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## ARTICLE

# AB-MH (Ammonia Borane - Metal Hydride) Composites: Systematic Understanding of Dehydrogenation Properties

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Dehydrogenation properties of AB-MH (Ammonia Borane - Metal Hydride, M = K, Na, Li, Ca, Mg, Al) composites were systematically investigated by thermal and mass analyses. The results suggest the Pauling electronegativity of M,  $\chi_p$  is a good indicator to predict the phases of composites, the dehydrogenation temperature and the amount of by-product gases (NH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>). The phases of composites were classified by  $\chi_p$  as follows. MBH<sub>4</sub> was formed for M = K, Na ( $\chi_p \leq 0.9$ ), MNH<sub>2</sub>BH<sub>3</sub> was formed for M = Na, Li ( $0.9 \leq \chi_p \leq 1.0$ ) and no new compounds were formed for M = Ca, Mg, Al ( $1.0 \leq \chi_p$ ). The 1st dehydrogenation temperatures of the samples (M = Na, Li, Ca, Mg) were 10 - 20 °C lower than that of AB itself ( $\chi_p \leq 1.2$ ). The amount of NH<sub>3</sub> was decreased when  $\chi_p$  was increased. On the other hand, the amount of B<sub>2</sub>H<sub>6</sub> was decreased when  $\chi_p$  was decreased. The emission of B<sub>3</sub>H<sub>6</sub>N<sub>3</sub> could occur by the reaction of NH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>. Finally, AB-MAIH<sub>4</sub> (M = Na, Li) composites, which were prepared based on the indicator, showed superior potentials as hydrogen storage materials because they did not desorb any by-product NH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub> and B<sub>3</sub>H<sub>6</sub>N<sub>3</sub>.

## 1. Introduction

Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) is an attractive candidate for hydrogen storage media because of its high hydrogen content (19.6 wt%, 0.145 kg/L).<sup>1-3</sup> It can desorb ~ 13 wt% of hydrogen below 200 °C.<sup>4-6</sup> The dehydrogenation of AB takes place in three steps within a single equivalent of hydrogen evolved in each step at *ca.* 70-110, 110-200, 400-900 °C in temperature ramping experiments.<sup>4-6</sup> One of the disadvantages for practical application is the emission of by-product gases such as ammonia (NH<sub>3</sub>), diborane (B<sub>2</sub>H<sub>6</sub>), and borazine (B<sub>3</sub>H<sub>6</sub>N<sub>3</sub>). For instance, release of ammonia causes damage to the fuel cell performance even at trace levels.<sup>7</sup> Worse yet, NH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> are harmful for living creatures.<sup>8,9</sup>

The dehydrogenation properties of AB-MH composites have been extensively studied, such as AB-LiH,<sup>10-18</sup> AB-NaH,<sup>10-13,19-21</sup> AB-LiH-NaH,<sup>12</sup> AB-KH,<sup>11,13,14,22</sup> AB-MgH<sub>2</sub>,<sup>23,24</sup> AB-CaH<sub>2</sub>,<sup>18,23,25</sup> AB-LiNH<sub>2</sub>,<sup>26</sup> AB-LiBH<sub>4</sub>,<sup>27</sup> AB-Li<sub>3</sub>AlH<sub>6</sub>,<sup>28</sup> AB-LiNH<sub>2</sub>-LiBH<sub>4</sub>,<sup>29</sup> in order to improve the dehydrogenation properties of AB. For example, AB-NaH composite desorbed hydrogen at 80-100 °C without the by-product diborane and borazine.<sup>20,21</sup> AB-LiNH<sub>2</sub> composite desorbed hydrogen as low as 60 °C without the by-product diborane and borazine.<sup>26</sup> However, systematic investigation on AB-MH composite has not been explored. On the other hand, thermodynamical stabilities of M(BH<sub>4</sub>)<sub>n</sub> and M(AlH<sub>4</sub>)<sub>n</sub> systems have been systematically investigated by using the Pauling electronegativity of M as an indicator.<sup>30-33</sup> The correlation between dehydrogenation temperature and Pauling electronegativity of M was found computationally and experimentally.<sup>30-33</sup> It is of great importance to understand the dehydrogenation properties of AB-MH composite

systematically in order to decrease dehydrogenation temperature and suppress by-product gas emission.

In this study, AB-MH (M=K, Na, Li, Ca, Mg, Al) composites were synthesized by ball milling method. Phases of AB-MH composites were determined by X-ray diffraction (XRD) analysis and dehydrogenation properties were discussed in terms of dehydrogenation temperature and amounts of hydrogen and by-product gas emissions. From the results, we proposed an indicator to predict the phases of composite, the dehydrogenation temperature and the amount of by-product gas emission (NH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>). Finally, we created superior composites according to the indicator and evaluated their dehydrogenation properties.

## 2. Experimental

The starting material NH<sub>3</sub>BH<sub>3</sub>, NaH, LiH, CaH<sub>2</sub>, NaAlH<sub>4</sub>, LiAlH<sub>4</sub> (purity 97 %, 55-65 % (moistened with oil), 95 %, 99.99 %, 90 %, 95 %, respectively) were purchased from Sigma Aldrich Co. Ltd. MgH<sub>2</sub> (purity 98 %) were purchased from Alfa Aesar. These materials were used as-received without any purification. AlH<sub>3</sub> was prepared by the chemical reaction between LiAlH<sub>4</sub> and AlCl<sub>3</sub> in ether solution.<sup>34</sup> KH was prepared according to ref. 35. All samples were handled in an argon glovebox without exposing samples to air. AB-MH (M = K, Na, Li, Ca, Mg, Al) and AB-MAIH<sub>4</sub> (M = Na, Li) composites were prepared by ball-milling under 0.1 MPa Ar with 400 rpm for 30 min, 1.0 MPa H<sub>2</sub> with 300 rpm for 5 min, respectively. Ball-milling processes were performed by using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls (7 mm in diameter) and 300 mg samples (ball :

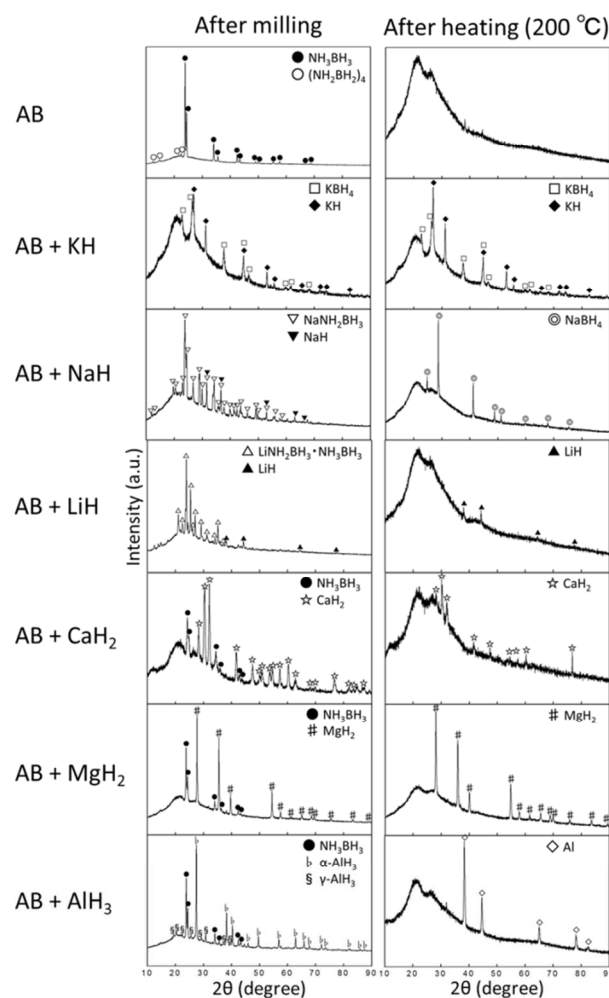
powder ratio = 70 : 1, by mass). The phase analysis was conducted by Powder X-ray diffraction (XRD, PANalytical, X'Pert-Pro with Cu K $\alpha$  radiation). The dehydrogenation properties were examined by thermal desorption mass spectrometry measurements (TDMS, ULVAC, BGM-102) combined with thermogravimetry and differential thermal analysis (TG-DTA, Bruker, 2000SA). Heating rate was 2 or 5 °C/min and helium gas flow rate was 300 mL/min. TDMS measurements combined with TG-DTA were performed twice for each sample. The amounts of hydrogen and by-product gases were defined by integrating the peaks of mass spectra. The value of integral for by-product gas was normalized by that for hydrogen. Then, the weight loss of each gas was estimated by the total weight loss obtained from TG results. All measurements were immediately performed after synthesizing AB-MH composite in order to prevent the composite from decomposing.

### 3. Results and Discussion

#### 3.1 Phase Analysis of AB-MH Composite

Fig. 1 shows the XRD patterns of each AB-MH composite and AB after milling and heating to 200 °C. Broad diffraction peaks around 20° and 27° in all profiles originate from the film and grease to prevent the sample oxidation. Small amount of (NH<sub>2</sub>BH<sub>2</sub>)<sub>4</sub> was observed in the milled AB. This phase was considered as impurity in as-received AB. After heating AB, there were no peaks in profile, indicating AB became amorphous state. For AB-NaH composite, peaks were consistent with sodium amidoborane (NaNH<sub>2</sub>BH<sub>3</sub>), which was confirmed by Xiong *et al.*<sup>10</sup> After heating, NaBH<sub>4</sub> was confirmed by XRD, which is different from the experimental results of previous investigators.<sup>19-21</sup> One of the possibilities of NaBH<sub>4</sub> formation would come from the different milling condition. There are some cases that non-equilibrium phases appear by mechanical ball milling.<sup>36</sup> As described in ref. 20, the formation of BH<sub>4</sub><sup>-</sup> ions may occur under the milling condition. For AB-LiH composite, peaks were consistent with lithium amidoborane - ammonia borane (LiNH<sub>2</sub>BH<sub>3</sub>·NH<sub>3</sub>BH<sub>3</sub>). This was the intermediate phase during the synthesis of LiNH<sub>2</sub>BH<sub>3</sub>, which was confirmed by Wu *et al.*<sup>17</sup> Thus, metal amidoborane (MNH<sub>2</sub>BH<sub>3</sub> (M = Na, Li)) was confirmed after milling for M = Na, Li. For AB-KH composite, KBH<sub>4</sub> was observed instead of potassium amidoborane (KNH<sub>2</sub>BH<sub>3</sub>) after milling. The wet chemical synthesis of KNH<sub>2</sub>BH<sub>3</sub> by stirring KH and AB in benzene for 2 days suggests the lower rotation speed and longer time of ball milling enables to generate KNH<sub>2</sub>BH<sub>3</sub>.<sup>22</sup> In cases of AB-MH (M = Ca, Mg, Al) composites, no new compounds were observed after milling. Only AB and each MH phase were observed. It was reported that more than 6 hours milling by using shaker mill can generate Ca(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>.<sup>25</sup> However, synthesis of Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub> by ball milling was unsuccessful.<sup>18</sup> After heating, only each MH phase was observed for M = Mg,

Ca. These results have good agreements with previous reports.<sup>23,24</sup> In case of M = Al, Al was observed after heating, which indicated AlH<sub>3</sub> desorbed hydrogen below 200 °C. From Fig. 1, we described the crystalline phases of AB-MH composites according to the Pauling electronegativity of M,  $\chi_p$  in Table 1. The previous study about the stability of M(NH<sub>2</sub>BH<sub>3</sub>)<sub>n</sub> by the computational method indicates electronegativity is a good indicator to understand the stability generally.<sup>13</sup> As shown in Table 1, MBH<sub>4</sub> was formed for M = K, Na ( $\chi_p \leq 0.9$ ), MNH<sub>2</sub>BH<sub>3</sub> was formed for M = Na, Li ( $0.9 \leq \chi_p \leq 1.0$ ) and no new compounds were formed for M = Ca, Mg, Al ( $1.0 \leq \chi_p$ ). This suggests the trend of the phases of AB-MH



**Fig. 1** Powder X-ray diffraction (XRD) profiles of AB-MH (M=K, Na, Li, Ca, Mg, Al) composites and AB after milling and heating to 200 °C.

**Table 1** Phases of AB-MH composites classified by the Pauling electronegativity of M. Decomposition temperature is the temperature at which crystalline phases after heating to 200 °C (KBH<sub>4</sub>, NaBH<sub>4</sub>, LiH, CaH<sub>2</sub>, and MgH<sub>2</sub>) desorb hydrogen. The peak dehydrogenation temperature in mass spectra was described. The heating rate was 5 °C/min.

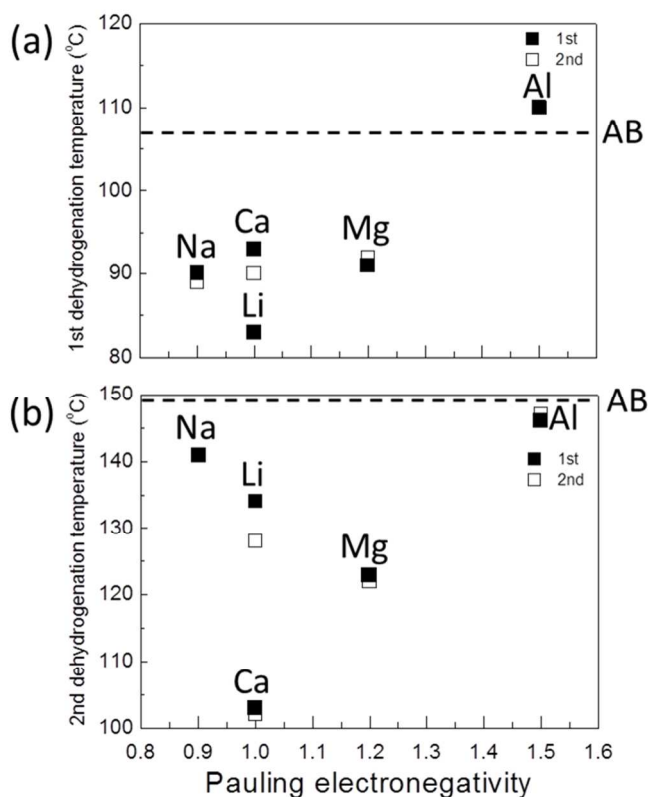
MH	KH	NaH	LiH	CaH <sub>2</sub>	MgH <sub>2</sub>	AlH <sub>3</sub>
Pauling electronegativity $\chi_p$ of M	0.8	0.9	1.0	1.0	1.2	1.5
Crystalline phases after milling	KBH <sub>4</sub>	NaNH <sub>2</sub> BH <sub>3</sub>	LiNH <sub>2</sub> BH <sub>3</sub> ·NH <sub>3</sub> BH <sub>3</sub>	CaH <sub>2</sub>	MgH <sub>2</sub>	AlH <sub>3</sub>
Crystalline phases after heating (200 °C)	KBH <sub>4</sub>	NaBH <sub>4</sub>	LiH	CaH <sub>2</sub>	MgH <sub>2</sub>	Al
Decomposition temperature /°C	425	400	555	627	446	n/a

composites follows the trend of  $\chi_p$ . MH tends to cause the reaction with AB faster when  $\chi_p$  decreases.

### 3.2 Dehydrogenation properties of AB-MH Composite

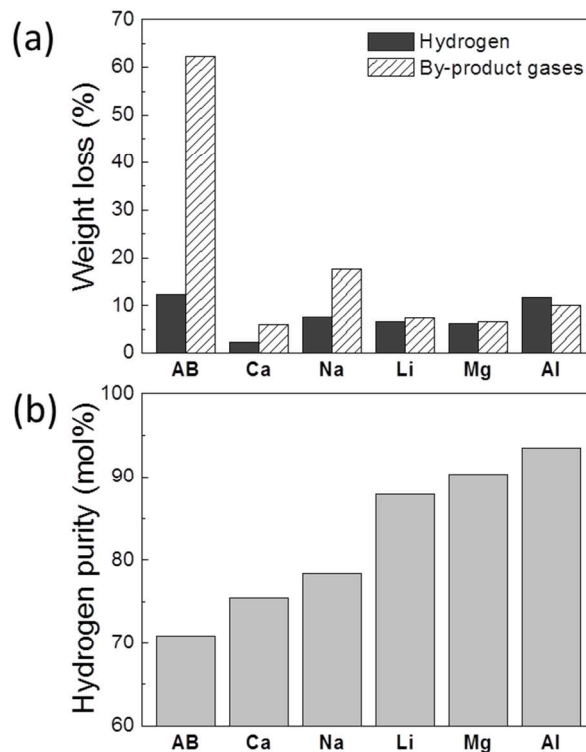
Fig. 2 shows the dehydrogenation temperatures of AB-MH (M = Na, Ca, Li, Mg, Al) composites below 200 °C. The results of AB-KH composite were not plotted because it did not desorb any gases during heating below 200 °C. The 1st and 2nd dehydrogenation peak temperatures in mass spectra were plotted to Fig. 2 (a) and (b), respectively. Dashed line shows the temperature of milled AB. As shown in Fig. 2(a), 1st temperatures for M = Na, Li, Ca, Mg ( $\chi_p \leq 1.2$ ) were decreased by 10-20 °C as compared with milled AB. These results have good agreements with other results.<sup>10,23,24</sup> 1st temperature for M = Al was not changed as milled AB. It is interesting to note that this trend is opposite to the trend in the dehydrogenation temperatures of  $M(\text{BH}_4)_n$  and  $M(\text{AlH}_4)_n$ .<sup>30-33</sup> 2nd temperatures for M = Ca, Mg, Al were correlated with electronegativity of M as shown in Fig. 2(b). It is difficult to compare the whole results of temperatures because phases are different between those for M = Na, Li and those for M = Ca, Mg, Al. AB-CaH<sub>2</sub> composite showed the lowest temperature of all the 2nd dehydrogenation temperatures. The dehydrogenation from AB-MH composites could be promoted by the solid-phase interaction between AB and MH. This interaction would affect the intramolecular N-H, B-H and B-N chemical bonds and intermolecular dihydrogen bond.

The amounts of hydrogen and by-product gases of AB-MH composites were investigated by TG-MASS. Fig. 3(a) shows the



**Fig. 2** Dehydrogenation temperatures of AB-MH composites below 200 °C classified by the Pauling electronegativity of M; (a) 1st peak temperatures, (b) 2nd peak temperatures. The heating rate was 2 °C/min. The black square symbol shows the result of 1st measurement and the white square symbol shows that of 2nd measurement.

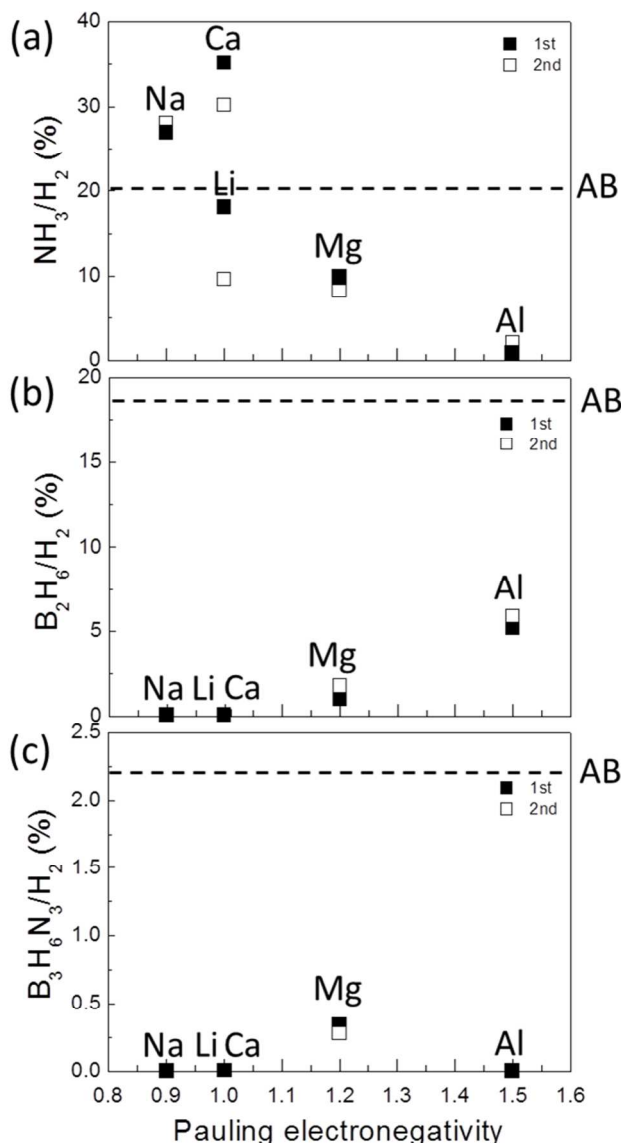
estimated weight losses of hydrogen and by-product gases below 200 °C. Milled AB desorbed by-product gases more than 60 %, indicating the substantial amount of by-product gas emission. All the AB-MH composites showed by-product gas emission of 6-18 %, suggesting the most of the by-product gases were suppressed. Fig. 3(b) shows the hydrogen purity of AB-MH composites. Purity of about 90 % was obtained for M = Li, Mg, Al. On the other hand, the purity for M = Na, Ca was only less than 80 %. In order to investigate the content of by-product gases, we estimated the amounts of by-product gases of  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$  and  $\text{B}_3\text{H}_6\text{N}_3$ . Fig. 4 shows the amounts of by-product gases of AB-MH composites.  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$  and  $\text{B}_3\text{H}_6\text{N}_3$  were measured by mass spectrometry. Dashed line shows the amount of milled AB. As shown in Fig. 4 (a), the amount of  $\text{NH}_3$  was decreased as  $\chi_p$  increased. AB- $\text{AlH}_3$  composite almost suppressed the emission of  $\text{NH}_3$ . On the other hand, the amount of  $\text{B}_2\text{H}_6$  was decreased as  $\chi_p$  decreased as shown in Fig. 4 (b). AB-MH (M = Na, Li, Ca ( $\chi_p \leq 1.0$ )) composites completely suppressed  $\text{B}_2\text{H}_6$ . Comparing the results of Fig. 3(b), it was indicated that the low hydrogen purity for M = Na, Ca ascribed to a large amount of  $\text{NH}_3$  emission. The emission process of  $\text{NH}_3$  in  $\text{NaNH}_2\text{BH}_3$  system was reported by Fijałkowski *et al.*,<sup>20</sup> which explained the formation and decomposition of the ionic salt caused the emission. The ionic radius of  $\text{M}^{n+}$  seems to be correlated with the emission of  $\text{NH}_3$ . The ionic radii of  $\text{Na}^+$  (102 pm) and  $\text{Ca}^{2+}$  (100 pm) are different from those of  $\text{Li}^+$  (76 pm),  $\text{Mg}^{2+}$  (72 pm), and  $\text{Al}^{3+}$  (54 pm).<sup>37</sup> The trend in the amount of  $\text{B}_2\text{H}_6$  was similar to that in case of  $M(\text{BH}_4)_n$ . In case of  $M(\text{BH}_4)_n$ , those for  $\chi_p \leq 1.5$  suppressed the emission of  $\text{B}_2\text{H}_6$ .<sup>30</sup> The previous study showed diammoniate of diborane (DADB),  $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$ , an ionic isomer of AB, is formed during the induction period before dehydrogenation of AB.<sup>38</sup> If DADB is regarded as a kind of borohydride, the emission process of  $\text{B}_2\text{H}_6$  in AB is considered to be similar to that in  $M(\text{BH}_4)_n$ . Further



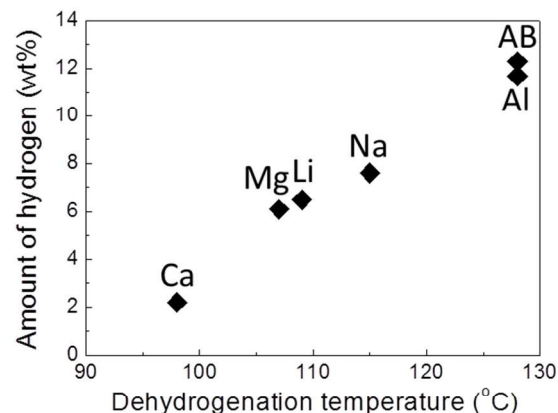
**Fig. 3** (a) Weight losses of hydrogen and by-product gases, (b) hydrogen purity of AB-MH composites below 200 °C. The heating rate was 2 °C/min.

investigations are needed to clarify the suppression mechanisms of  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$  emission in AB-MH composites. Fig. 4 (c) showed only AB-MgH<sub>2</sub> composite desorbed  $\text{B}_3\text{H}_6\text{N}_3$ . The emission of  $\text{B}_3\text{H}_6\text{N}_3$  may correlate with the emission of  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$ .  $\text{B}_3\text{H}_6\text{N}_3$  can be generated by the reaction between  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$  with a molar ratio of 2 : 1.<sup>39</sup> AB-MgH<sub>2</sub> composite desorbed  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$ , then they would react to form  $\text{B}_3\text{H}_6\text{N}_3$ . In the other composites, either emission of  $\text{NH}_3$  or  $\text{B}_2\text{H}_6$  was suppressed, which would result in the suppression of  $\text{B}_3\text{H}_6\text{N}_3$  emission. As a result,  $\chi_p$  would be a good indicator to predict the dehydrogenation temperatures and the amounts of by-product gases. We summarized the dehydrogenation properties of composites in Fig. 5. Fig. 5 shows the amounts of hydrogen desorbed below 200 °C versus dehydrogenation temperatures. AB-CaH<sub>2</sub> composite showed the lowest dehydrogenation temperature and AB-AlH<sub>3</sub> composite showed the largest amount of hydrogen of all the composites. However, it was

indicated that there were no materials fulfilling large amounts of hydrogen desorbed at low temperatures. In order to accomplish these requirements, further investigations, e.g. combining AB with more than two metal hydrides, will be needed.



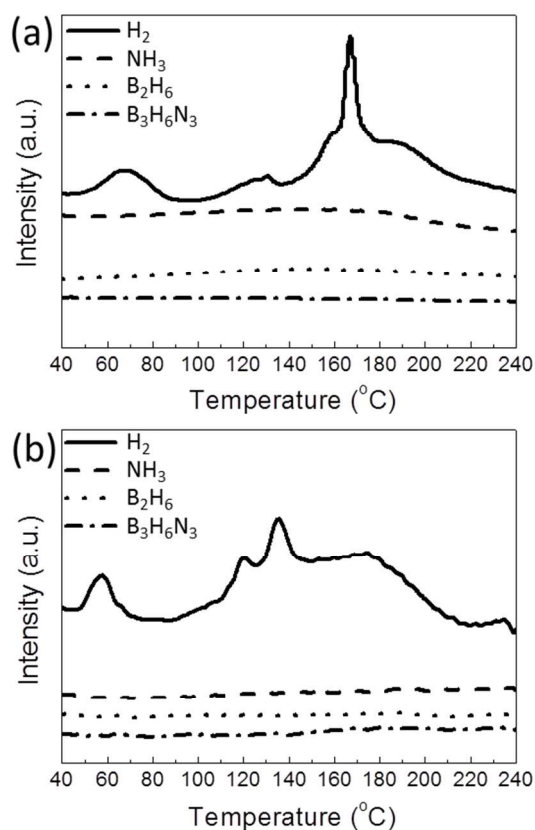
**Fig. 4** The amounts of by-product gases desorbed by AB-MH composites classified by the Pauling electronegativity of M; (a) ammonia ( $\text{NH}_3$ ), (b) diborane ( $\text{B}_2\text{H}_6$ ), and (c) borazine ( $\text{B}_3\text{H}_6\text{N}_3$ ). The heating rate was 2 °C/min. The black square symbol shows the result of 1st measurement and the white square symbol shows that of 2nd measurement.



**Fig. 5** The amounts of hydrogen desorbed by AB-MH composites below 200 °C versus dehydrogenation temperatures. The average temperatures between 1st and 2nd temperatures were plotted. The heating rate was 2 °C/min.

### 3.3 Creation of AB-MH composite based on the indicator

From the basis for the indicator described in section 3.2, we created superior AB-MH composites. As shown in Fig. 4, the emissions of  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$  were suppressed by combining



**Fig. 6** The mass spectra of (a) AB-NaAlH<sub>4</sub> composite and (b) AB-LiAlH<sub>4</sub> composite. The heating rate was 5 °C/min.

with  $\text{AlH}_3$  and  $\text{NaH}$  ( $\text{LiH}$ ), respectively. Therefore, we thought the idea of combining  $\text{MAIH}_4$  ( $M = \text{Na, Li}$ ) with  $\text{AB}$  because  $\text{MAIH}_4$  ( $M = \text{Na, Li}$ ) is the compound consisting of  $\text{MH}$  ( $M = \text{Na, Li}$ ) and  $\text{AlH}_3$ . The milling conditions of  $\text{AB-MAIH}_4$  composites are written in experimental part. The milling time of 5 min would be appropriate because milling for 30 min resulted in the decomposition of composites during milling. The mass spectra of  $\text{AB-NaAlH}_4$  and  $\text{AB-LiAlH}_4$  composites are shown in Fig. 6. It is interesting that both composites did not desorb  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$  and  $\text{B}_3\text{H}_6\text{N}_3$  at all within the accuracy of our apparatus. Only hydrogen gas was desorbed. About 4 wt% of hydrogen was desorbed below 240 °C in both composites. The suppression of by-product gas emission was also confirmed in  $\text{AB-Li}_3\text{AlH}_6$  composites.<sup>28</sup> Thus,  $\text{AB-MAIH}_4$  ( $M = \text{Na, Li}$ ) composites showed superior potentials as hydrogen storage materials. Investigations of the reaction processes of both composites are currently in progress.

#### 4. Conclusion

In order to decrease dehydrogenation temperature and suppress by-product gas emission, we investigated the phases and dehydrogenation properties of  $\text{AB-MH}$  composites prepared by ball-milling.  $\text{MBH}_4$  was formed for  $M = \text{K, Na}$  ( $\chi_p \leq 0.9$ ),  $\text{MNH}_2\text{BH}_3$  was formed for  $M = \text{Na, Li}$  ( $0.9 \leq \chi_p \leq 1.0$ ) and no new compounds were formed for  $M = \text{Ca, Mg, Al}$  ( $1.0 \leq \chi_p$ ). 1st dehydrogenation temperatures for  $M = \text{Na, Li, Ca, Mg}$  ( $\chi_p \leq 1.2$ ) were decreased by 10-20 °C as compared with the milled one. The amount of  $\text{NH}_3$  was decreased when electronegativity was increased.  $\text{AB-AlH}_3$  composite almost suppressed the emission of  $\text{NH}_3$ . On the other hand, the amount of  $\text{B}_2\text{H}_6$  was decreased when electronegativity was decreased.  $\text{AB-MH}$  ( $M = \text{Na, Li, Ca}$  ( $\chi_p \leq 1.0$ )) composites completely suppressed  $\text{B}_2\text{H}_6$ .  $\text{B}_3\text{H}_6\text{N}_3$  emission was observed for  $M = \text{Mg}$ . The emission could be occurred by the reaction between  $\text{NH}_3$  and  $\text{B}_2\text{H}_6$ . These results suggested that Pauling electronegativity of  $M$ ,  $\chi_p$  is a good indicator to predict the phases of composites, dehydrogenation temperature and the amount of by-product gas emission ( $\text{NH}_3$  and  $\text{B}_2\text{H}_6$ ).  $\text{AB-MAIH}_4$  ( $M = \text{Na, Li}$ ) composites, which were prepared based on the indicator, showed superior potentials as hydrogen storage materials because they did not desorb any by-product  $\text{NH}_3$ ,  $\text{B}_2\text{H}_6$  and  $\text{B}_3\text{H}_6\text{N}_3$ . These results would be helpful for clarifying the improvement mechanism of dehydrogenation properties and designing new hydrogen storage materials.

#### Notes and References

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