An experimental study of neat and ionic liquid-aided ammonia borane thermolysis

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ABSTRACT

This paper reports hydrogen (H_2) yield and reaction rate measurements of ammonia borane (AB) thermolysis in the neat form as well as facilitated by the presence of an ionic solvent, 1-butyl-3-methylimidazolium chloride (bmimCl). The measurements were conducted at various temperatures between 85 and 120 °C under quasi-isothermal conditions. The details of fast hydrogen evolution at the initial stage of the thermolysis process were captured for the first time. The presence of bmimCl led to significant increases in both the rate and the amount of hydrogen released, compared to the corresponding quantities at identical temperatures for neat AB thermolysis. Measurements reported in the literature are in qualitative agreement with this observation but lack the time resolution necessary for the quantitative comparisons. At 120 °C, the measured gravimetric H_2 storage capacity from the neat AB thermolysis was 9.9 wt% (material base) and that from the AB/bmimCl mixture (80/20 wt%) thermolysis was 11.2 wt%. Also, the reaction rate of the thermolysis of AB/bmimCl mixture (80/20 wt%) was twice as fast as that of the neat AB thermolysis at this temperature. In the bmimCl (20 wt%) aided AB thermolysis, a significant increase in the H_2 yield occurred at temperatures over 107 °C.

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1. Introduction

Chemical hydrides, such as ammonia borane (NH_3BH_3, AB), can be used in hydrogen-powered applications for the release of hydrogen (H_2) on demand. Various methods are being developed for vehicular hydrogen storage in AB, including thermolysis and catalytic hydrolysis of AB.

AB is soluble in water and can react with water in the presence of catalysts to rapidly release hydrogen at room temperature. Catalytic AB hydrolysis in dilute and concentrated aqueous solutions [1–3] as well as in AB/water slurries [4] have been investigated thoroughly. The theoretical maximum gravimetric hydrogen storage capacity (material base) of AB hydrolysis is 9.0 wt% while the measured maximum storage capacity was 7.5 wt%, when 92% hydrogen yield was achieved in the hydrolysis of a (1:2.37) AB/water slurry [4].

AB thermolysis processes in the neat form [5–13] and in the presence of ionic solvents [14–16] provide the highest known gravimetric hydrogen storage capacities (7–11 wt%) for temperatures under 120 °C. Operations in this temperature range provide the exciting possibility of waste heat recovery from internal combustion engines and PEM fuel cells.

The reaction of neat AB thermolysis involves the thermal decomposition of AB liberating H_2 and a sequence of competing reactions [7,17,18] forming volatile byproducts (as impurities in the H_2), including monomeric aminoborane (BH_2NH_2), borazine (($BHNH$)$_3$), and diborane (B_2H_6). The extent of volatile byproducts evolved increases as the heating rate is increased [12].

With heating rates in the range of 1–10 K min^{-1}, the decomposition of AB initiates below 97 °C as an exothermic process [9]. During this step, the material loses its crystalline form and birefringence but without evolution of H_2, resulting in a mobile form of AB and the diammoniate of diborane ($[NH_3BH_2NH_3]^+[BH_4]^-$) as follows [8],

$$3NH_3BH_3 \underset{crystal}{} \rightarrow \underset{mobile}{NH_3BH_3} + [NH_3BH_2NH_3] + [BH_4]^- \quad (1)$$
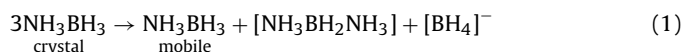
Recent studies revealed that the formation of diammoniate of diborane in the initial stage, although without H_2 evolution, is a key step of the overall AB dehydrogenation process [8,16].

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The endothermic AB melting process that initiates at ~102 °C limits the rise in temperature and the AB melts completely at ~112 °C [7]. An exothermic decomposition process occurs in the temperature range between 107 and 117 °C, liberating 1.1 ± 0.1 mol of H_2 per mole of AB [9]. This step is accompanied with the formation of polymeric aminoborane $(NH_2BH_2)_x$ as described below [7,9,19],

$$NH_3BH_{3(s)} \rightarrow NH_3BH_{3(l)} \qquad (2)$$

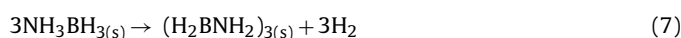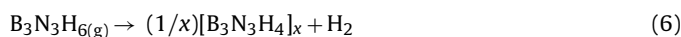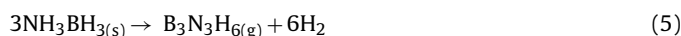$$NH_3BH_3 \rightarrow \frac{1}{x}(NH_2BH_2)x + H_2 \qquad (3)$$
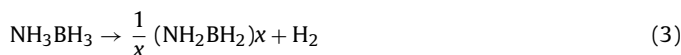
where the subscripts 's' and 'l' represent solid and liquid phases, respectively.

A second mole of H_2 is released during another exothermic step that initiates before the first dehydrogenation step terminates and spans a broader temperature range approximately from 127 to 180 °C. This step is accompanied with the formation of polyiminoborane-like material $(NHBH)_x$, a small amount of toxic gaseous borazine $((BHNH)_3)$ [7,17] and sometimes diborane (B_2H_6) [9,17].

$$(NH_2BH_2)_x \rightarrow (NHBH)_x + xH_2 \qquad (4)$$

The first and second dehydrogenation steps together yield (2.2 ± 0.1) mol of H_2 per mole of AB. In order to extract all 3 mol of H_2 stored in 1 mol of AB, temperatures above 500 °C are needed to decompose AB to form boron nitride (BN) and H_2 [11,17]. This final step is not of interest to the present work since the required temperature is significantly above the highest waste heat temperature of the PEM fuel cells and the product BN has high thermal and chemical stability.

An alternative decomposition route of AB is by formation of cyclic polymeric compounds, such as borazine, polyborazylene $(B_3N_3H_4)_x$, and cyclotriborazane $(H_2BNH_2)_3$. The hydrogen release reactions that form cyclic polymeric compounds are as follows [13],

$$3NH_3BH_{3(s)} \rightarrow B_3N_3H_{6(g)} + 6H_2 \qquad (5)$$

$$B_3N_3H_{6(g)} \rightarrow (1/x)[B_3N_3H_4]_x + H_2 \qquad (6)$$

$$3NH_3BH_{3(s)} \rightarrow (H_2BNH_2)_{3(s)} + 3H_2 \qquad (7)$$

where subscript 'g' represents the gas phase.

It is difficult to ascertain which of the above-mentioned decomposition routes and competing reactions dominate. Formation of the amino and iminoborane-like polymers involves multiple reactions (chain initiation, propagation and termination) [20] and foaming effects during reaction also add to the complexity [16]. The exact kinetics and mechanism of neat AB thermolysis are hence, complicated [18].

Neat AB thermolysis under isothermal conditions was investigated before. AB decomposition initiated after 3 and 1 h heating at 85 and 95 °C, respectively [14]; and the material tended to foam during dehydrogenation. Catalysis is difficult to use in the solid phase reactions because it is virtually impossible to have all the material access a catalytic site, but additives have been developed to be mixed into the AB powder to increase H_2 release rate and purity. For example Li-AB $(LiNH_2BH_3)$ was obtained by a lithium metal substitution of the hydrogen on the N-atom in AB [21]. Mass spectrometry showed that H_2 was released from Li-AB at 92 °C (instead of at 108 °C from AB) with much faster H_2 release rate. In addition, the chemical structure of Li-AB does not allow volatile byproducts; thus suppressing the borazine impurity within the H_2 gas [21].

Ionic liquids facilitate milder reaction temperatures and better reaction control in AB thermolysis, since ionic liquids significantly enhance the formation of diammoniate of diborane $([NH_3BH_2NH_3]^+[BH_4]^-)$, which is the key intermediate ionic species in AB thermolysis [16]. In the work presented here, 1-butyl-3-methylimidazolium chloride (bmimCl) enhanced the H_2 release rate as well as yield from AB significantly. Ionic liquids have negligible vapor pressures and are thermally stable at elevated temperatures and recyclable with little loss of efficacy. These properties make their applications in hydrogen storage systems very attractive [14,19,22]. A possible AB dehydrogenation pathway with the presence of ionic liquid was discussed in detail in Ref. [16].

BmimCl is a solid at room temperature but melts above 70 °C [23–25]. AB thermolysis tests with varying proportions of bmimCl (0, 20, 30 and 50 wt%) in the temperature range from 75 to 120 °C were reported in the pioneering work by Sneddon and co-workers [5,14,16,26]. The volumes of accumulated H_2 were recorded either intermittently using a Toepler pump apparatus or continuously using an automated gas burette. For the thermolysis of 50/50 wt% AB/bmimCl mixture at 95 °C, 1.6 mol of H_2 per mole of AB were generated after 22 h of heating in one test [14] while 2.2 mol of H_2 per mole of AB were generated after 161 min of heating in another test [26]. For AB/bmimCl mixture thermolysis at 110 °C, it was observed that the initial dehydrogenation rate increased with increasing bmimCl in the mixture from 20 to 30 wt% but then decreased with increasing bmimCl from 30 to 50 wt% [26]. For the thermolysis of 80/20 wt% AB/bmimCl mixture at 120 °C, 2.2 mol of H_2 per mole of AB were generated after 100 min of heating; thus a breakthrough material-based H_2 storage capacity of 11.4 wt% with desired release rate was achieved [16]. In these bmimCl aided AB thermolysis tests, the initial rapid H_2 release process, however, was not captured by the Toepler pump apparatus [5,14,26] or was not captured correctly by the automated gas burette apparatus [16,26], where rapid unphysical spikes were recorded.

Being used in conjunction with ionic liquids, metal catalysts can further enhance the hydrogen release rate of AB thermolysis and lower the release temperature. For instance, the addition of 5 mol% rhodium (Rh) in a 50/50 wt% AB/bmimCl mixture enhanced the initial hydrogen release rate from 0.7 mol H_2 per hour to 1 mol H_2 per hour at 85 °C [5].

AB thermolysis, neat or ionic liquid-aided, is accompanied by foaming [5,21], which limits the ability to engineer a solid AB system. Proton sponge in ionic liquids was shown to both increase the release rate of the second mole of H_2 and suppress foaming [5]. Other additives, which suppress foaming and enable morphological stability during AB thermolysis, have also been investigated [21].

To further understand details of bmimCl aided AB thermolysis, H_2 generation measurements for AB thermolysis under atmospheric pressure and quasi-isothermal conditions were conducted in the present study. The hydrogen yields and release rates (particularly, in the first 5 min) from the thermolysis of neat AB and AB/bmimCl mixtures (50/50 and 80/20 wt%) in a temperature (T) range between 85 and 120 °C were measured. The temperature range was selected with the consideration of utilizing waste heat from an internal combustion engine or a PEM fuel cell. The specific objectives of the present work were to:

1. Capture the initial H_2 release process in neat and bmimCl aided AB thermolysis;
2. Investigate the effects of temperature on H_2 release rate and yield in bmimCl aided AB thermolysis; and
3. Investigate the effects of impurity and aging of bmimCl on H_2 yield.

2. Experimental

2.1. Materials

Ammonia borane (Aviabor, Dzerzhinsk, Nizhny Novgorod, Russia) and bmimCl (≥99% purity, Lot # 1409627, Fluka Analytical)
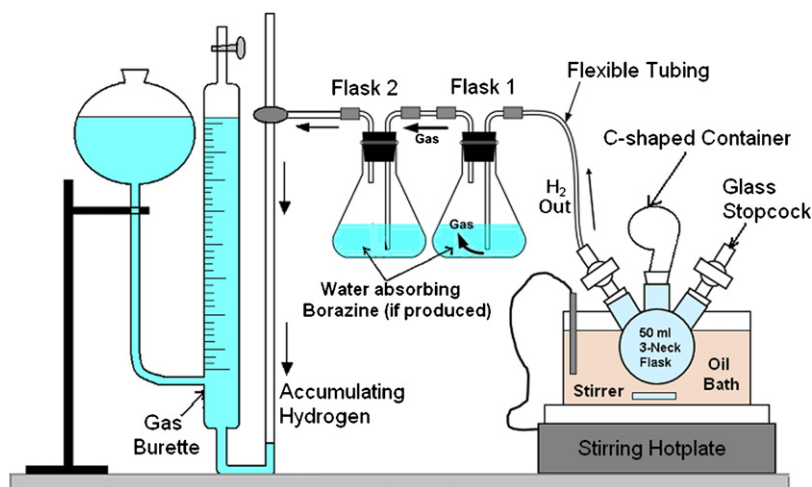
Fig. 1. Experimental apparatus.

were used as received in the AB thermolysis measurements. Another grade of bmimCl ($\geq$98% purity, Lot # 1411922, Fluka Analytical) was used as received to study the effect of bmimCl purity on the reaction. A small amount of AB (136 ± 0.5 mg) was used in each experiment such that the evolved volume of H_2 could be accommodated in a 250 ml gas burette. Also, 34 ± 0.5 mg and 136 ± 0.5 mg bmimCl were used in 80/20 and 50/50 AB/bmimCl mixture thermolysis, respectively.

BmimCl is very sensitive to the moisture and oxygen in air. It should be stored under argon atmosphere; otherwise it becomes lumped and the H_2 yield from the thermolysis of AB is lowered significantly. Even stored in an argon environment (1 mbar pressure, 0.1 ppm H_2O, and 0.1 ppm O_2) after approximately 5 weeks, the bmimCl salt became lumped and deactivated. In a 0.1 ppm O_2 environment, there exists greater than 10^{12} molecules per cm^3 of O_2 atoms. These O_2 atoms may react with the ions of bmimCl while it was stored causing a decrease in the yield of the thermolysis reaction. Therefore all data from using bmimCl presented in this paper are limited to fresh bmimCl received from the vendor.

2.2. Apparatus, procedure, and operating conditions

The experimental apparatus is shown schematically in Fig. 1. A glass container (500 ml) was loaded with soybean cooking oil (Pure Wesson Vegetable Oil, Con Agra, NE) and a stirring bead. The oil bath was seated on a hot-plate magnetic stirrer and the oil was heated to the desired reaction temperature. The stirring bead was rotated at a speed of 550 rpm. A c-shaped glass container (2 ml) was pre-loaded with the desired amount of AB. A 50 ml 3-necked reaction flask was pre-loaded with desired amount of bmimCl and stored in a glove box under argon atmosphere (1 mbar pressure, 0.1 ppm H_2O, 0.1 ppm O_2). After being taken out of the glove box, the flask was immediately submerged in the pre-heated oil bath and a nitrogen purge was connected at the central neck. An open stopcock was seated on one of the two side-necks of the flask to allow any trapped air (being replaced by the N_2) to flow out of the flask. The other side-neck of the flask was sealed with a rubber septum and a hypodermic type-T thermocouple (copper constantan, accuracy 0.5 K, with a stainless steel sheath) pierced through it to measure the reaction temperature. When the thermocouple was not used, the side-neck was covered by a glass stopcock. The flask was allowed to attain the oil bath temperature for about 10 min and was continuously purged with N_2 during this period of time.

After pre-heating of the flask, the open stopcock that was used as the vent was removed and that side-neck was connected to a gas burette using a glass stopcock and tubing. The nitrogen source was removed from the central neck and the AB was gently poured into the reaction flask through the central neck from the c-shaped glass container. The c-shaped container was seated on and clamped to the central neck, and the stopwatch (for time recording) started. The oil bath temperature was maintained constant within a variation of $\pm 1\,°C$.

The evolving H_2 was passed through two successive flasks of water that could absorb and condense the trace amounts of gaseous byproducts formed during the thermolysis, such as borazine [16]. Subsequently, the H_2 was collected in the gas burette with a resolution of 1.0 ml. The accumulated H_2 volume in the gas burette was monitored and recorded using a high-density video camcorder (HV20 Canon; Zoom 6.1–61 mm, video lens with $10\times$ optical zoom and instant autofocus, 2.96 megapixel image sensor, filter size 43 mm, 24p cinema mode). The temperature of the H_2 gas accumulated in the burette was measured at the end of each experiment.

The recorded tape was replayed at the end of each experiment. The display was zoomed at the gas burette graduated marks. The hydrogen evolution data, from which the reaction rates were calculated, were acquired by pausing and noting down the volume graduations and corresponding time instants from the recorded video. The amount of collected hydrogen in the burette was calculated using the ideal gas law with the consideration of pressure variation caused by the change of water column height [2].

The operating temperatures for the thermolysis of neat AB, 80/20 AB/bmimCl mixture, and 50/50 AB/bmimCl mixture are listed in Table 1. The present apparatus was able to maintain the reaction at the desired temperature within a variation of $\pm 2\,°C$ for most part of the reaction. In the AB/bmimCl mixture tests at temperatures higher than $105\,°C$, within less than 30 s after 2–4 min from the beginning of the heating, the temperature quickly increased by 5–25 $°C$ followed by a rapid return to the isothermal condition, resulting in a sharp spike in the reaction temperature profile.

Table 1
Experimental conditions of AB thermolysis.

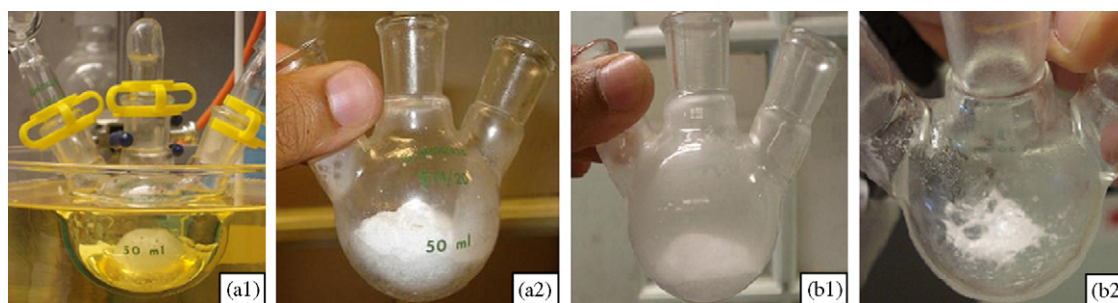| Material	Oil bath temperature ($°C$)
Neat AB	100, 105, 115, 120
80/20 AB/bmimCl	85, 95, 105, 107, 108, 110, 115, 120
50/50 AB/bmimCl	120

Fig. 2. Photographs of 50 ml flask with materials of: (a1) neat AB during thermolysis, (a2) product of neat AB thermolysis right after the completion of the reaction, (b1) product of 80/20 AB/bmimCl mixture thermolysis right after the completion of the reaction, and (b2) product of 80/20 AB/bmimCl mixture thermolysis 24 h after the completion of the reaction.

2.3. Experimental uncertainty

It was estimated that the instrumentation inaccuracy for the hydrogen gas temperature and volume measurements caused ±1.4% bias error in the moles of hydrogen collected or the moles of AB consumed. Based on three repeated 80/20 AB/bmimCl experiments under the same conditions at 100 °C, the overall random error caused by the measurements of time, the mass of AB, and the mass of bmimCl, led to an experimental uncertainty of 3.8% (with 95% confidence). As a result, the overall experimental uncertainty in the moles of hydrogen collected or the moles of AB consumed were estimated to be 4.0% with 95% confidence.

3. Results and discussion

3.1. Experimental observation

Fig. 2 demonstrates photographs of the 50 ml 3-necked flask with materials of: (a1) neat AB during thermolysis, (a2) product of neat AB thermolysis right after the completion of the reaction, (b1) product of 80/20 AB/bmimCl mixture thermolysis right after the completion of the reaction, and (b2) product of 80/20 AB/bmimCl mixture thermolysis 24 h after the completion of the reaction.

The reactants (AB/bmimCl mixture or neat AB) occupied approximately 2 ml in the 50 ml reaction flask at the start of reaction. During the thermolysis reaction, frothing was observed and the reaction mixture (reactants and byproducts) expanded as shown in photograph (a1). For neat AB thermolysis, the reaction byproducts occupied approximately 25 ml in the flask (or 12 times volume expansion) at the end of reaction as shown in photograph (a2). For the 80/20 AB/bmimCl mixture thermolysis, the reaction byproducts occupied approximately 15 ml in the flask (or seven times volume expansion) at the end of reaction as shown in photograph (b1). The presence of 20 wt% bmimCl suppressed the extent of volume expansion of the byproducts by approximately 40%. For the spent fuel mixture with bmimCl, the frothing-with-volume expansion effect subsided after approximately 24 h as shown in photograph (b2).

With a small change of heating temperature from 105 to 107 °C, significant H_2 yield increase was observed during the thermolysis of the 80/20 AB/bmimCl mixture. The 80/20 AB/bmimCl mixture is a slurry at temperatures above 85 °C with some of the AB dissolved in bmimCl. The significant H_2 yield increase with the small change of heating temperature may be caused by the melting of AB, which completes around 112 °C. With the present quasi-isothermal apparatus, the reaction temperature exceeded 112 °C for a very short period of time with the heating temperature of 107 °C. We assumed that the solid–liquid phase AB/bmimCl slurry changed into a liquid phase within the first 2 min of heating and that most of the dehydrogenation process occurred in the liquid phase. As the H_2

release progressed, a solid byproduct (most likely polyiminoborane based on literature and limited spent fuel chemical analysis of the products of the present experiments) began to form and the mixture solidified during the evolution of the second equivalent of H_2. In other words, the thermolysis of AB/bmimCl slurry is accompanied with changes in phase from (a) solid AB crystals, to (b) molten AB/bmimCl mixture, to (c) solid byproduct. The process is also accompanied with competing reactions, frothing and volume expansion effects.

3.2. Effect of bmimCl mass fraction

Fig. 3 depicts the measured AB thermolysis processes in the presence of different proportions of bmimCl (0, 20, and 50 wt%) at 120 °C, as represented by the moles of H_2 released (nH_2) per mole of initial AB ($n_{AB,0}$) as a function the reaction time (t). As illustrated in Fig. 3a, the present measurements are consistent with the data
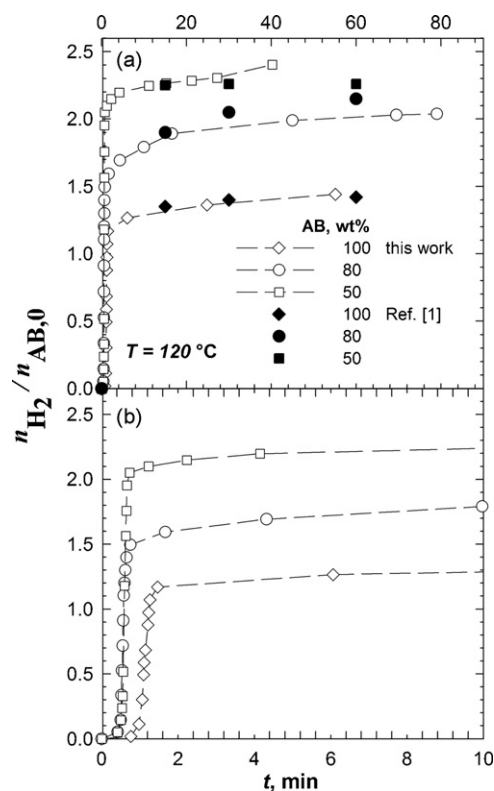

Fig. 3. Hydrogen release rate for AB thermolysis with different proportions of bmimCl at 120 °C: (a) time between 0 and 90 min of reaction and (b) time between 0 and 10 min showing the initial H_2 evolution. The present experimental data are compared to those reported in Ref. [5].
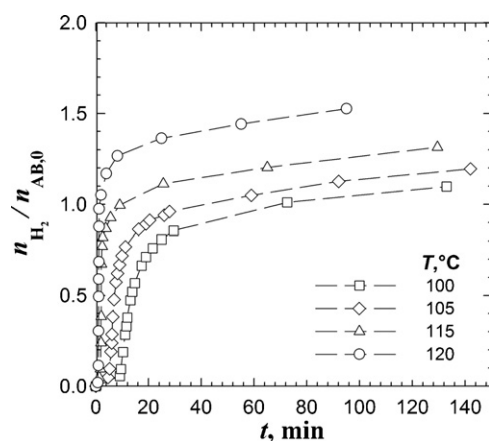
Fig. 4. Thermolysis of neat AB.

reported in Ref. [5], where the reaction flask was plunged into a hot oil bath without pre-heating, thermolysis started under vacuum conditions, and volatile non-hydrogen byproducts were captured using a liquid nitrogen trap.

At 120 °C, for 50/50 AB/bminCl mixture, 80/20 AB/bmimCl mixture, and neat AB tests, 2.4, 2.1, and 1.4 mol of H_2 per mole of AB were released after 40, 80, and 56 min of heating, respectively. The increase in H_2 yield with increasing mass fraction of bmimCl in the mixture suggests that the yield increases with the amount of initial AB dissolving in the ionic liquid. The highest measured hydrogen storage capacity was 11.2 wt% from the thermolysis of 80/20 AB/bmimCl mixture at 120 °C, which is within uncertainty limits of the highest ever reported (11.4 wt%) in Ref. [16]. Considering its high hydrogen storage capacity, remaining studies of the effects of temperature and bmimCl addition were focused on the 80/20 AB/bmimCl mixture.

The dehydrogenation process during its earliest time step was successfully captured by the present experimental approach as shown in Fig. 3b, where the first 10 min of the process are detailed. For the two bmimCl aided tests at 120 °C, there was a very slow dehydrogenation period at the beginning of the reaction. Then there was a rapid hydrogen release process approximately within the following 30 s. Most of the hydrogen was released at this stage, followed by a slow dehydrogenation process during which a smaller amount of additional hydrogen was released.

3.3. Effect of temperature

3.3.1. Neat AB thermolysis

Under the quasi-isothermal conditions of the experiments, dehydrogenation of neat AB was observed within 30 min of heating between 95 and 100 °C. A detailed plot of neat AB thermolysis in the temperature range from 100 to 120 °C is depicted in Fig. 4. Both the H_2 yield and the release rate increase with increasing temperature in this range. A gravimetric hydrogen storage capacity of 9.9 wt% was achieved at 120 °C after 100 min of heating. The induction time and hydrogen yields of neat AB thermolysis at various temperatures were summarized in Table 2.

Table 2
Induction time and hydrogen yields of neat AB thermolysis under quasi-isothermal conditions at atmospheric pressure.

Temperature (°C)	Induction time (min)	H_2 yield (mol H_2/mol AB)
100	10	1.1
105	5	1.2
115	1.5	1.3
120	1	1.5

3.3.2. BmimCl aided AB thermolysis

Fig. 5a shows the normalized moles of H_2 released per mole of AB as a function of time for thermolysis of the 80/20 AB/bmimCl mixture at eight temperatures in the range from 85 to 120 °C. With the addition of 20 wt% bmimCl, dehydrogenation occurred right away at temperatures as low as 85 °C. At higher temperatures the thermolysis processes were very rapid and the data of Fig. 5a need to be deciphered with a magnified scale as shown in Fig. 5b, where very short induction periods for thermolysis at higher temperatures are revealed. Both the H_2 release rate and the final yield increased with increasing temperature in the present experimental range. For temperatures above 107 °C, a brief relatively slow dehydrogenation period progressively decreased from 2.5 to 0.5 min with increasing temperature was observed. This slow dehydrogenation period was followed by a rapid hydrogen release process lasting less than 0.5 min. Most of the hydrogen was generated during this 0.5 min period with the reaction temperature profile showing a sharp exothermic temperature spike followed by a rapid return to the isothermal condition. The dehydrogenation rates, represented by slopes of the curves in Fig. 5b, also showed a spike within the 0.5 min period when the nominal oil bath temperature increased within a narrow range from 105 to 107 °C. The less than 0.5 min rapid hydrogen release process was followed by a slower dehydrogenation process providing the final yield of over 2 mol of hydrogen per mole of AB. In this final stage, the formation of polymers (amino and imino boranes) may impede the reaction speed. These observations suggest changes in the underlying reaction mechanisms deserving of future detailed studies.
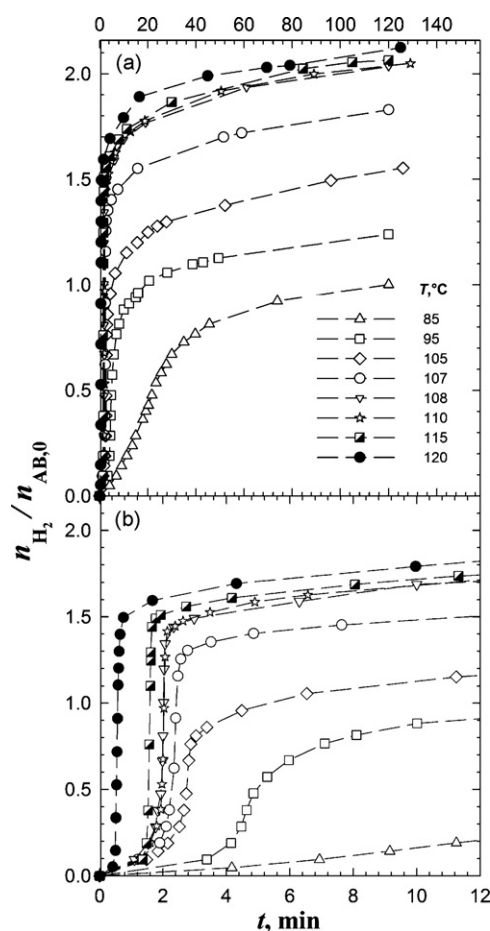

Fig. 5. Thermolysis of a mixture of 20 wt% bmimCl (99% purity) and 80 wt% AB: (a) time between 0 and 140 min of reaction and (b) time between 0 and 12 min showing the initial H_2 evolution.
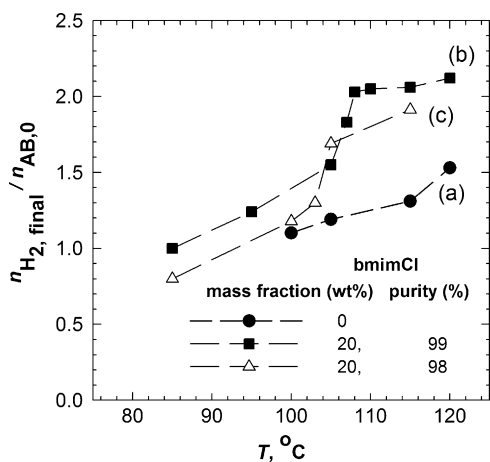
Fig. 6. Final hydrogen yields from the thermolysis of: (a) neat AB, (b) 80:20 wt% mixture of AB and 99% purity bmimCl, and (c) 80:20 wt% mixture of AB and 98% purity bmimCl.

The H_2 yields, defined as moles of H_2 per mole of AB at the end of the thermolysis process, are plotted as a function of reaction temperature in Fig. 6. Results of three different sets of experiments: (a) neat AB, (b) 80/20 mixture of AB in 99% purity bmimCl, and (C) 80/20 mixture of AB in 98% purity bmimCl are shown. The variation of final H_2 yield with temperature shows an almost linear increase within the present experimental range for the neat AB. The two sets of experiments (b) and (c) with bmimCl clearly show a dramatic increase in the yield at all temperatures including a rapid increase in a narrow 2 °C range around 107 °C. The high sensitivity of the results to bmimCl purity is also clearly underscored by the data in Fig. 6. Both experiments with 98% and 99% purity samples (curves b and c) illustrate the dramatic qualitative and quantitative change in the H_2 yield and its temperature dependence.

The gravimetric hydrogen storage capacities (material base) and initial H_2 release rates of neat and bmimCl (20 wt%, 99% purity) aided AB thermolysis under atmospheric pressure in the temperature range from 85 to 120 °C are summarized in Table 3. The initial H_2 release stage is defined as the time of the first 0.5 mol of hydrogen released per mole of AB. For neat AB thermolysis, the initial H_2 release rate increased from 0.04 (mol H_2/mol AB) per minute at 100 °C to 0.45 (mol H_2/mol AB) per minute at 120 °C. For the 80/20 AB/bmimCl mixture, the initial H_2 release rate increased from 0.02 (mol H_2/mol AB) per minute at 85 °C to 0.94 (mol H_2/mol AB) per minute at 120 °C. At reaction temperatures of 105 and 120 °C, the initial H_2 release rates more than doubled by the addition of 20 wt% bmimCl. The results from Table 3 show that using bmimCl solvent for AB, the hydrogen storage capacity can be increased by over neat AB.

4. Conclusions

In the present experimental study, neat and bmimCl aided AB thermolysis under quasi-isothermal conditions in the temperature range from 85 to 120 °C was investigated. Dehydrogenation of neat AB was observed with less than 30 min induction period between 95 and 100 °C. At 120 °C, the measured gravimetric hydrogen storage capacity of neat AB thermolysis was 9.9 wt%. With a 20 wt% addition of bmimCl, (1) dehydrogenation occurred right away at a lower temperature of 85 °C; (2) the measured hydrogen storage capacity of the 80/20 AB/bmimCl mixture was 11.2 wt% at 120 °C; and (3) foaming during AB thermolysis was partially suppressed. These features make the bmimCl aided AB thermolysis a very attractive hydrogen storage approach, although hydrogen yield reduction caused by impurity and aging of bmimCl should be further addressed. Also, bmimCl aided thermolysis should be implemented at sufficiently high temperature (>107 °C) to achieve a noticeable gain in the hydrogen storage capacity when comparing to the neat AB thermolysis.

References

[1] M. Chandra, Q. Xu, A high-performance hydrogen generation system: transition metal-catalyzed dissociation and hydrolysis of ammonia–borane, J. Power Sources 156 (2006) 190–194.
[2] S. Basu, A. Brockman, P. Gagare, Y. Zheng, P.V. Ramachandran, W.N. Delgass, J.P. Gore, Kinetics of Ru-catalyzed ammonia borane hydrolysis, J. Power Sources 188 (2009) 238–243.
[3] A. Brockman, Y. Zheng, J.P. Gore, A study of catalytic hydrolysis of concentrated ammonia borane solutions, Int. J. Hydrogen Energy 35 (2010) 7350–7356.
[4] A. Brockman, Amonia Borane Hydrolysis Based Hydrogen Storage: Engineering Considerations, M.S. Thesis, Purdue University, West Lafayette, Indiana, May 2008.
[5] L.G. Sneddon, Amineborane-based Chemical Hydrogen Storage, 2008 DOE Hydrogen Program Review, Project ID: ST7, http://www.hydrogen. energy.gov/pdfs/review08/st_7_sneddon.pdf, 2008.
[6] M.G. Hu, R.A. Geanangel, W.W. Wendlandt, The thermal decomposition of ammonia borane, Thermochim. Acta 23 (1978) 249–255.
[7] G. Wolf, J. Baumann, F. Baitalow, F.P. Hoffmann, Calorimetric process monitoring of thermal decomposition of B–N–H compounds, Thermochim. Acta 343 (2000) 19–25.
[8] M. Bowden, T. Autrey, I. Brown, M. Ryan, The thermal decomposition of ammonia borane: a potential hydrogen storage material, Curr. Appl. Phys. 8 (2008) 498–500.
[9] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Roßler, G. Leitner, Thermal decomposition of B–N–H compounds investigated by using combined thermoanalytical methods, Thermochim. Acta 391 (2002) 159–168.
[10] A.T. Raissi, Hydrogen from ammonia and ammonia–borane complex for fuel cell applications, in: Proceedings of the 2002 US DOE Hydrogen Program Review, NREL/CP-610-32405, http://www.eere.energy.gov/ hydrogenandfuelcells/pdfs/32405b15.pdf, 2002.
[11] F.H. Stephens, V. Pons, R.T. Baker, Ammonia–borane: the hydrogen source par excellence? Dalton Trans. (2007) 2613–2626.
[12] N. Mohajeri, A.T. Raissi, K.K. Ramasamy, Thermal conductivity of ammonia borane complex and its composites with aluminum powder, Thermochim. Acta 452 (2007) 28–30.
[13] C.R. Miranda, G. Cedar, Ab initio investigation of ammonia–borane complexes for hydrogen storage, J. Chem. Phys. 126 (2007) 184703-1–184703-11.
[14] M.E. Bluhm, M.G. Bradley, R. Butterick, U. Kusari, L.G. Sneddon, Amineborane-based chemical hydrogen storage: enhanced ammonia borane dehydrogenation in ionic liquids, J. Am. Chem. Soc. 128 (2006) 7748–7749.
[15] L.G. Sneddon, Amine-borane Based Chemical Hydrogen Storage, 2007 DOE Hydrogen Program Review, Project ID: ST27, http://www.hydrogen.energy.gov/pdfs/review07/sat_27_sneddon.pdf, 2007.

Table 3
Measured H_2 storage capacities (wt%) and initial H_2 release rates for AB thermolysis under quasi-isothermal conditions at atmospheric pressure.

T (°C)	Neat AB thermolysis		80/20 AB/bmimCl thermolysis	
	Wt%	Initial H_2 release rate (mol H_2/mol AB) min^{-1}	Wt%	Initial H_2 release rate (mol H_2/mol AB) min^{-1}
85			5.1	0.02
95			6.4	0.10
100	7.1	0.04		
105	7.7	0.07	8	0.18
107			9.2	0.22
108			10.4	0.24
110			10.5	0.25
115	8.5	0.24	10.6	0.32
120	9.9	0.45	11.2	0.94

[16] D.W Himmelberger, L.R. Alden, M.E. Bluhm, L.G. Sneddon, Ammonia borane hydrogen release in ionic liquids, Inorg. Chem. 48 (2009) 9883–9889.
[17] N. Mohajeri, A.T. Raissi, O. Adebiyi, Hydrolytic cleavage of ammonia–borane complex for hydrogen production, J. Power Sources 167 (2007) 482–485.
[18] M.R. Mallery, U. Pasaogulari, C.F. Mallery, J. Tessitore, Multiphysics model of ammonia borane pyrolysis to H_2 gas for fuel cell applications, AIAA paper number, 2008 2008-4907.
[19] A. Karkamkar, C. Aardahl, T. Autrey, Recent developments on hydrogen release from ammonia borane, Mater. Matters 2 (2) (2007) 6–10.
[20] R.J. Young, P.A. Lovell, Introduction to Polymers, 2nd ed., CRC Press, Boca Raton, Florida, 1991.
[21] C. Aardahl, T. Autrey, D. Camaioni, D. Dubois, J. Linehan, A. Karkamkar, S. Rassat, R. Zheng, W. Shaw, J. Li, D. Heldebrandt, R. Potter, M. Mock, A. Luedtke, T. Smurthwaite, Chemical hydrogen storage research at PNNL, in: DOE Hydrogen Program FY 2008 Annual Progress Report, 2008, pp. 565–569, http://www.hydrogen.energy.gov/pdfs/progress08/iv_b_1c_aardahl.pdf.
[22] J Dupont, R.F. DeSouza, P.A.Z. Suarez, Ionic liquid (molten salt) phase organometallic catalysis, Chem. Rev. 102 (2002) 3667–3692.
[23] A. Takada, K. Imaichi, T. Kagawa, Y. Takahashi, Abnormal viscosity increment observed for an ionic liquid by dissolving lithium chloride, J. Phys. Chem. B 112 (2008) 9660–9662.
[24] A.P. Dadi, C.A. Schall, S. Varanasi, Mitigation of cellulose recalcitrance to enzymatic hydrolysis by Ionic liquid pretreatment, Appl. Biochem. Biotechnol. 137–140 (2007) 407–421.
[25] O. Yamamuro, Y. Minamimoto, Y. Inamuro, S. Hayashi, H. Hamaguchi, Heat capacity and glass transition of an ionic liquid 1-butyl-3-methylimidazolium chloride, Chem. Phys. Lett. 423 (2006) 371–375.
[26] L.G. Sneddon, Amineborane-based Chemical Hydrogen Storage, 2009 DOE Hydrogen Program Review, Project ID: ST16, Available online at http://www.hydrogen.energy.gov/pdfs/review09/st_16_sneddon.pdf, 2009.