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Article

# Surface-Controlled Conversion of Ammonia Borane from Boron Nitride

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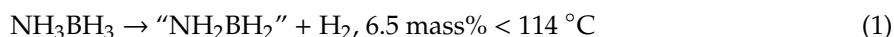
**Abstract:** “One-pot regeneration”, which is simple regeneration method of ammonia borane (AB) using hydrazine and liquid ammonia, enables conversion of AB from hexagonal boron nitride (h-BN) after milling hydrogenation. Solution <sup>11</sup>B-NMR revealed the presence of AB after NH<sub>3</sub>/N<sub>2</sub>H<sub>4</sub> treatment of milled h-BN (BNH<sub>x</sub>) although the yield of AB was less than 5%. The conversion mechanism was clarified as B-H bonds on the h-BN surface created by ball-milling under hydrogen pressure have an ability to form AB, which was confirmed by Thermogravimetry-Residual Gas Analysis (TG-RGA) and Infrared (IR) analysis. The reaction routes are also the same as regeneration route of polyborazylene because intermediates of AB such as (B(NH<sub>2</sub>)<sub>3</sub>) and hydrazine borane were found by solution <sup>11</sup>B-NMR after soaking BNH<sub>x</sub> in liquid NH<sub>3</sub> and hydrazine, respectively. Because of the fact that all reactions proceed on the h-BN surface and no reaction proceeds when neat h-BN is treated, breaking of B<sub>3</sub>N<sub>3</sub> ring structure and then creation of B-H bond is the key issue to increase conversion yield of AB.

**Keywords:** hydrogen storage; ammonia borane; boron nitride; milling; nuclear magnetic resonance; hydrogenation

## 1. Introduction

In the future, a major hurdle of realizing carbon constraining world is storage and transportation of energy. While there are many potential green sources of electrical energy generation (e.g., solar and wind), both the intermittency and remoteness of these sources will severely limit their practical application at large scale [1]. Storage of the electric energy produced by intermittent sources would allow a leveling of the supply that should enable the “green-grid”. There are many possible ways to store the energy, but chemical bonds represent perhaps the cheapest option. Hydrogen generated from electrolysis suffers from several drawbacks: it is a gas and therefore requires either large volumes or high pressures to store [2]. Similar issues arise in the application of hydrogen as a fuel in automotive applications. Although the commercial hydrogen fuel cell vehicle can store 70 MPa of hydrogen with about 5.5 mass% including tank, improvement of hydrogen storage technology with higher hydrogen density (U.S. DOE ultimate target: 6.5 mass% of system) is required [2]. The promising way to store hydrogen with high density is hydrogen storage material; therefore, many different hydrogen

storage media have been considered to improve their gravimetric and volumetric density of usable hydrogen [3]. One of the recent high profile candidates is ammonia borane (AB;  $\text{NH}_3\text{BH}_3$ ) because of its 19.6 mass% of hydrogen capacity and moderate initial dehydrogenation temperature ( $\sim 110^\circ\text{C}$ ) [4]. AB desorbs hydrogen over a wide range of temperatures in three idealized steps, as follows [5]:



In reality, the decomposition pathway of AB is more complicated and the “ $\text{NH}_2\text{BH}_2$ ” and “ $\text{NHBH}$ ” species are better represented as polymers. While, on the face of it, AB looks like an excellent material for hydrogen storage, there are several issues to be overcome before practical use could be a reality [6]. Issues with the kinetics of hydrogen release have been well-examined by many research groups using a wide range of approaches such as catalysts [7], Lewis and Brønsted acids [8], metal hydrides [9], proton sponge activation [10], ionic liquids [11], confinements [12], and metal-substitution as metal amidoboranes [13]. However, the major limitation of AB has always been the exothermic nature of hydrogen release although this nature has advantages from a technological point of view, in that no extra energy is required to obtain hydrogen from AB. This nature prohibits the direct rehydrogenation of the dehydrogenated material form back to AB by simple pressurizing hydrogen gas. Only chemical recycle route (regeneration) is possible to recharge hydrogen into dehydrogenated AB. The dehydrogenated material, or “spent fuel” as it is often called, is a complex mixture of polymeric  $\{\text{BNH}_x\}_n$  species (polyborazylene: PB), generally containing hydrogen. PB has linear or  $\text{B}_2\text{N}_3$  ring structures with many degrees of polymerization, which depends on amount and condition of released hydrogen. The full release of hydrogen from AB, which is the ceramic boron nitride (h-BN), is also spent fuel, but h-BN was considered too robust to be ever converted back to AB due to quite strong bonds in  $\text{B}_3\text{N}_3$  ring structure. Therefore, less than 2.5 equivalents of hydrogen released from AB would be favorable for regeneration, which means hydrogen in the  $\{\text{BNH}_x\}_n$  species would facilitate the chemical reformation of AB. The proto-typical spent fuel, which is ring-structured PB made from borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ) [14], has been successfully converted back to AB by using benzenethiol [15] as a digesting agent followed by tin hydrides [16] for hydrogen transfer. Moreover, we eventually established a quite simple one-pot AB regeneration technique from PB using hydrazine (Hz) in liquid ammonia (liq.  $\text{NH}_3$ ) as the hydrogen transfer reagent [17]. This “one-pot regeneration” rapidly proceeds within 24 h via two reaction routes: hydrazine reacts with PB to form hydrazine borane ( $\text{N}_2\text{H}_4\text{BH}_3$ ) and then AB forms by the ligand exchange from  $\text{N}_2\text{H}_4$  to  $\text{NH}_3$  [17];  $\text{HB}(\text{NH}_2)_2$  forms by the reaction between PB and ammonia in the liquid ammonia and then AB and  $\text{B}(\text{NH}_2)_3$  form by the disproportionation of  $\text{HB}(\text{NH}_2)_2$  [18]. The theoretical approach indicates that only B-H bond can react with  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  [17,18], which means that B-H bonding is mandatory for regeneration.

While some reports of AB regeneration [19–21] and lithium amidoborane ( $\text{LiNH}_2\text{BH}_3$ ) [22] have been published, there is still a great challenge remaining which is full-regeneration of AB from hexagonal boron nitride (h-BN). Based upon simple thermodynamic argument, h-BN is too far downhill to be considered as a precursor for AB (endothermic reaction,  $\Delta H = 215.4 \text{ kJ/mol}$ ) due to full-dehydrogenated state of AB [23,24]. Another fact, that h-BN has no B-H bonding, is also a big issue for regeneration. Therefore, direct hydrogenation of bulk h-BN to AB might be difficult to proceed. Graphite, which has similar structure to h-BN, is also difficult to hydrogenate directly at room temperature but ball-milling under hydrogen pressure, a strong hydrogenation tool, realizes hydrogenation of carbon at room temperature (RT) [25]. Even ball-milling hydrogenation method has been employed, no AB formed but only surface on h-BN was hydrogenated taking the form of “ $\text{BNH}_x$ ”, which still has many  $\text{B}_3\text{N}_3$  rings ( $hklm = 0002$ ) supported by X-ray diffraction (XRD) [26]. The hydrogenation of h-BN during the ball milling process relies upon the formation of defects at the surface of h-BN, which is an apparently thermodynamic favorable process. Although  $\text{BNH}_x$  is smaller hydrogen coordination ( $x < 0.5$ ) than PB

( $x = 1.0$ ) and has a similar structure to that of PB (Figure 1), the infrared (IR) spectrum of  $\text{BNH}_x$  showed both B-H and N-H stretching peaks with a structure similar to polyaminoborane (PAB;  $\{\text{BH}_2\text{NH}_2\}_n$ ). Therefore,  $\text{BNH}_x$  is different from PAB in terms of  $\text{BH}_2$  species and number of  $\text{B}_3\text{N}_3$  ring structure. Now activated  $\text{BNH}_x$  is no longer as thermodynamically stable as h-BN and direct chemical conversion to AB using  $\text{N}_2\text{H}_4/\text{NH}_3$  is possible. Hence, the purpose in this study is to transform back to AB upon  $\text{N}_2\text{H}_4/\text{NH}_3$  treatment from B-H bonds in milling hydrogenated h-BN. We also investigated the reaction mechanism of this transformation including the reaction route.

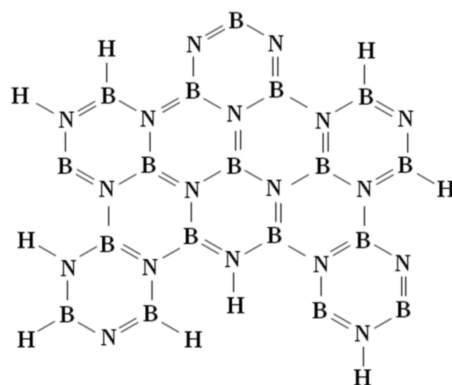


Figure 1. Structures of  $\text{BNH}_x$ .

## 2. Materials and Methods

The starting material, h-BN nanopowder (<150 nm, 99%, Aldrich Co. Ltd.) was used as received or after dried at 200 °C for 8 h under vacuum condition.  $\text{BNH}_x$  and  $\text{BN-NH}_x$  (N-H bonding coated h-BN) were synthesized by using the ball milling method under 1 MPa of  $\text{H}_2$  or 0.8 MPa of  $\text{NH}_3$  at RT for 80 h using vibration milling (SEIWA GIKEN Co. Ltd., RM-10) as the previous report [26]. In a typical reaction, 100 mg of each sample (neat h-BN,  $\text{BNH}_x$ , and  $\text{BN-NH}_x$ ) was placed into stainless steel vessel (about 50 mL) and cooled down to  $-78$  °C using a dry ice/ethanol mixture. Then  $\text{NH}_3$  was condensed into the container. After the addition of about 30 mL of liquid  $\text{NH}_3$ , 200  $\mu\text{L}$  of anhydrous hydrazine (98%, Aldrich Co. Ltd.) was added. The reaction vessel was then sealed and heated at 40 °C for 1 week. These vessels were opened under atmospheric pressure containing condensed  $\text{NH}_3$  by cooling in liquid nitrogen before opening to prevent blowing up sample in the container. After warming up and the evaporation of  $\text{NH}_3$  under atmospheric pressure for 5 h, residual  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  were completely removed under dynamic vacuum maintained for 5 h. All procedures were carried out without exposing air.

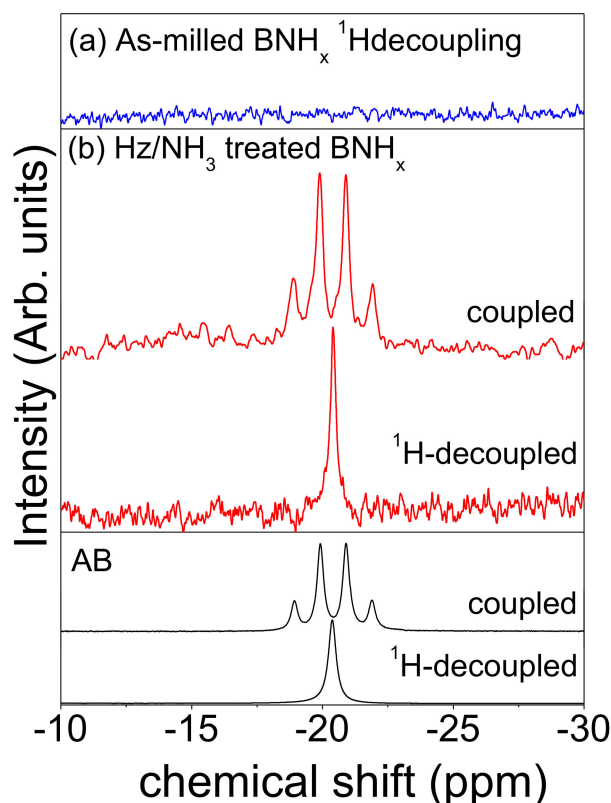
$^{11}\text{B}$  and  $^1\text{H}$  solution nuclear magnetic resonance (NMR: Bruker, AVANCE 300, 96.29 MHz for  $^{11}\text{B}$  and 300.13 MHz for  $^1\text{H}$ ) of  $\text{BNH}_x$  and  $\text{N}_2\text{H}_4/\text{NH}_3$  treated samples were performed at room temperature using  $d_8$ -THF as the solvent. Samples for NMR were prepared by filtering by THF (about 50 mL) then dynamic evacuation of filtered solution. External calibration of  $^{11}\text{B}$  NMR was performed using  $\text{BF}_3$ -etherate standard (0.0 ppm). We also measured  $^{11}\text{B}$  solution NMR (Bruker, AVANCE 400, 128.38 MHz) of  $\text{BNH}_x$  after soaking in each solvent ( $\text{NH}_3$  and  $\text{N}_2\text{H}_4$ ) at RT for 24 h in order to confirm intermediates.

Thermogravimetric analysis (TGA) of  $\text{BNH}_x$  after the  $\text{N}_2\text{H}_4/\text{NH}_3$  treatment (whole sample including soluble and insoluble species) was performed by LABSYS evo (SETARAM). At the same time, gas analyses were performed by residual gas analyzer (RGA: INFICON, Transpector<sup>®</sup> CPM) and infrared (IR: Thermo Nicolet, AVATAR 360 FT-IR) TGA-RGA measurement of  $\text{BNH}_x$  before the treatment and residual (after removal of AB) treated  $\text{BNH}_x$  was simultaneously performed by TG 8120 (Rigaku) coupled with M-QA200TS (Canon Anelva Corporation). Both measurements were performed with a scanning rate of 10 °C/min. Powder X-ray diffraction (XRD) measurements were operated by RINT-2100 (Rigaku,  $\text{Cu K}\alpha$  radiation) for  $\text{BNH}_x$  and D8 Discover (Bruker,  $\text{Cu K}\alpha$  radiation) for

$\text{N}_2\text{H}_4/\text{NH}_3$  treated  $\text{BNH}_x$ . All procedures have been performed without exposing the samples to air by handling in the Ar-filled glovebox except the TGA-RGA-IR measurement of  $\text{BNH}_x$  after the treatment, where the exposure time was minimized (<10 sec).

### 3. Results and Discussion

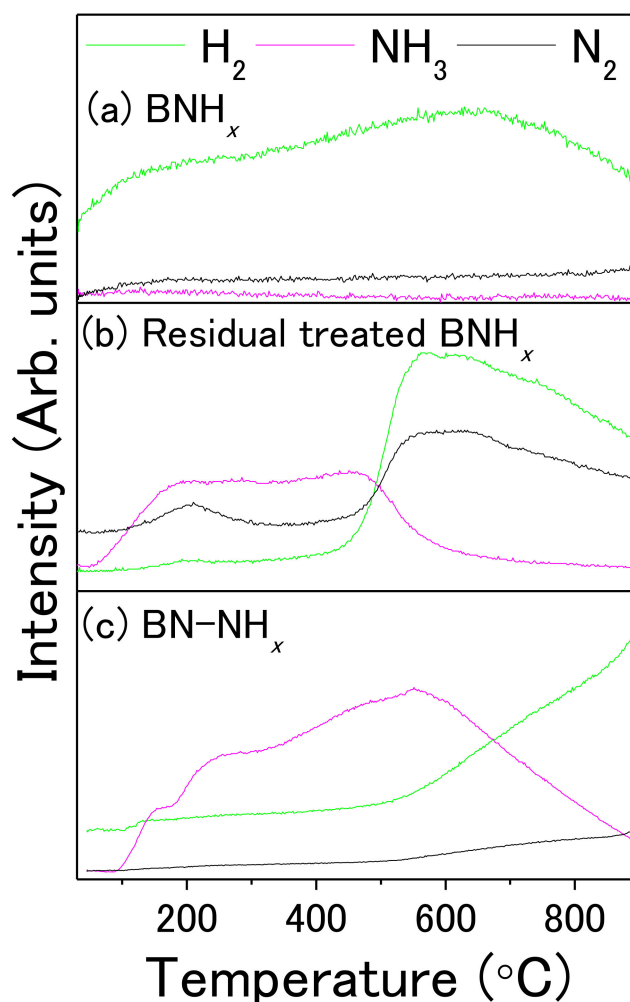
The regeneration of AB is most simply followed by  $^{11}\text{B}$  solution NMR. The reaction of neat h-BN with  $\text{N}_2\text{H}_4/\text{NH}_3$  showed no evidence of the formation of AB or any other molecular species even after prolonged time (Figure S1a in supplementary materials). Extraction of  $\text{BNH}_x$ , hydrogenated h-BN by ball milling, with THF yielded no observable B-H species in solution (Figure 2a). In contrast, when  $\text{BNH}_x$  was treated with  $\text{N}_2\text{H}_4/\text{NH}_3$  for 1 week, a soluble  $\text{BH}_3$  containing species ( $-20.4$  ppm,  $J_{\text{B,H}} = 94$  Hz) is presented (Figure 2b). This resonance is identified as AB by comparison with commercial AB. In addition, mixture of this soluble species and the commercial AB showed single peak in  $^{11}\text{B}$  NMR spectrum (Figure S1b). Although hydrazine borane (HzB) can be produced as an intermediate compound or by the reaction between AB and  $\text{N}_2\text{H}_4$ , in liquid  $\text{NH}_3$  all of HzB can be converted to AB by metathesis (Figure 2b). The  $^1\text{H}$  NMR spectrum of this product also shows the presence of resonances identified as triplet  $\text{NH}_3$  species in AB at 4ppm (Figure S2).



**Figure 2.**  $^{11}\text{B}$  solution NMR spectra of (a) as-milled  $\text{BNH}_x$  with  $^1\text{H}$ -decoupled and (b)  $\text{BNH}_x$  after  $\text{N}_2\text{H}_4/\text{NH}_3$  treatment with  $^1\text{H}$ -coupled and decoupled. Profiles of ammonia borane (AB) as a reference are also shown.

Unfortunately, the yield of AB is not significant overall being less than 5% based upon the mass of treated  $\text{BNH}_x$ . It is important to reveal the mechanism of this reaction in order to improve AB yield using this method. It is likely that only the surface of h-BN is hydrogenated during the ball milling process and only this surface is susceptible to be attacked by  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$ . We have reported that  $\text{BNH}_x$ , hydrogenated h-BN by ball milling, is still dominated by the hexagonal  $\text{N}_3\text{B}_3$  ring structure of h-BN, even after 80 h milling [26]. Indeed, our X-ray diffraction analysis (XRD) of  $\text{BNH}_x$  and the product after  $\text{N}_2\text{H}_4/\text{NH}_3$  treatment have diffraction peaks corresponding to h-BN ring structure

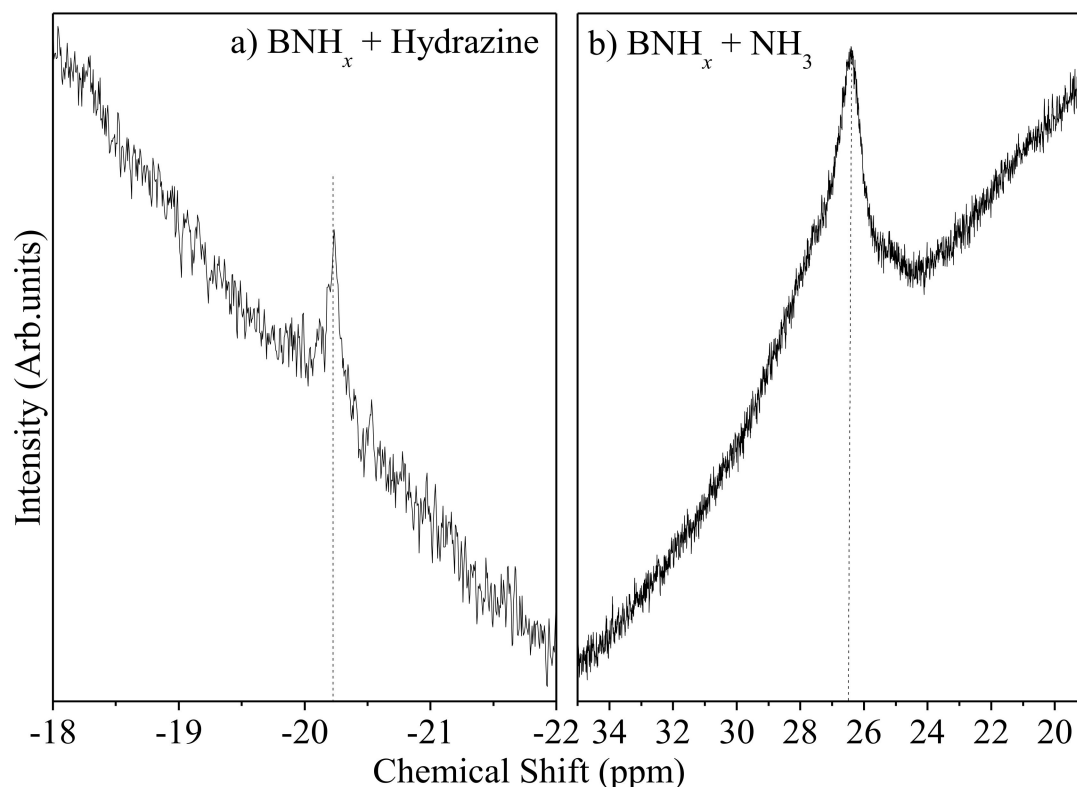
( $hklm = 0002$ , Figure S3).  $\text{BN-NH}_x$ , which is milled h-BN under ammonia pressure for 80 h [22], has not been shown in our hands to generate AB by the  $\text{Hz}/\text{NH}_3$  treatment (Figure S1c), which is the same as the failure of neat h-BN to show any reaction with  $\text{N}_2\text{H}_4/\text{NH}_3$ . This is part of the evidence that presence of the B-H bonds is critical to this reaction as confirmed. Moreover, the calculation results in the previous report support that B-H bonds are only reactive with  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  but not N-H bonds [17,18]. TG-RGA-IR analysis could support this speculation. RGA profile of  $\text{BNH}_x$  shows wide temperature range of hydrogen (and small amount of  $\text{N}_2$  and  $\text{NH}_3$ ) release (Figure 3a). On the other hand, residue ( $\text{N}_2\text{H}_4/\text{NH}_3$  treated  $\text{BNH}_x$  after removal of AB) desorbed mainly  $\text{NH}_3$  (and small amount of  $\text{N}_2$  and  $\text{H}_2$ ) below  $500^\circ\text{C}$  (Figure 3b), which is similar to that of  $\text{BN-NH}_x$  denoted in Figure 3c. This phenomenon indicates that weak B-H bond in  $\text{BNH}_x$  was substituted from  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  during treatment. Increase of  $\text{BNH}_x$  mass after the treatment (100 to 170 mg) can be this evidence. Additional evidence has been found in IR results because the residue has weaker B-H (about  $2500\text{ cm}^{-1}$ ) and stronger N-H peaks (about  $3500\text{ cm}^{-1}$ ) than these  $\text{BNH}_x$  peaks (Figure S4). Overall untreated  $\text{BNH}_x$  loses about 2.5 mass% up to  $900^\circ\text{C}$  whereas the residue loses 11.5 mass% mostly due to  $\text{NH}_3$  desorption. This is also evidence of substitution from B-H to N-H bonds.



**Figure 3.** TG-RGA profiles of (a)  $\text{BNH}_x$ , (b) residue of  $\text{N}_2\text{H}_4/\text{NH}_3$  treated  $\text{BNH}_x$ , and (c)  $\text{BN-NH}_x$ .

The reaction path is also an important issue to be clarified for improvement of this method. As mentioned, the intermediate of  $\text{N}_2\text{H}_4$  route is  $\text{N}_2\text{H}_4\text{BH}_3$ , while the intermediates of  $\text{NH}_3$  route are  $\text{HB}(\text{NH}_2)_2$  and  $\text{B}(\text{NH}_2)_3$  (decomposition product of  $\text{HB}(\text{NH}_2)_2$ ). The simple way to confirm their presence is NMR measurement after soaking  $\text{BNH}_x$  in liquid  $\text{NH}_3$  or  $\text{N}_2\text{H}_4$ .  $^1\text{H}$ -decoupled  $^{11}\text{B}$  solution

NMR spectra (solvent: THF) after soaking in both  $\text{N}_2\text{H}_4$  and liquid  $\text{NH}_3$  had a weak peak at  $-20.2$  ppm (Figure 4a) and a strong peak at  $26.5$  ppm with a small shoulder (Figure 4b), respectively. Although the signals in the coupled spectrum of  $\text{N}_2\text{H}_4$ -soaked sample were too weak to identify, this peak position is close to  $\text{N}_2\text{H}_4\text{BH}_3$ . The peak in the NMR spectrum in liquid  $\text{NH}_3$ -soaked sample locates almost the same as  $\text{B}(\text{NH}_2)_3$ . Other peak was not observed in both spectra. Thus, regeneration route of  $\text{BNH}_x$  could be the same as PB regeneration route as we reported.



**Figure 4.**  $^{11}\text{B}\{^1\text{H}\}$  solution NMR spectra of  $\text{BNH}_x$ , after soaking in (a)  $\text{N}_2\text{H}_4$  and (b) liquid  $\text{NH}_3$  (solvent: THF).

When we consider these observations, a probable reaction mechanism for the formation of the AB from h-BN can be envisioned. Firstly, all of the reactions, from the ball milling through to the reactions with  $\text{N}_2\text{H}_4/\text{NH}_3$ , only occur at the BN surface. Previous calculations indicate that only the B-H bonds in  $(\text{BNH}_x)_n$  have an ability to form AB on reaction with  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$ , while the  $\text{B}_3\text{N}_3$  ring structure is unaffected by them. Once B-H bonds created by milling are attacked by  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$ ,  $\text{N}_m\text{H}_n$  bonds are formed resulting in release of AB and an  $\text{N}_m\text{H}_n$  coated surface. The sample mass may increase due to this substitution reaction. The coated  $\text{N}_m\text{H}_n$  surface could be similar to  $\text{BN-NH}_x$ . The B-H bonds reacted with  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  could be weak bond energy with N atom. Considering the main B-H bond in  $\text{BNH}_x$  is PAB ( $\{\text{BNH}_2\}_n$ ), this weak B-H bond could be  $\text{BH}_2$ . A schematic depiction of this model is displayed in Figure 5 but the real reaction might be more complicated because the edge of  $\text{BNH}_x$  would have many kinds of structure. We need to identify “active” edge by the theoretical approach to clarify deeper reaction mechanism of this regeneration method. Further experimental work is also necessary to minimize or break the volume of  $\text{N}_3\text{B}_3$  ring structure and therefore increase the amount of B-H bonds in the  $\text{BNH}_x$  by ball-milling (or other method).

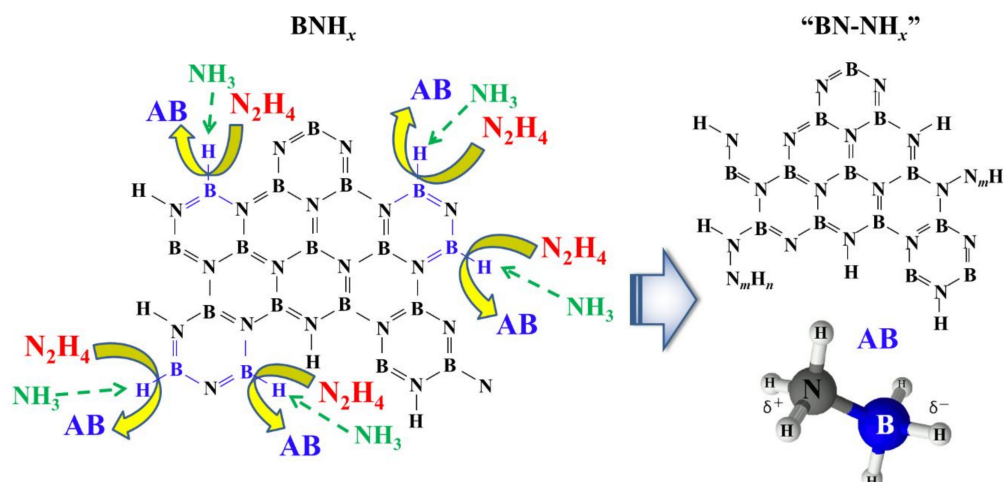


Figure 5. Conversion model of AB from  $\text{BNH}_x$  by the  $\text{N}_2\text{H}_4/\text{NH}_3$  treatment.

#### 4. Conclusions

In this study, the synthesis of AB from h-BN was successful using ball milling under hydrogen pressure and then soaked in  $\text{N}_2\text{H}_4$ -liquid  $\text{NH}_3$  solution. The THF-soluble product of this reaction was shown by  $^{11}\text{B}$  NMR to be AB.  $\text{H}_2\text{H}_4/\text{NH}_3$  treated  $\text{BNH}_x$  which removed AB, had similar RGA profile to  $\text{BN-NH}_x$  below  $500^\circ\text{C}$ , indicating substitution of N-H bonds for B-H bonds proceeded. The key aspect of this chemistry is the creation of the defects by breaking  $\text{B}_3\text{N}_3$  ring at the surface of h-BN during the milling under  $\text{H}_2$ . This phenomenon enables the formation of B-H species that can be attacked by both  $\text{H}_2\text{H}_4$  and  $\text{NH}_3$  to form AB. These B-H bonds in  $\text{BNH}_x$  would be low bond energy with N atom likewise broken  $\text{B}_3\text{N}_3$  ring structure, which can desorb hydrogen below  $500^\circ\text{C}$ . The presence of intermediates ( $\text{N}_2\text{H}_4\text{BH}_3$  and  $\text{B}(\text{NH}_2)_3$ ) in NMR indicates that their reaction routes could be the same as those of PB regeneration. Although this method is not commercially useful immediately, unless there is improvement of its low production yield (about 5%), such surface chemistry could open up new possibilities of other thermodynamically tough chemical reactions. Of course, it may be possible to envision a hydrogen storage system using full hydrogen from AB (19.6 mass%  $\text{H}_2$ ) if high AB yield of regeneration using our method is realized. If an effective method to break the strong bonding in  $\text{B}_3\text{N}_3$  ring and then create B-H bonding is found, this “one-pot regeneration” probably gives high yield of AB.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/1996-1073/13/21/5569/s1>.

**Author Contributions:** Conceptualization, Y.K. and A.K.B.; methodology and investigation, T.N., H.U., and H.M.; writing—original draft preparation, T.N.; writing—review and editing, A.K.B., T.I., and B.L.D.; project administration, A.K.B., T.I. and Y.K.; funding acquisition, A.K.B., T.N., and Y.K. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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