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Discrepancy in the thermal decomposition/dehydrogenation of ammonia borane screened by thermogravimetric analysis

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Abstract

Ammonia borane NH_3BH_3 (AB), in pristine or destabilized state, has been much investigated as a solid-state chemical hydrogen storage material. The potential of such compound for thermolytic dehydrogenation (and decomposition) can be fast and reliably screened and assessed by thermogravimetric (TG) analysis via descriptors like both the onset temperature of dehydrogenation and the overall weight loss over the temperature range 100-200°C. However, comparisons to results reported in the open literature need to be done with caution. The objective of the present article is thus to show that the thermolytic properties of AB determined by TG analysis are much dependent on the operation conditions. We have observed that much different results are obtained by changing the analyzer, and especially the crucible (comparable to a semi-closed reactor in one case or similar to an open reactor in the second case). For example, a stable AB sample is able to suffer a weight loss of 18.4 wt% starting from 116.5°C when a semi-closed crucible is used, *versus* a weight loss of 51.9 wt% starting from 91°C with the utilization of an open crucible. Our main results are reported herein in the form of a short technical communication: it aims at sharing our experimental observations in order to avoid misinterpretation and misunderstanding as for the TG analyses of AB and of any kind of derivatives. The present work should help in comparing the data available in the open literature with care and, from now on, should be regarded as a key study to report comparable TG results for AB thermolytic dehydrogenation.

Keywords

Ammonia borane; Hydrogen storage; Thermal decomposition; Thermogravimetric analysis; Thermolysis.

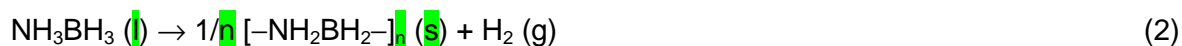
1. Introduction

Ammonia borane (or borazane, NH_3BH_3 ; denoted AB) is a key material in the field of solid-state chemical hydrogen storage owing to its solid state at ambient conditions, stability under inert atmosphere, high hydrogen density (19.5 wt% H and $146 \text{ g}_\text{H} \text{ L}^{-1}$) and ability to dehydrogenate/decompose from about 100°C [1-3]. It is however thermodynamically unrealistic to target the recovery of all of the hydrogen (because of the formation of the highly stable boron nitride [4]). In ideal thermolytic conditions it may be expected an effective gravimetric hydrogen storage capacity of at best 13 wt% (corresponding to 4 out of 6 H of NH_3BH_3) [5,6].

Under heating, the transformation of pristine AB starts with melting occurring between 97 and 119°C :



The discrepancy in the melting temperature is due to different factors like the heating rate (1 - $10^\circ\text{C} \text{ min}^{-1}$), the sample purity and the pre-dimerization of the borane [1]. The melting is concomitant with the first decomposition [7,8] whose weight loss measured by thermogravimetric (TG) analysis is roughly comparable to 6.5 wt% [9,10], suggesting that AB mainly dehydrogenates:



Decomposition into e.g. aminoborane NH_2BH_2 , ammonia NH_3 and diborane B_2H_6 also occurs in some extent [11]. From about 130°C (and up to about 200°C), the second decomposition takes place, being characterized by an important weight loss (>20 wt%) [12]. AB decomposes into the undesired gaseous products NH_3 , B_2H_6 and borazine $\text{B}_3\text{N}_3\text{H}_6$ [13,14]. Dehydrogenation also takes place such as [7]:



Such thermolytic properties do not match the requirements for solid-state chemical hydrogen storage in terms of hydrogen purity and operation temperatures. Thereupon, innovative strategies (i.e. homogeneous catalysis [15,16], doping [17,18], nanoconfinement [19,20], nanosizing [21,22], and chemical modification [23,24]) have been developed to mitigate, even suppress, the decomposition of AB and concomitantly to improve the dehydrogenation properties. The benefits of such destabilization strategies can be evaluated by several techniques, including TG analysis.

Thus far, we have studied four of the aforementioned strategies and a number of AB-based materials and derivatives had been prepared. In our laboratory the thermolytic properties of each any AB-based material is systematically evaluated by TG analysis, which is a simple

and effective way for screening fast and reliably the aforementioned compounds. Despite the complexity of AB thermal decomposition [5], the TG results allow to select or discard the screened materials on the basis of the onset temperature of decomposition and the weight losses occurring between 80 and 200°C (Figure 1). However, comparisons to results reported in the open literature need to be considered with caution. Indeed, in the present work, it is reported that much different results can be collected by changing the analyzer and the crucible (comparable to a semi-closed reactor or to an open reactor). For a same AB sample it is for instance possible to see much different weight losses at 200°C (differential of more than 30 wt%) and incomparable onset temperatures of dehydrogenation (e.g. 91°C vs. 116.5°C). This is a critical situation, and to our knowledge, it has not been reported and discussed before.

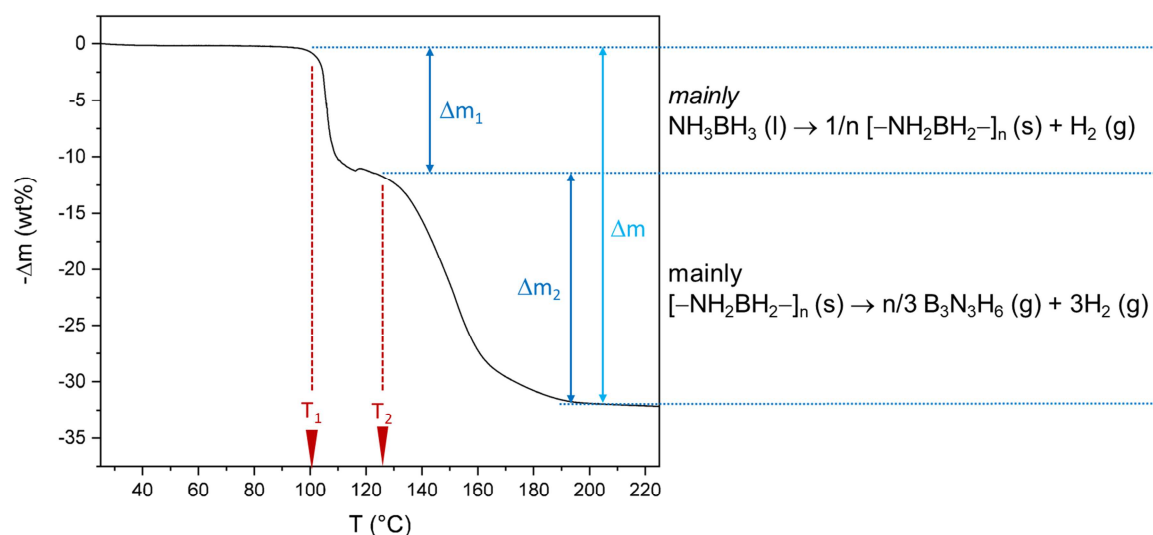


Figure 1. Typical TG analysis curve for AB: focus on the descriptors T_1 (the onset temperature of the first main decomposition), Δm_1 (the weight loss of the first main decomposition), T_2 (the onset temperature of the second main decomposition), Δm_2 (the weight loss of the second main decomposition) and Δm (the overall weight loss from 80 to 200°C).

With the present technical communication we aim at sharing our experimental observations about the aforementioned discrepancies, that is, about the differences observed in the thermolytic dehydrogenation properties of AB by just changing the TG analyzer. Such a report should be of importance to avoid, in the future, misinterpretation and misunderstanding as for the TG analyses of AB and of any kind of AB derivatives.

2. Materials and methods

Four different samples of AB were synthesized. The samples denoted **1**, **2** and **3** were prepared by metathesis-dehydrogenation using borohydride and ammonium salts (all from Sigma-Aldrich) and an anhydrous organic solvent. The reactions were performed at 35°C for 2 days. For **1** (purity $\geq 99\%$), lithium borohydride LiBH_4 , ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ and 1,4-dioxane (Sigma-Aldrich) were used. For **2** (purity $\geq 99\%$), sodium borohydride NaBH_4 , $(\text{NH}_4)_2\text{CO}_3$ and tetrahydrofuran (Acros) were used. For **3** (purity $\geq 97\%$), LiBH_4 , ammonium chloride NH_4Cl and 1,4-dioxane were used. The sample denoted **4** (purity 100%) was prepared by base displacement reaction involving dimethylsulfide borane $(\text{CH}_3)_2\text{S}\cdot\text{BH}_3$ (2 M solution in toluene; Sigma-Aldrich), ammonia NH_3 (Alpha Gaz) and anhydrous toluene (Acros). The bubbling of NH_3 in the borane solution was performed at 0°C for 15 min. Details about the syntheses, the samples purity and the respective characterizations are available in reference [9]. The samples were stored in an argon-filled glove box (MBraun M200B, $\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm).

The screening of the different AB samples (i.e. thermal stability and thermogravimetric features) was done by using TG analysis. In our laboratory, a Texas Instruments Q500 analyzer (denoted **A**), located in a room, is available. It works under nitrogen flow (50 mL min^{-1}). We use aluminum crucibles because they can be sealed in the argon-filled glove box. Typically, a crucible and a lid are put in the glove box to be loaded with the AB sample to be analyzed. The crucible is loaded with a maximum of 2-3 mg (because of the foaming of the borane under heating) of AB, is sealed and is taken out the glove box. Just before starting the TG analysis, the lid is pierced with a needle to allow the evolving gas to escape through the as-obtained pinhole. The experiments are carried out from 25 to 200°C at a heating rate of 1 or 5°C min^{-1} . During the progress of our work, we had an access to another TG analyzer, a Rigaku thermoplus TG 8120 (denoted **B**). It is located in an argon-filled glove-box (MIWA MDB-1B, $\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). It works under a helium flow (50 mL min^{-1}). With this apparatus, we used an alumina crucible that is unnecessary to seal. The sample mass was again limited to 2-3 mg. All of the steps for an experiment with this analyzer are realized in the glove box. The experiments are carried out from 25 to 200°C at a heating rate of 1°C min^{-1} .

A TG analysis of AB can be described through five descriptors (Figure 1): the onset temperature of the first decomposition (T_1), the weight loss for the first decomposition (Δm_1), the onset temperature of the second decomposition (T_2), the weight loss for the second

decomposition (Δm_2), and the overall weight loss at 200°C (Δm). Herein, for clarity, the TG curves will be discussed in terms of T_1 and Δm mainly.

3. Results and discussion

The first reports about the thermal stability of pristine AB studied by TG analysis point out the effect of the heating rate on the results [13,25-27]. Generally, T_1 and T_2 increase when the heating rate is increased (e.g. from 1 to 5°C min⁻¹ [26]). Such a change may be explained by the low decomposition kinetics of AB [28,29]. Also, with rising heating rate, the overall weight loss Δm generally increases. Weismiller et al. [30] have plotted Δm as a function of the heating rate (range 2 to 50°C min⁻¹) and have found a nearly logarithmic evolution. According to Baumann et al. [27], the amount of evolved H₂ is independent of the heating rate whereas the amount of the volatile by-products strongly increases. This is confirmed by Weismiller et al. [30]. A similar conclusion comes from Héлары et al. who, besides, have suggested variations in the degradation pathways according to the heating rate [31].

The impact of the heating rate (1 vs. 5°C min⁻¹) is verified in our experimental conditions. For that the analyzer **A** was used. The TG curves for our four samples are shown in Figure 2. On the one hand, we confirm that the increase of the heating rate results in a shift of T_1 (as well as of T_2) to higher values. With **1**, T_1 is equal to 107°C at 1°C min⁻¹ while it is 116.5°C at 5°C min⁻¹ (ΔT_1 of 9.5°C). The difference is even more important for **3** and **4** as T_1 increases by 16 and 21°C respectively. On the other hand, the weight losses are impacted by the change of the heating rate. The decomposition is favored with the increase of the heating rate. For example, Δm for the sample **1** is about 18 wt% at 1°C min⁻¹ and 42 wt% at 5°C min⁻¹. For **2**, **3** and **4**, the weight losses at 1 and 5°C min⁻¹ are as follows: 31.9 and 48.3 wt%; 14.8 and 19.3 wt%; 20.3 and 39.8 wt%. This is in agreement with the higher decomposition extent (i.e. more of the unwanted by-product borazine) as reported elsewhere [13,26].

We elsewhere have discussed the interest of investigating various AB samples [9]. Our objective was to find the suitable synthesis method for getting pure AB with improved decomposition properties (i.e. showing lower T_1). The sample **1** has for example been found to be the most stable AB, with T_1 as high as 116.5°C (at 5°C min⁻¹). It has been directly compared to **2**, considered as the least stable pure AB ($T_1 = 104^\circ\text{C}$). With respect to **3**, it has shown the lowest T_1 (93.5°C) because of traces of impurities (LiCl). With respect to **4**, it has

been found to be less stable ($T_1 = 98^\circ\text{C}$) than **1**, which is explained by differences at the molecular scale. For more details about the purity of AB and its impact on the TG results, the reader is invited to scrutinize ref. [9] where in fact twelve different AB samples have been compared. In the present work, **1**, **2**, **3** and **4** are further studied but with another TG analyzer, the apparatus **B**. Our objective is initially to confirm the differences between the samples we observed with the apparatus **A**. Two major observations stand out (Figure 3). At first sight, the TG curves obtained with the analyzer **B** and those collected with the other analyzer are similar in their allure. However a further exploration shows that the curves cannot be superimposed: there are three main differences.

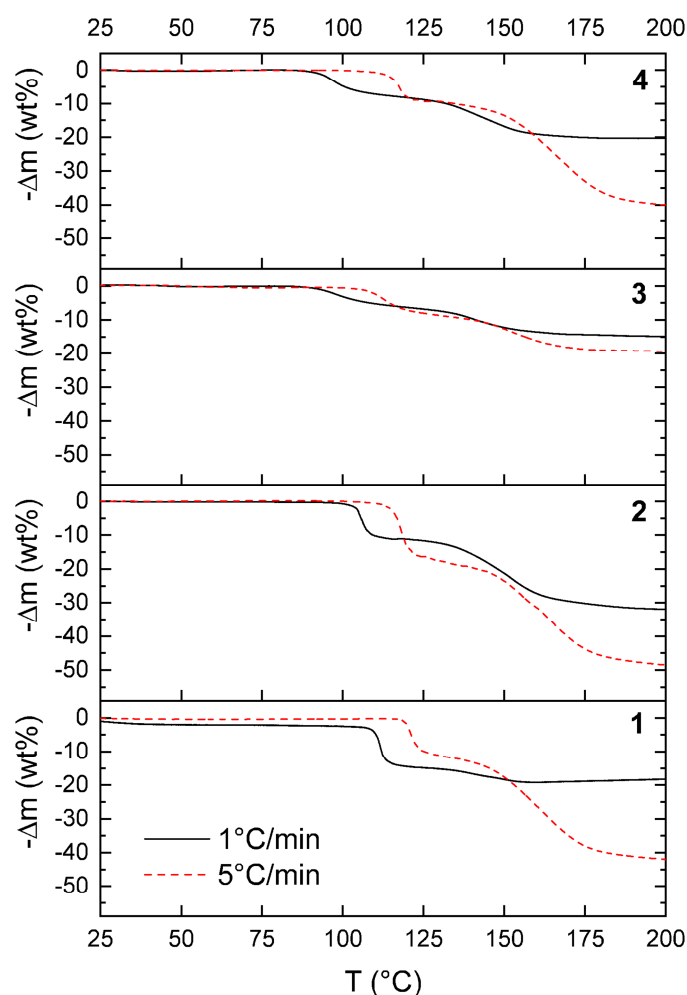


Figure 2. TG curves of the AB samples **1**, **2**, **3** and **4** studied with the analyzer **A** at two heating rates: 1 and 5°C min^{-1} .

First, the TG curves obtained with **B** confirm that the most stable AB is still **1** ($T_1 = 91^\circ\text{C}$). The other samples are less stable. For example, T_1 for **3** is about 65°C . In other words, the

ranking of **1** and **2** (as well as of **3** and **4**) in terms of thermal stability is not dependent on the TG analyzers, the present results confirming our previous conclusions [9].

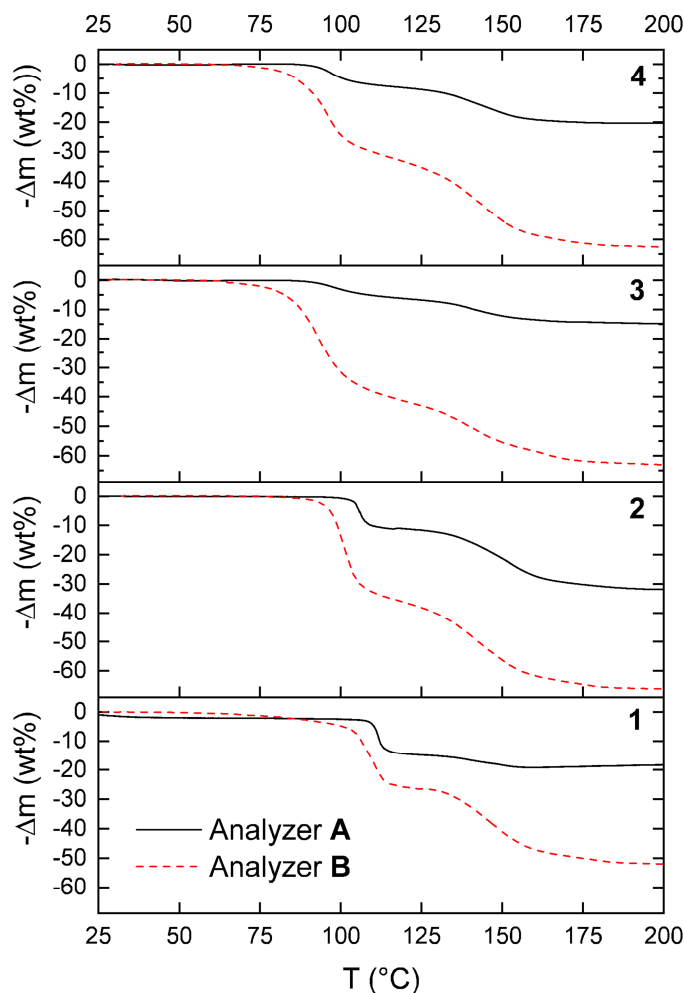


Figure 3. TG curves of the AB samples **1**, **2**, **3** and **4** studied with the analyzers **A** and **B** at $1^{\circ}\text{C min}^{-1}$.

Second, the temperatures T_1 are significantly decreased when the analyzer **B** is considered. In comparison to the data collected with the analyzer **A**, there is a gap of about 15, 20, 27 and 24°C for **1**, **2**, **3** and **4** respectively. With **3** and **4**, T_1 is even slightly lower than 65°C . Such onset temperatures are comparable to those found with a destabilized AB, that is, AB doped with a metal chloride [32] or for an AB nanoconfined into the open porosity of mesoporous silica [33]. This observation may challenge the reliability and relevancy of cross-comparisons of TG results.

Third, the weight losses are affected (Table 1). With the analyzers **A** and **B**, Δm is found to be respectively 18.4 and 51.9 wt% for **1**, 31.9 and 66.1 wt% for **2**, 14.8 and 63 wt% for **3**, and

20.3 and 62.6 wt% for **4**. The weight losses are clearly much higher with **B**. This demonstrates that the decomposition extent of an AB sample is strongly dependent on the analyzer and that TG results obtained with different systems must be compared with care.

Table 1. Weight losses found at 200°C for the samples **1**, **2**, **3** and **4** with the analyzers **A** and **B** (based on the curves in **Figure 3**). The weight losses are given in wt% as well as in equivalent of H₂ (such as 13 wt% = 2 equivalent of H₂).

Analyzer	Weight loss in wt% / Weight loss in equiv. H ₂			
	Sample 1	Sample 2	Sample 3	Sample 4
A	18.4 / 2.8	31.9 / 4.9	14.8 / 2.3	20.3 / 3.1
B	51.9 / 8	66.1 / 10.2	63 / 9.7	62.6 / 9.7

At the scale of our experiments using two different TG analyzers, the crucible can be seen as the main difference. With **A**, the aluminum crucible is sealed and the gas evacuation is done through a pinhole ($\varnothing < 1$ mm) made to the lid. With **B**, the alumina crucible is not sealed. The former may thus be seen as a semi-closed “reactor” and the latter may be an open “reactor”, which makes a difference.

With the open crucible of **B**, the evacuation of the forming gases is favored because the TG flowing gas leaches the surface of the sample. The gases have a short residence time in the crucible “cloud”. Hence, a dehydrogenation by-product like NH₂BH₂ and a decomposition by-product like NH₃ or B₂H₆, both forming during the first weight loss, are favorably passed into the TG exhaust (**Figure 4**). This is also true for the trimeric gaseous by-product B₃N₃H₆ mainly forming during the second weight loss.

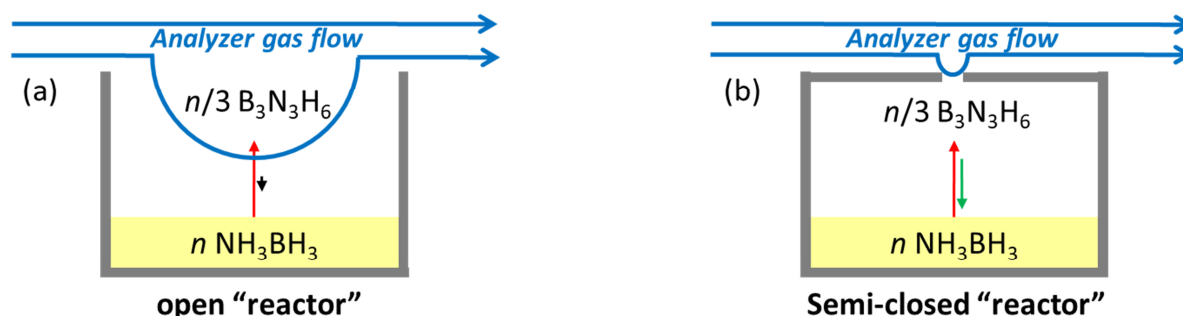


Figure 4. Schematic representation of a so-called (a) open “reactor” and of a (b) semi-closed “reactor”.

In contrast, with the semi-closed crucible of **A**, the evacuation of the forming gases is more difficult. Their residence time in the crucible “cloud” is much longer than for the previous analyzer. During the first weight loss, equilibria between the gaseous by-products (mainly NH_2BH_2 , NH_3 , B_2H_6) and the decomposing AB are likely to take place (Figure 4). The former gases may then be involved in further reactions with the remaining solid towards the formation polymeric solid residues [5]. This is also true for $\text{B}_3\text{N}_3\text{H}_6$, mainly evolving during the second weight loss, a fraction of it being then able to polymerize into polyborazylene (a solid thermolytic residue).

In our conditions, the use of both types of crucibles has led to significantly different TG profiles despite the use of the same AB samples. Though TG analysis is an easy-to-use and fast tool for screening chemical hydrogen storage materials, care must be taken with the collected data. Direct comparisons of TG results are possible and reliable if, and only if, the conditions of the TG experiments are equivalent. Otherwise any attempt to make direct comparison will result in misinterpretations and erroneous conclusions. For example, the low weight loss recorded for **1** (18.4 wt%) with the analyzer **A** could let us imagine that the sample would be suitable for boron nitride formation with high ceramic yield (<81%). However when the results obtained with **B** are considered it is obvious that the ceramic yield will be much lower (<48%). One way to think about this is that the semi-closed “reactor” would allow higher ceramic yields.

In the field dedicated to thermolytic decomposition of AB, the present findings add complexity to the interpretations of the reported results. Up to now, the complexity lied in the heating rate of the TG experiment [13,25-31] and/or in the purity (molecular composition) of the AB sample. For example, the ionic dimer of AB, i.e. diammoniate of diborane $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$, that may form during the synthesis of AB is known to be less stable than AB and to release much less volatile by-products [34]. A mixture of AB and DADB has then a different thermal behavior in comparison to pure AB [35]. From now, the aforementioned complexity lies, also, in the operating/use conditions of TG analysis.

4. Conclusion

For screening different AB samples as well as any chemical hydrogen storage materials, TG analysis is an easy-to-use, efficient and reliable tool. However, the results are much dependent on the operating conditions. In the present work we have shown that significantly different TG profiles can be obtained for a given AB sample by changing the analyzer and

the way of preparing the crucible. For example, an AB sample, considered as being stable, is able to suffer a weight loss of 18.4 wt% starting from 116.5°C with one TG analyzer, versus a weight loss of 51.9 wt% starting from 91°C with another analyzer. On the one hand (for the former analyzer), a sealed aluminum crucible (with a pinhole) has been used; it may be compared to a semi-closed “reactor”. On the other hand (for the latter analyzer), an alumina crucible (not sealed) has been handled; it may be compared to an open “reactor”. This makes a difference that makes big differences in TG results. We have thus shown, for the first time, that one given AB sample is able to show much different thermolytic behaviors depending on the TG analyzer and the crucible that is used. In consequence, care must be taken when TG results in the open literature are compared and when comparative discussions are done about both AB stability and thermolytic dehydrogenation. This also applies to any boron- and/or nitrogen-based materials investigated for chemical hydrogen storage. Direct comparisons can be possible if the operating conditions are much comparable. This is the best approach to avoid misinterpretations and erroneous conclusions.

Acknowledgments

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References

- [1] Zhang J, Lee JW. Progress and thermolytic dehydrogenation of ammonia borane for mobile applications. *Korean J Chem Eng* 2012;29:421-31.
- [2] Li H, Yang, Chen X, Shore SG. Ammonia borane, past as prolog. 2014;751:60-6.
- [3] Akbayrak S, Özkar S. Ammonia borane as hydrogen storage materials. *Int J Hydrogen Energy* 2018;43:18592-606.
- [4] Frueh S, Kellett R, Mallery C, Molter T, Willis WS, King'onde C, Suib SL. Pyrolytic decomposition of ammonia borane to boron nitride. *Inorg Chem* 50;2011:783-92.
- [5] Al-Kukhun A, Hwang HT, Varma A. Mechanistic studies of ammonia borane dehydrogenation. *Int J Hydrogen Energy* 2013;38:169-79.
- [6] Demirci UB. Ammonia borane, a material with exceptional properties for chemical hydrogen storage. *Int J Hydrogen Energy* 2017;42:9978-10013.

- [7] Hu MG, Geanangel RA, Wendlandt. The thermal decomposition of ammonia borane. *Thermochim Acta* 1978;23:249-55.
- [8] Baitalow F, Wolf G, Grolier JPE, Dan F, Randzio SL. Thermal decomposition of ammonia-borane under pressures up to 600 bar. *Thermochim Acta* 2006;445:121-5.
- [9] 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;41:14562-70.
- [10] Neiner D, Karkamkar A, Linehan JC, Arey B, Autrey T, Kauzlarich SM. Promotion of hydrogen release from ammonia borane with mechanically activated hexagonal boron nitride. *J Phys Chem C* 2009;113:1098-103.
- [11] Jepsen LH, Skibsted J, Jensen TR. Investigations of the thermal decomposition of $MBH_4-2NH_3BH_3$, $M = Na, K$. *J Alloys Compd* 2013;580:5287-91.
- [12] Geanangel RA, Wendlandt WW. A TG-DSC study of the thermal dissociation of $(NH_2BH_2)_x$. *Thermochim Acta* 1985;86:375-8.
- [13] Wolf G, Baumann J, Baitalow F, Hoffmann FP. Calorimetric process monitoring of thermal decomposition of B-N-H compounds. *Thermochim Acta* 2000;343:19-25.
- [14] Biliškov N, Vojta D, Kótai L, Szilágyi IM, Hunyadi D, Pasinszki T, Grgac SF, Borgschulte A, Züttel A. High influence of potassium bromide on thermal decomposition of ammonia borane. *J Phys Chem C* 2016;120:25276-88.
- [15] Erickson KA, Wright DS, Waterman R. Dehydrocoupling of amine boranes via tin(IV) and tin(II) catalysts. *J. Organomet. Chem.* 2014;751:541-5.
- [16] Glüer A, Förster M, Celinski VR, Schmedt auf der Günne J, Holthausen MC, Schneider S. Highly active iron catalyst for ammonia borane dehydrocoupling at room temperature. *ACS Catal* 2015;5:7214-7.
- [17] Zhang Y, Shimoda Z, Miyaoka H, Ichikawa T, Kojima Y. Thermal decomposition of alkaline-earth metal hydride and ammonia borane composites. *Int J Hydrogen Energy* 2010;35:12405-9.
- [18] Ploszajski AR, Billing M, Nathanson AS, Vickers M, Bennington S. Freeze-dried ammonia borane-polyethylene oxide composites: phase behaviour and hydrogen release. *Int J Hydrogen Energy* 2018;43:5645-56.
- [19] Moussa G, Bernard S, Demirci UB, Chiriac R, Miele P. Room-temperature hydrogen release from activated carbon-confined ammonia borane. *Int J Hydrogen Energy* 2012;37:13437-45.
- [20] Diaz LB, Hanlon JM, Bielewski M, Milewska A, Gregory DH. Ammonia borane based nanocomposites as solid-state hydrogen stores for portable power applications. *Energy Technol* 2018;6:583-94.

- [21] Lai Q, Rawal A, Quadir Z, Cazorla C, Demirci UB, Aguey-Zinsou KF. Nanosizing ammonia borane with nickel: a path toward the direct hydrogen release and uptake of B-N-H systems. *Adv Sust Syst* 2018;2:1700122.
- [22] Lai Q, Aguey-Zinsou KF, Demirci UB. Nanosizing ammonia borane with nickel – An all-solid and all-in-one approach for H₂ generation by hydrolysis. *Int J Hydrogen Energy* 2018;43:14498-506.
- [23] Nakagawa Y, Shinzato K, Nakagawa T, Nakajima K, Isobe S, Goshome K, Miyaoka H, Ichikawa T. Synthesis, structural characterization, and hydrogen desorption properties of Na[Al(NH₂BH₃)₄]. *Int J Hydrogen Energy* 2017;42:6173-80.
- [24] Møller KT, Jørgensen M, Andreasen JG, Skibsted J, Łodziana Z, Filinchuk Y, Jensen TR. Synthesis and thermal decomposition of potassium tetraamidoboranealuminum, K[Al(NH₂BH₃)₄]. *Int J Hydrogen Energy* 2018;43:311-21.
- [25] Sit V, Geanangel RA, Wendlandt WW. The thermal dissociation of NH₃BH₃. *Thermochim Acta* 1987;113:379-82.
- [26] 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.
- [27] Baumann J, Baitalow F, Wolf G. Thermal decomposition of polymeric aminoborane (H₂BNH₂)_x under hydrogen release. *Thermochim Acta* 2005;430:9-14.
- [28] He T, Xiong Z, Wu G, Chu H, Wu C, Zhang T, Chen P. Nanosized Co- and Ni-catalyzed ammonia borane for hydrogen storage. *Chem Mater* 2009;21:2314-8.
- [29] Miranda CR, Ceder G, Ab initio investigation of ammonia-borane complexes for hydrogen storage, *J Chem Phys* 2007;126:184703.
- [30] Weismiller MR, Wang SQ, Chowdhury A, Thynell ST, Yetter RA. Confined rapid thermolysis of ammonia borane. *Thermochim Acta* 2013;551:110-7.
- [31] Hélyary J, Salandre N, Saillard J, Poullain D, Beaucamp A, Autissier D. A physico-chemical study of an NH₃BH₃-based reactive composition for hydrogen generation. *Int J Hydrogen Energy* 2010;34:169-73.
- [32] Nakagawa Y, Zhang T, Kitamura M, Isobe S, Hino S, Hashimoto N, Ohnuki S. A systematic study of the effects of metal chloride additives on H₂ desorption properties of ammonia borane. *J Chem Eng Data* 2016;61:1924-9.
- [33] Sullivan JA, Herron R, Phillips AD. Towards an understanding of the beneficial effect of mesoporous materials on the dehydrogenation characteristics of NH₃BH₃. *Appl Catal Environ. B* 2017;201:182-8.
- [34] Fang Z, Luo J, Kang X, Xia H, Wang S, Wen W, Zhou X, Wang P. Facile solid-phase synthesis of the diammoniate of diborane and its thermal decomposition behavior. *Phys Chem Chem Phys* 2011;13:7508-13.

- [35] Petit JF, Dib E, Gaveau P, Miele P, Alonso B, Demirci UB. ^{11}B MAS NMR study of the thermolytic dehydrocoupling of two ammonia boranes upon the release of one equivalent of H_2 at isothermal conditions. *Chem Select* 2017;2:9396-401.