Effect of Boric Acid on Thermal Dehydrogenation of Ammonia Borane: H_2 Yield and Process Characteristics

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We have recently demonstrated that boric acid (H_3BO_3, BA) is a promising additive to decrease onset temperature as well as to enhance hydrogen release kinetics for thermolysis of ammonia borane (NH_3BH_3, AB). The observations suggest that tetrahydroxyborate ion released by heating BA serves as Lewis acid and catalyzes AB dehydrogenation. Using this approach, we obtained high H_2 yield at 85°C, along with rapid kinetics. Various operating conditions were investigated, such as reactor temperature, AB wt %, and particle size of BA. Even in the presence of 10 wt % BA, high H_2 yield (13 wt %) and trace amount of ammonia (10–20 ppm) were obtained at 80°C, proton exchange membrane (PEM) fuel cell operating temperature. To our knowledge, such H_2 yield value is higher than from any other method using AB with additive or catalyst at PEM fuel cell operating temperatures. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3359-3364, 2013
Keywords: ammonia borane, boric acid, dehydrogenation, hydrogen, hydrogen storage

Introduction

Hydrogen is an important alternative to address some adverse aspects of current hydrocarbon-liquid fuels for transportation applications because, with oxygen in fuel cells to generate electricity, its only product is water. To develop hydrogen-powered vehicles, however, safe, light weight, and energy efficient methods for on-board hydrogen storage are required.

Ammonia borane (NH_3BH_3, AB) has attracted considerable interest as a promising hydrogen storage candidate because of its high hydrogen content (19.6 wt %), hydrogen release under moderate conditions, and stability at room temperature.[1–3] Hydrogen can be released from AB by hydrolysis, thermolysis, or hydrothermolysis.[4–6] Among the AB dehydrogenation methods, thermolysis provides potentially high hydrogen yield, significantly reduced ammonia production, and no B—O bond formation which is preferred from the spent fuel regeneration viewpoint.[3,5,7–9] In general, relatively high operating temperature, long-induction period, low H_2 yield, and slow kinetics still remain challenges for AB thermolysis.

Various additives have been developed to decrease onset temperature and induction period of AB thermolysis. Gutowska et al.[10] reported that a nanocomposite of mesoporous silica and AB releases hydrogen at 50°C with a half-reaction time of 85 min, as compared to half-reaction time of 290 min at 80°C for neat AB. Heldebrant et al.[11] found that addition of diammoniate of diborane ($[NH_3BH_2NH_3][BH_4]$, DADB) to neat AB significantly decreases the induction time and onset temperature at which hydrogen is released. Nanophase boron nitride (nano-BN) additives to AB play a similar role as DADB and also serve as a scaffold, both decreasing the onset temperature of H_2 release.[12] Himmelberger et al.[13] found that AB reactions in bmimCl (ionic liquid) containing 5.3 mol % (28 wt %) bis(dimethylamino) naphthalene [proton sponge (PS)] released two equivalent of H_2 in 171 min at 85°C. Dispersed metal nanoparticle catalysts such as Pd, Ni, and Pt were deposited on a silica-based mesoporous material to improve kinetic properties of AB thermolysis.[14] Unfortunately, these methods involve relatively large amount of expensive additives, which increase the overall system weight. Zhang et al.[15,16] reported that CO_2 enhances the kinetics of AB thermoloysis and 1.33 H_2 equivalent was measured at 85°C and 4 bar but separation and recycle of CO_2 from H_2 stream must be considered for its practical uses. Metal halides have been also used as catalysts to destabilize AB, which allow H_2 release at moderate temperatures.[17,18] Kalidindi et al.[18] obtained 9 wt % overall H_2 yield using 20 wt % (5 mol %) $CuCl_2$ at 60°C in 6.5 h. However, the stability of the catalysts at room temperature or in the presence of water must be resolved.

We have recently demonstrated that boric acid (BA) can decrease onset temperature of AB thermolysis to below PEM fuel cell operating temperatures and increase H_2 yield along with rapid kinetics as well.[19] Using this approach, 11.5 wt % overall hydrogen yield (2.23 H_2 equivalent) was obtained at 85°C. In addition, trace amount of NH_3 (20–30 ppm) was detected in the gaseous product.[19] It is believed that tetrahydroxyborate ion released by heating BA serves as Lewis acid, which catalyzes AB dehydrogenation[20]

$$H_3BO_3 \overset{\text{heat}}{\rightarrow} HBO_2+H_2O \tag{1}$$

$$H_3BO_3+H_2O \rightarrow B(OH)_4^- +H_3O^+ \tag{2}$$

In our prior work, mechanistic studies were carried out to understand the reaction mechanism of AB dehydrogenation

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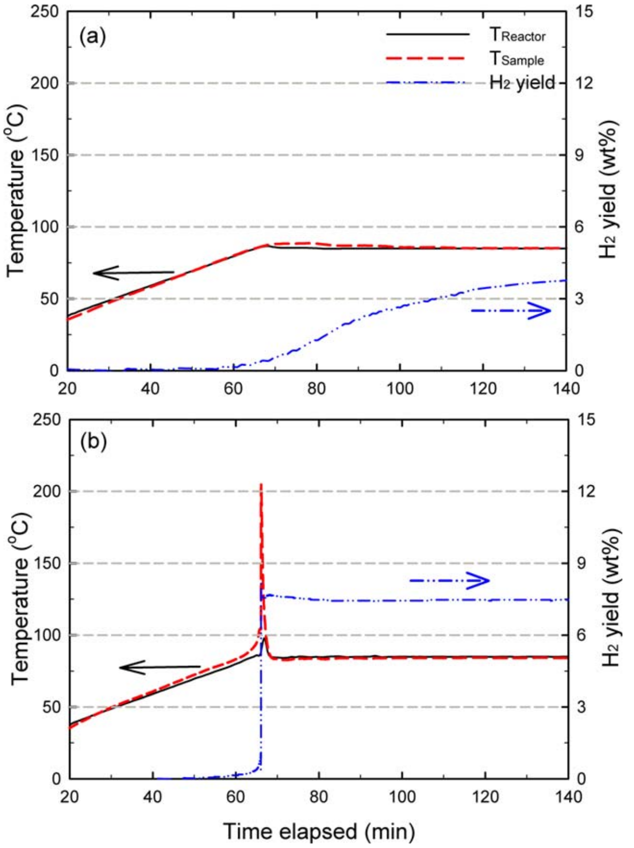

Figure 1. H_2 yield and temperature profiles for T_{SP}=85°C, P_i=14.7 psia, and heating rate=2°C/min (a) neat AB, (b) 50 wt % AB (AB:BA=1:1).

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in the presence of BA. In this work, H_2 yield and process characteristics were studied by varying operating conditions, such as reactor temperature, AB wt %, and particle size of BA, to determine the efficacy of BA as an additive.

Experimental

The experiments were conducted in a stainless steel reactor (Parr Instrument Company, Model 4592; volume 70 mL) with external heating. The samples were prepared by mixing AB (NH_3BH_3, 97% pure, Sigma Aldrich) with BA (H_3BO_3, 99.9% pure, Mallinckrodt), or anhydrous iron chloride ($FeCl_2$, 98% pure, Sigma Aldrich), or anhydrous nickel chloride ($NiCl_2$, >98% pure, Sigma Aldrich), or anhydrous cobalt chloride ($CoCl_2$, 98% pure, Sigma Aldrich) and placed in a small glass vial (5 mL) inside the reactor. Starting at room temperature, with 2°C/min heating rate, the reaction vessel was maintained for 60-min hold at the set point value (T_{SP}). The reactor pressure and temperatures (sample and reactor) were monitored using an online pressure transducer and thermocouples. For transient mass-spectrometry (MS, Hiden Analytical HPR-20) analysis of gaseous products, a fixed volumetric flow of Ar (120 cc/min) was introduced to the reactor using a mass flow controller and gas generation was analyzed with time using MS. For hydrogen release measurements, the reactor was operated in a batch mode, while argon gas was continuously injected into the reactor for the transient analysis. After cooling the reactor to room temperature at the end of the experiment, the product gas was collected in a sampling bag and then NH_3 concentration was measured using Drager tube. To examine the dehydration properties of BA, thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) (TA Instruments, SDT Q600) was used and the exit gas was analyzed by MS. Particle size of BA was characterized by a light-scattering particle-size distribution analyzer (Horiba-950). Additional experimental details are discussed elsewhere.[7,21,22]

Results and Discussion

Effect of reactor temperature and AB concentration

Figure 1 shows the profiles of typical temperature and overall H_2 yield (i.e., accounting for weights of both AB and additive) for neat AB and 50 wt % AB (AB:BA=1:1) at 14.7 psia and heating rate 2°C/min for reactor set point temperatures (T_{SP}) 85°C. For neat AB thermolysis without BA, hydrogen gradually evolved with time after reaching the set point temperature and only ~2.3 wt % H_2 yield was achieved in 30 min as shown in Figure 1a. On the other hand, for 50 wt % AB, hydrogen yield ~7.4 wt % was achieved and stabilized quickly after sharp heat evolution (Figure 1b). It was found that the sample temperature increased sharply up to ~200°C (sufficient to release the second H_2 mole from AB), with simultaneous evolution of H_2. It is known that the release of first and second hydrogen from AB via thermolysis is exothermic.[5] Thus, it is expected that the heat released during the first dehydrogenation step drives the second step.

Figure 2 shows the effect of reactor set point temperature on H_2 yield for different AB wt%. It may be seen that reactor set point temperature at which sharp H_2/heat evolution occurred decreases with decreasing AB wt% (or AB/BA ratio). For 33 and 50 wt % AB, the sharp evolution was observed for all the reactor set point temperatures tested in this study, while it was measured to be 80 and 95°C for 67 and 80 wt % AB, respectively. On the other hand, for 90 wt % and neat AB, H_2 yield increases with reactor temperature but no sharp evolution was observed. It was also found that when the sharp evolution occurs, H_2 yield is independent of

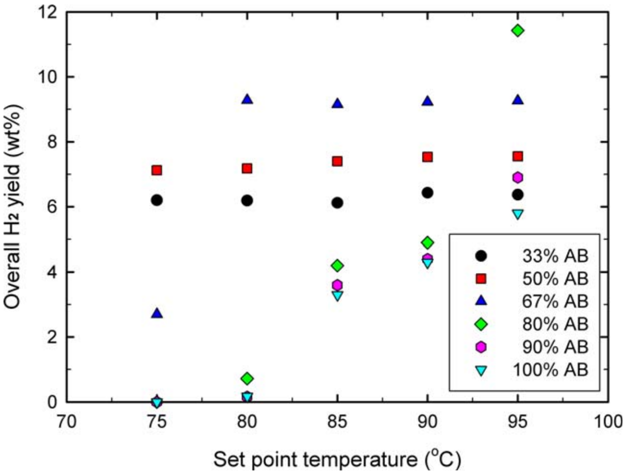

Figure 2. Effect of reactor temperature and AB concentration on H_2 yield (P_i=14.7 psia, heating rate=2°C/min, and d_{BA}=380 μm).

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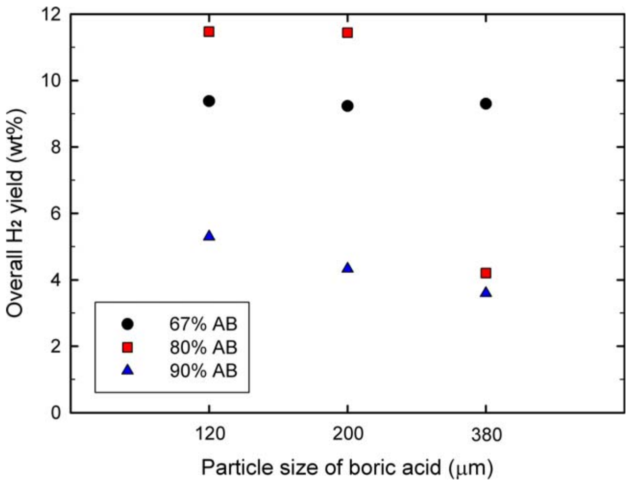

Figure 3. Effect of BA particle size on H_2 yield for different AB concentrations (T_{SP}=85°C, P_i=14.7 psia, and heating rate=2°C/min).

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the reactor set point temperature. The H_2 yields after sharp evolution were measured to be ∼6.3, 7.4, 9.2, and 11.4 wt % for 33, 50, 67, and 80 wt % AB, respectively. These results agree with the hypothesis that tetrahydroxyborate ion serves as Lewis acid, which catalyzes AB dehydrogenation. With heating, BA forms these ions along with some water released from BA itself (Eqs. 1 and 2). Note that amount of water from BA in the temperature range 75–95°C is small, as compared to BA itself, so that amount of Lewis acid generated is proportional to that of water. It is apparent that the amount of water liberated, hence the amount of Lewis acid formed, increases with increasing set point temperature and BA content.

Effect of reactor BA particle size

To investigate the effect of BA particle size (d_{BA}) on hydrogen release kinetics, BA was used as received or treated using mortar and pestle or ball-milling. The average d_{BA} values were measured to be 380, 200, and 120 μm, respectively. In these experiments, samples with different d_{BA} were tested at 85°C for 67, 80, and 90 wt % AB. As shown in Figure 3, it was found that H_2 release kinetics is enhanced by decreasing d_{BA}. For 67 wt %, sharp H_2/heat evolution was observed for all the particle sizes tested in this study and ∼9.2 wt % H_2 yield was obtained after the sharp heat evolution. Interestingly, by decreasing d_{BA} to ≤200 μm, sharp H_2/heat evolution was observed for 80 wt % AB which did not exhibit sharp evolution for d_{BA}=380 μm. Adding 20 wt % BA, high H_2 yield ∼11.5 wt % was achieved along with rapid kinetics at 85°C. On the other hand, for 90 wt % AB, no sharp evolution occurred even with d_{BA}=120 μm, although H_2 yield gradually increased with decreasing particle size from 3.6 to 5.3 wt % H_2. The TGA/DSC/MS analysis for different size of neat BA was conducted, as shown in Figure 4, where note that data for d_{BA}=120 μm was presented in our prior work.[19] It can be seen that the weight change of BA is closely related to dehydration of BA (Figure 4b). From these results, it is clearly seen that by decreasing its particle size, water release from BA is enhanced, suggesting that formation of Lewis acid catalyzing AB dehydrogenation, is also facilitated.

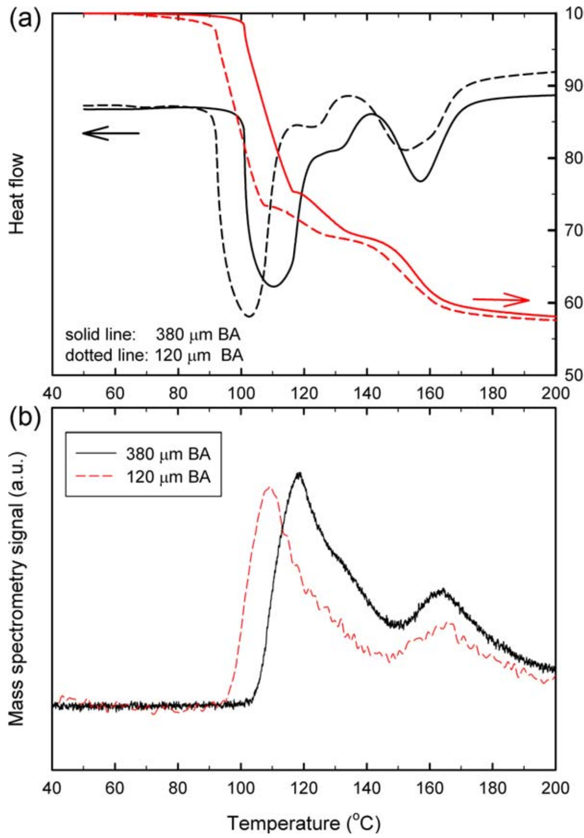

Figure 4. Transient analysis of TGA/DSC-MS for different BA particle sizes (a) TGA/DSC, and (b) MS.

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Effect of sample configuration

Although sharp heat evolution resulting in high H_2 yield was not observed for 90 wt % AB, another experiment for the same AB wt% was conducted with a different sample configuration. In this case, some 1:1 AB-BA mixture was placed at the bottom, while the remaining neat AB was added at the top. This arrangement (Figure 5a) permits heat

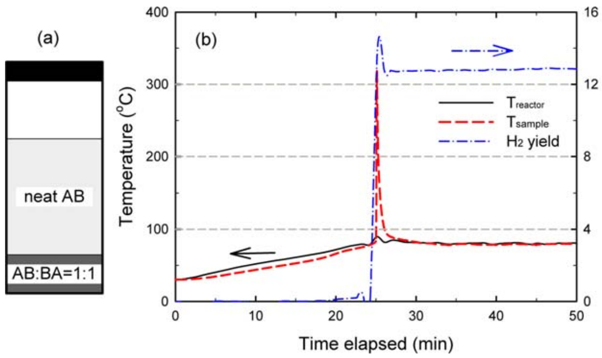

Figure 5. (a) Configuration of AB-BA mixture (b) H_2 yield and temperature profiles obtained for 90 wt % AB at T_{SP}=80°C, P_i=14.7 psia, heating rate=2°C/min, and d_{BA}=120 μm.

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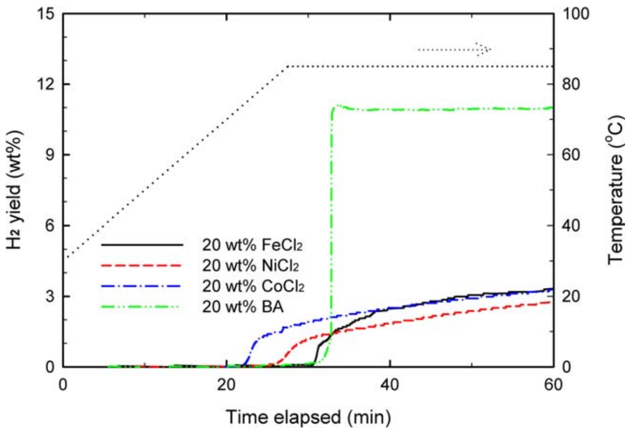

Figure 6. H_2 yield profiles from mixture of AB and different additives or catalysts for 80 wt % AB, T_{SP}=85°C, P_i=14.7 psia, and heating rate=2°C/min.

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generated from the AB-BA mixture to flow upward and initiate neat AB thermolysis. Figure 5b shows the temperature and H_2 profiles with time for 90 wt % AB – 10 wt % BA mixture at 14.7 psia, T_{SP} 80°C, and heating rate 2°C/min. Remarkably, high H_2 yield (13 wt %) was obtained along with rapid heat evolution, indicating that the behavior of AB thermolysis can be influenced by sample configuration. To our knowledge, the 13 wt % H_2 yield is higher than from any other method using AB at PEM fuel cell operating temperatures.

Effect of catalysts and comparison with BA addition

Some catalysts (e.g., metal halide, hydride, etc.) have been used to destabilize AB, which allow H_2 release at below PEM fuel cell operating temperatures.[23–25] In particular, metal chlorides have been reported to be active for AB thermolysis.[17,18] For this reason, catalytic performance of several metal chlorides such as $FeCl_2$, $NiCl_2$, and $CoCl_2$ was compared with that of BA. The powdered metal chlorides tested in this study were used as received, and samples were prepared under inert environment of glove box due to high sensitivity to moisture in air. Figure 6 shows the hydrogen release profiles for 80 wt % AB with 20 wt % catalyst/additive ($FeCl_2$, $NiCl_2$, $CoCl_2$, or BA) at 85°C. As compared to BA, all the metal chlorides showed lower onset temperature of AB dehydrogenation ($NiCl_2$, and $CoCl_2$) or higher initial dehydrogenation rate ($FeCl_2$). Thus, AB with $NiCl_2$ or $CoCl_2$ starts to release H_2 even at 72 and 81°C, respectively. In contrast, both $FeCl_2$ and BA release H_2 after reaching reactor set point temperature (85°C) but initial dehydrogenation rate for $FeCl_2$ was higher than that for BA. Unlike BA case, however, sharp H_2/heat evolution was not observed with any metal chlorides and H_2 yields gradually increased with time and were 3.3, 2.7, and 3.3 wt % in 30 min at 85°C for $FeCl_2$, $NiCl_2$, and $CoCl_2$, respectively.

Ammonia formation

For use in PEM fuel cell applications, ammonia must be removed from the H_2 stream.[7,26] It is known that even thermolysis of neat AB produces some ammonia.[7,8] We recently reported that for 80 wt % AB – 20 wt % BA, NH_3 concentration in gaseous product was only 20–30 ppm, much less than that observed in neat AB thermolysis.[19] In this study, we also measured ammonia formation using Drager tubing after cooling the reactor to room temperature at the end of the experiment. Each data point is an average of two to four experiments. As shown in Figure 7, NH_3 concentration increased with increasing BA wt %, indicating that AB or its thermolysis products react with water released from BA. When sharp evolution occurred, NH_3 concentration in the gaseous product decreased from 2.3% to 25 ppm with increasing AB wt% from 33 to 80 wt %. On the other hand, relatively high NH_3 formation of 3500 and 800 ppm were measured for 90 wt % and neat AB, respectively, which did not show sharp evolution. It was also found that both H_2 yield and NH_3 formation for 90 wt % AB are higher than those for neat AB, indicating that water released from BA contributes to both hydrolysis and catalytic thermolysis of AB. Figure 7 also shows the NH_3 formation for 90 wt % AB with different sample configuration (shown in Figure 5a). It is remarkable that in this case, only trace amount of NH_3 (10–20 ppm) was detected in the gaseous product. This result suggests that both the extent of AB hydrolysis and amount of water from BA are very small because most of the water from BA is expected to react vigorously with spent products of AB thermolysis (e.g., polyaminoborane, borazine, polyborazylene, etc.) due to their high reactivity with moisture.[27,28] Thus, assuming that no AB hydrolysis occurs for 80 and 90 wt % AB, we obtained ~2.2 H_2 equivalent from AB along with rapid kinetics at PEM fuel cell operating temperatures.

Transient analysis of gaseous products

Figure 8 shows transient MS analysis for both neat AB and 80 wt % AB-20 wt % BA, where a fixed volumetric flow of Ar was introduced through the reactor and gas generation was measured with time. Figure 8a also shows the set point temperature with time during the experiment. In these experiments, different reactor set point temperatures, 85 and 150°C, were applied for 80 wt % AB and neat AB, respectively. It is expected that both 80 wt % AB and neat AB release similar amount of H_2 (14–15 wt % H_2 based on AB only) under these conditions. Apart from H_2, we also

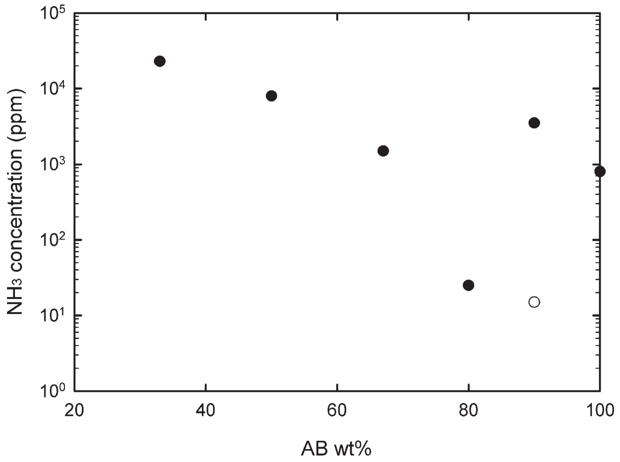

Figure 7. Effect of AB concentration on NH_3 formation for T_{SP}=85°C, P_i=14.7 psia, and heating rate=2°C/min.

Hollow symbol represents different sample configuration shown in Figure 5.

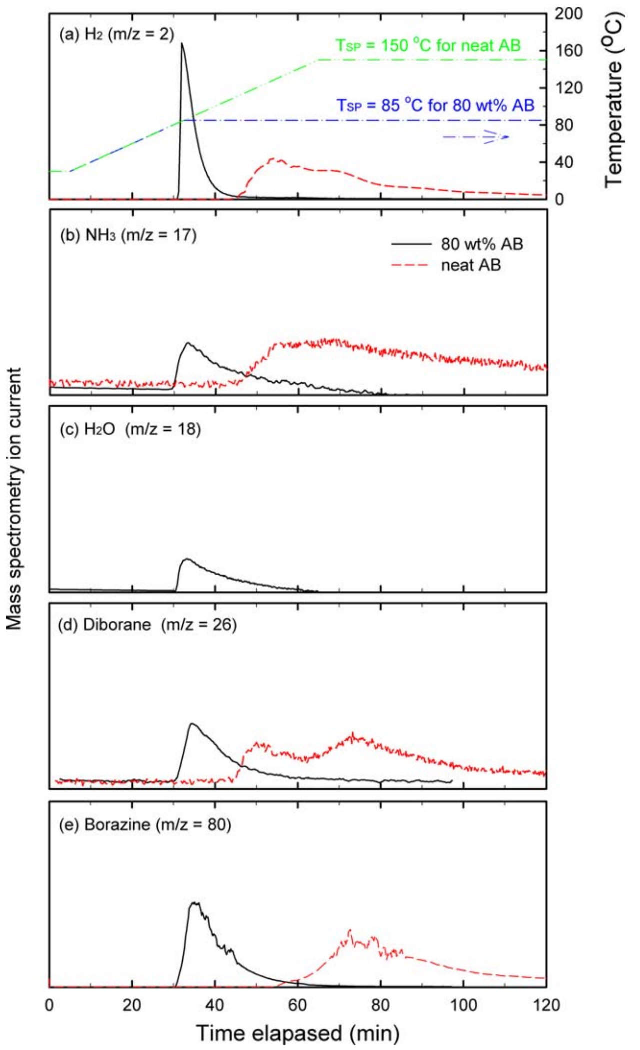

Figure 8. MS transient analysis for neat AB and 80 wt % AB-20 wt % BA mixture (a) hydrogen, (b) ammonia, (c) H_2O, (d) diborane, and (e) borazine (AB=0.2 g and heating rate=2°C/min).

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analyzed formation of other gaseous products (e.g., borazine, diborane, ammonia) which must be removed for use in PEM fuel cells.[1–3,7,26,29]

For neat AB, hydrogen release started at ~110°C and evolved gradually with time. It is clear from Figures 8a, b that release of NH_3 and H_2 follow the same pattern. Similarly, diborane is formed along with NH_3 and H_2 but it appears that more diborane is generated during second H_2 release from AB (Figure 8d). It is known that borazine is produced during the second hydrogen release by AB thermolysis,[5,30] which is in good agreement with our result (Figure 8e). Unlike neat AB, all gaseous products are quickly generated during sharp evolution for 80 wt % AB. Figure 8 shows that as compared to neat AB, 80 wt % AB produces comparable amount of borazine along with less ammonia and diborane. As expected, some water formation was also observed during the sharp evolution for 80 wt % AB (Figure 8c).

Comparison of different AB dehydrogenation methods

Table 1 summarizes the operating conditions and results of H_2 yield and NH_3 formation from different AB dehydrogenation methods.[7,19,22] It also shows the AB+additive [i.e., water, bmimCl, PS, nano-BN, quartz wool (QW), BA] weight required to generate 5.8 kg H_2 (350 miles drive with 50% fuel cell efficiency) from maximum H_2 yield corresponding to each method. Table 1 also summarizes the total weight of AB+additive along with the NH_3 removal weight requirements.[7,19,22] For these calculations, NH_3 adsorbent was used and its capacity was taken as 5 wt% NH_3. Thus, considering all factors including operating temperature and total weight requirement, the AB-BA and AB-QW systems are found to be the most promising among the various methods described in Table 1. As compared to gasoline internal combustion engines, assuming 25 mpg, the mass of gasoline required to drive 350 miles is ~40 kg, suggesting that the two AB-based hydrogen storage approaches are attractive for PEM fuel cell vehicle applications.

Conclusions

In recent work, we demonstrated that BA is a promising additive to decrease onset temperature as well as to enhance hydrogen release kinetics for thermolysis of AB.[19] The observations suggest that tetrahydroxyborate ion released by heating BA serves as Lewis acid and catalyzes AB dehydrogenation. In this work, this approach was investigated over various operating conditions such as reactor temperature, AB wt %, and particle size of BA. Even in the presence of relatively low 10 wt % BA, high overall H_2 yield (13 wt %) was obtained at 80°C, PEM fuel cell operating temperature. In addition, only trace amount of NH_3 (10–20 ppm) was detected in the gaseous product. Furthermore, the spent AB

Table 1. Comparison of Different Approaches for AB Dehydrogenation

AB Dehydrogenation Method	AB Concentration (wt %)	*T*sp (°C)	*P*$_i$ (psia)	Maximum OverallH$_2$ Yield (wt %)	NH$_3$ Concentration (mol% or ppm)[a]	WeightAB+ Additive (kg)	Weight of NH$_3$ Removal (kg)	Total Weight Requirement (kg)
Hydrothermolysis[7]	77	85	200	13.5	1.0%	43	10	53
AB/bmimCl+3 wt % moisture[7]	90	110	14.7	13	0.2%	45	2	47
AB/bmimCl/PS+3 wt % moisture[7]	49[b]	85	14.7	7.6	0.5%	76	5	81
AB/nano-BN[7]	80	150	14.7	12	0.3%	48	3	51
Neat AB[7]	100	85	14.7	2.7	0.04%	215	0.5	215.5
Neat AB[7]	100	150	14.7	15	0.1%	39	1.2	40.2
Neat AB+QW[21]	83	90	14.7	12	10 ppm	49	0.01	49
AB+BA[18]	80	85	14.7	11.5	25 ppm	51	0.03	51
AB+BA	90	80	14.7	13	15 ppm	45	0.01	45

[a] Measured at AB concentration which provides maximum H_2 yield.
[b] AB: 250mg, bmimCl: 250 mg, PS: 10 mg.

solid product was found to be polyborazylene-like species,[19] which can be efficiently regenerated using currently developed methods.[9] To our knowledge, such H_2 yield value is higher than from any other method using AB with additive or catalyst at PEM fuel cell operating temperatures. The results suggest that the hydrogen storage approach described in this work is promising for PEM fuel cell vehicle applications.

Acknowledgment

One of us (AV) recalls with great fondness the period of his graduate studies under the direction of "The Chief." We thank Ahmad Al-Kukhun for assistance with some experiments.

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