilly JJ. Direct and reversible synthesis of  $\text{AlH}_3$ -triethylenediamine from Al and  $\text{H}_2$ . *J Phys Chem C* 2007;111:19148-52. <https://doi.org/10.1021/jp076804j>

[31] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. I. Versuche zur darstellung eines borazol-homologen "alazols"  $\text{Al}_3\text{N}_3\text{H}_6$ . *Z Naturforsch B* 1955;10:229-30. <https://doi.org/10.1515/znb-1955-0409>

[32] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. II. Zur kenntnis eines aluminiumtriamids  $\text{Al}(\text{NH}_2)_3$ . *Z Naturforsch B* 1955;10:230-32. <https://doi.org/10.1515/znb-1955-0410>

[33] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. III. Versuche zur darstellung eines trimethyl-alazols ( $\text{AlHNR}_3$ )<sub>3</sub>. Z Naturforschg B 1955;10:232-34. <https://doi.org/10.1515/znb-1955-0411>

[34] Wiberg E, Graf H, Uson R. Über monomeren Aluminiumwasserstoff  $\text{AlH}_3$ . Z. Anorg. Allg. Chem. 1953;272:221-32. <https://doi.org/10.1002/zaac.19532720124>

[35] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. V. Das verhalten von aluminiumwasserstoff gegenüber pyridin. Z Naturforschg B 1955;10:236-37. <https://doi.org/10.1515/znb-1955-0413>

[36] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. VI. Zur kenntnis von alazanen des typus  $\text{AlH}_3\cdot\text{NR}_3$ . Z Naturforschg B 1955;10:237-38. <https://doi.org/10.1515/znb-1955-0414>

[37] Wiberg E, May A. Notizen: Über die umsetzung von aluminiumwasserstoff mit ammoniak und aminen. IV. Zur kenntnis einer verbindungsreihe  $\text{AlH}_3\cdot n[\text{N}(\text{CH}_3)_2]_n$ . Z Naturforschg B 1955;10:234-35. <https://doi.org/10.1515/znb-1955-0412>

[38] Ruff JK, Hawthorne MF. The amine complexes of aluminum hydride. I. J Am Chem Soc 1960;82:2141-4. <https://doi.org/10.1021/ja01494a013>

[39] Ehrlich R, Young AR, Lichstein BM, Perry DD. The chemistry of alane. I. Some observations on the effect of the coordinating base on the aluminum-hydrogen absorption in the infrared. Inorg Chem 1963;2:650-2. <https://doi.org/10.1021/ic50007a064>

[40] Marsh CMB, Schaefer III HF. Trimethylamine alane and its dissociation products. J Phys Chem 1995;99:195-206. <https://doi.org/10.1021/j100001a033>

[41] Laubengayer AW, Wade K, Lengnick G. Aluminum-nitrogen polymers. The formation and condensation of adducts of triphenylalane with methylamine and dimethylamine. Inorg Chem 1962;1:632-7. <https://doi.org/10.1021/ic50003a036>

[42] Fetter NR, Bartocha B, Brinckman Jr FE, Moore DW. Some reactions of organoaluminum compounds with nitrogen-containing bases. *Can J Chem* 1963;41:1359-67. <https://doi.org/10.1139/v63-186>

[43] Marlett EM, Park WS. Dimethylethylamine-alane and *N*-methylpyrrolidine-alane. A convenient synthesis of alane, a useful selective reducing agent in organic synthesis. *J Org Chem* 1990;55:2968-9. <https://doi.org/10.1021/jo00296a078>

[44] Ehrlich R, Young II AR, Lichstein BM, Perry DD. The chemistry of alane. II. Polyiminoalanes. *Inorg Chem* 1964;3:628-31. <https://doi.org/10.1021/ic50015a004>

[45] Li H, Meziani MJ, Kitaygorodskiy A, Lu F, Bunker CE, Shiral Fernando KA, Guliants EA, Sun YP. Preparation and characterization of alane complexes for energy applications. *J Phys Chem C* 2010;114:3318-22. <https://doi.org/10.1021/jp911859z>

[46] Wong BM, Lacina D, Nielsen IMB, Graetz J, Allendorf MD. Thermochemistry of alane complexes for hydrogen storage: A theoretical and experimental investigation. *J Phys Chem C* 2011;115:7778-86. <https://doi.org/10.1021/jp112258s>

[47] Ni C, Yang L, Muckerman JT, Graetz. Aluminum hydride separation using *N*-alkylmorpholine. *J Phys Chem C* 2013;117:14983-91. <https://doi.org/10.1021/jp404397v>

[48] Ochi A, Kent Bowen H, Rhine WE. The synthesis of aluminum nitride from aluminum hydride. *Mater Res Soc Symp Proc* 1988;121:663-6. <https://doi.org/10.1557/PROC-121-663>

[49] Maya L. Synthetic approaches to aluminum nitride via pyrolysis of a precursor. *Adv Ceram Mater* 1986;1:150-3. <https://doi.org/10.1111/j.1551-2916.1986.tb00007.x>

[50] Janik JF, Paine RT. The systems  $\text{LiAlH}_4/\text{NH}_4\text{X}$  and  $\text{N}_2\text{H}_5\text{Cl}$  as precursor sources for AlN. *J Organomet Chem* 1993;449:39-44. [https://doi.org/10.1016/0022-328X\(93\)80104-J](https://doi.org/10.1016/0022-328X(93)80104-J)

- [51] Zhang H, Loo YS, Geerlings H, Lin J, Chin WS. Hydrogen production from solid reactions between  $\text{LiAlH}_4$  and  $\text{NH}_4\text{Cl}$ . *Int J Hydrogen Energy* 2010;356:176-80. <https://doi.org/10.1016/j.ijhydene.2009.10.070>
- [52] Zheng X, Zheng J, Ma Q, Liu S, Feng X, Lin X, Guo X. Study on dehydrogenation properties of the  $\text{LiAlH}_4\text{-NH}_4\text{Cl}$  system. *J Alloys Compd* 2013;551:508-11. <https://doi.org/10.1016/j.jallcom.2012.11.051>
- [53] Wang X, Wu C, Zhang Y, Chen Y. Hydrogen generation behaviors of  $\text{LiAlH}_4$  and  $\text{NH}_4\text{Cl}$  in  $\text{Et}_2\text{O}$ , THF or DME. *Int J Hydrogen Energy* 2016;41:6825-32. <http://dx.doi.org/10.1016/j.ijhydene.2016.03.081>
- [54] Wang X, Chen Y, Kong Q, Feng W, Li Z, Wu Y, Liu Y, et al. Low-temperature hydrogen release through  $\text{LiAlH}_4$  and  $\text{NH}_4\text{F}$  react in  $\text{Et}_2\text{O}$ . *Int J Hydrogen Energy* 2000;45:8774-8782. <https://doi.org/10.1016/j.ijhydene.2020.01.102>
- [55] Marsh CMB, Hamilton TP, Xie Y, Schaefer HF. Ammonia alane. *J Chem Phys* 1992;96:5310-7. <https://doi.org/10.1063/1.462716>
- [56] Davy RD, Jaffrey KL. Aluminium-nitrogen multiple bonds in small  $\text{AlNH}$  molecules: Structures and vibrational frequencies of  $\text{AlNH}_2$ ,  $\text{AlNH}_3$  and  $\text{AlNH}_4$ . *J Phys Chem* 1994;98:8930-6. <https://doi.org/10.1021/j100087a019>
- [57] Leboeuf M, Russo N, Salahub DR, Toscano M. A density functional study of borane and alane monoammoniate ( $\text{BH}_3\text{NH}_3$ ,  $\text{AlH}_3\text{NH}_3$ ). *J Chem Phys* 1995;103:7408-13. <https://doi.org/10.1063/1.470312>
- [58] Marsh CMB, Schefer III HF. Absence of dative bonds in bis(ammonia)alane. *J Phys Chem* 1995;99:14309-15. <https://doi.org/10.1021/j100039a018>
- [59] Czerw M, Goldman AS, Krogh-Jespersen K. Addition of ammonia to  $\text{AlH}_3$  and  $\text{BH}_3$ . Why does only aluminum form 2:1 adducts? *Inorg Chem* 2000;39:363-9. <https://doi.org/10.1021/ic990961i>

[60] Horvath V, Kovacs A, Hargittai I. Structural aspects of donor-acceptor interactions. *J Phys Chem A* 2003;107:1197-202. <https://doi.org/10.1021/jp022072d>

[61] Grant DJ, Dixon DA. Thermodynamic properties of molecular borane phosphines, alane amines, and phosphine alanes and the  $[\text{BH}_4^-][\text{PH}_4^+]$ ,  $[\text{AlH}_4^-][\text{NH}_4^+]$ , and  $[\text{AlH}_4^-][\text{PH}_4^+]$  salts for chemical hydrogen storage systems from ab initio electronic structure theory. *J Phys Chem A* 2005;109:10138-47. <https://doi.org/10.1021/jp054152y>

[62] Mitrasinovic PM. Invariant description of the behavior of electrons in donor-acceptor molecules. *Chem Phys Lett* 2004;392:419-27. <https://doi.org/10.1016/j.cplett.2004.05.085>

[63] Nguyen VS, Swinnen S, Nguyen MT, Dixon DA. Computational study of molecular complexes based on ammonia alane for chemical hydrogen storage. *J Phys Chem C* 2009;113:18914-26. <https://doi.org/10.1021/jp904344p>

[64] Nguyen VS, Matus MH, Ngan VT, Nguyen MT, Dixon DA. Theoretical study of the hydrogen release from ammonia alane and the catalytic effect of alane. *J Phys Chem C* 2008;112:5662-71. <https://doi.org/10.1021/jp7103374>

[65] Nguyen VS, Majumdar D, Leszczynski J, Nguyen MT. Hydrogen release from ammonia alane-based materials: Formation of cyclotrialazane and alazine. *J Phys Chem C* 2015;119:4524-39. <https://doi.org/10.1021/jp511668z>

[66] Mayer E. Symmetrical cleavage of diborane by ammonia in solution. *Inorg Chem* 1972;11:866-9. <https://doi.org/10.1021/ic50110a044>

[67] Shore SG, Parry RW. The crystalline compound ammonia-borane,  $\text{H}_3\text{NBH}_3$ . *J Am Chem Soc* 1955;77:6084-5. <https://doi.org/10.1021/ja01627a103>



[68] Heldebrant DJ, Karkamkar A, Linehan JC, Autrey T. Synthesis of ammonia borane for hydrogen storage applications. *Energy Environ Sci* 2008;1:156-160. <https://doi.org/10.1039/B808865A>

[69] Hoon CF, Reynhardt EC. Molecular dynamics and structures of amine boranes of the type  $R_3N \cdot BH_3$ : I. X-ray investigation  $H_3N \cdot BH_3$  at 295 K and 110 K. *J Phys C: Solid State Phys* 1983;16:6129-36. <https://doi.org/10.1088/0022-3719/16/32/007>

[70] Gutowsk M, Autrey T. Computational studies of boron/nitrogen and aluminum/nitrogen compounds for chemical hydrogen storage. *Prepr Pap Am Chem Soc Div Fuel Chem* 2004;49:275-6.

[71] Frueh S, Kellett R, Mallery C, Moller T, Willis WS, Kong'ondou C, Suib SL. Pyrolytic decomposition of ammonia borane to boron nitride. *Inorg Chem* 2011;50:783-92. <https://doi.org/10.1021/ic101020k>

[72] Chandra M, Xu Q. Dissociation and hydrolysis of ammonia-borane with solid acids and carbon dioxide: an efficient hydrogen generation system. *J Power Sources* 2006;159:855-60. <https://doi.org/10.1016/j.jpowsour.2005.12.033>

[73] Hwang HT, Varma A. Effect of boric acid on thermal dehydrogenation of ammonia borane: mechanistic studies. *Int J Hydrogen Energy* 2012;38:1925-31. <https://doi.org/10.1016/j.ijhydene.2012.11.046>

[74] Özkar S. Magnetically separable transition metal nanoparticles as catalysts in hydrogen generation from the hydrolysis of ammonia borane. *Int J Hydrogen Energy* 2021;46:21383-400. <https://doi.org/10.1016/j.ijhydene.2021.03.241>

[75] Semenenko KN, Bulychev B., Shevlyagina EA. Aluminium hydride. *Russ Chem Rev* 1966;35:649-58 <https://doi.org/10.1070/RC1966v035n09ABEH001513>

[76] Summerscales OT, Gordon JC. Regeneration of ammonia borane from spent fuel materials. *Dalton Trans* 2013;42:10075-84. <https://doi.org/10.1039/C3DT50475A>

[77] Lale A, Bernard S, Demirci UB. Boron nitride for hydrogen storage. *ChemPlusChem* 2018;83:893-903. <https://doi.org/10.1002/cplu.201800168>

[78] Miyaoka H, Ichikawa T, Fujii H, Kojima Y. Hydrogen desorption reaction between hydrogen-containing functional groups and lithium hydride. *J Phys Chem C* 2010;114:8668-74. <https://doi.org/10.1021/jp101533z>

[79] Li J, Kathmann SM, Hu HS, Schenter GK, Autrey T, Gutowski M. Theoretical investigations on the formation and dehydrogenation reaction pathways of  $H(NH_2BH_2)_nH$  ( $n = 1-4$ ) oligomers: importance of dihydrogen interactions. *Inorg Chem* 2010;49:7710-20. <https://doi.org/10.1021/ic100418a>

[80] Luo J, Kang X, Wang P. Synthesis, formation mechanism, and dehydrogenation properties of the long-sought  $Mg(NH_2BH_3)_2$  compound. *Energy Environ Sci* 2013;6:1018-25. <https://doi.org/10.1039/C3EE23627G>

[81] Castilla-Martinez CA, Roussignol L, Demirci UB. Magnesium hydrazinidoborane: Synthesis, characterization and features for solid-state hydrogen storage. *Int J Hydrogen Energy* 2021;46:33164-75. <https://doi.org/10.1016/j.ijhydene.2021.07.169>

[82] Wang Q, Sun Q, Jena P and Kawazoe Y. Potential of AlN nanostructures as hydrogen storage materials. *ACS Nano* 2009;3:621-6. <https://doi.org/10.1021/nn800815e>

[83] Moradi M, Naderi N. First principle study of hydrogen storage on the graphene-like aluminum nitride nanosheet. *Struct Chem* 2014;25:1289-96. <https://doi.org/10.1007/s11224-014-0410-x>

[84] Kojima Y, Kawai Y, Ohba. Hydrogen storage of metal nitrides by a mechanochemical reaction. *J Power Sources* 2006;159:81-7. <https://doi.org/10.1016/j.jpowsour.2006.04.024>