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Hydrogen desorption properties of NH_3BH_3-MH_n mixtures: How to control by-product gases

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Introduction

Hydrogen storage is a big challenge for a future hydrogen energy society. Currently, the compressed hydrogen gas tanks are utilized for fuel cell vehicles. For future applications, more compact and lightweight storage of hydrogen is demanded. Therefore, novel hydrogen storage materials should be explored.

Summary

Chapter 1 shows the introduction part of this thesis. Ammonia borane (NH_3BH_3, AB) is a promising hydrogen storage material because of its high hydrogen capacities. Nevertheless, its poor recyclability, sluggish kinetics and by-product gas emissions (ammonia (NH_3), diborane (B_2H_6) and borazine ($B_3H_6N_3$)) are disadvantages for its applications. To overcome these disadvantages, ammonia borane - metal hydride (AB-MH_n) mixtures, such as AB-LiH and AB-MgH_2, have been extensively studied.[1-2] However, systematic investigation on these mixtures has not been explored. In this study, various kinds of AB-MH_n (M = K, Na, Li, Ca, Mg, Al) mixtures were synthesized. The objectives of the thesis are following three parts; (1) Exploring important factors to reduce H_2 desorption temperature and amounts of by-product gas emissions from the systematic investigation on H_2 desorption properties, (2) Synthesizing advanced AB-MH_n mixtures based on the factors and investigating their H_2 desorption properties, (3) Investigating H_2 desorption processes of the advanced mixtures.

In chapter 2, six kinds of AB-MH_n (M = K, Na, Li, Ca, Mg, Al) mixtures were synthesized by ball-milling and the crystalline phases and H_2 desorption properties of the mixtures were systematically investigated. The crystalline phases were analyzed by power X-ray diffraction (XRD) and H_2 desorption properties were examined by thermogravimetry – differential thermal analysis – mass spectrometry (TG-DTA-MS). The results revealed that the Pauling electronegativity of metal, χ_p, is an important factor to predict the crystalline phases, H_2 desorption temperatures and amounts of by-product gas emissions. The correlation between H_2 desorption temperatures and χ_p was observed. Coulombic attraction between $H^{\delta-}$ of MH_n and $H^{\delta+}$ of AB would result in the temperature decrease. The amounts of hydrogen and by-product gases were normalized by integrating the peaks of mass spectra. The value of integral for by-product gases was normalized by that for hydrogen. The weight loss of each gas was estimated by using these

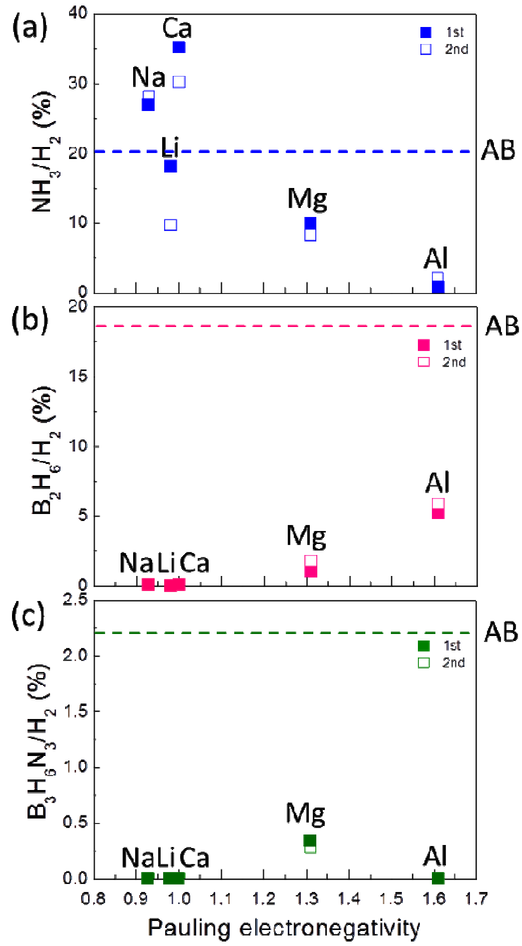

Fig. 1 The amounts of by-product gases desorbed from AB-MH_n mixtures classified by the Pauling electronegativity of M; (a) ammonia (NH_3), (b) diborane (B_2H_6) and (c) borazine ($B_3H_6N_3$). The heating rate was 2 °C min^{-1}. The filled squares show the results of 1st measurement and the white square shows the results of 2nd measurement.

integral values and the total weight loss obtained from TG results. Fig. 1 shows the amounts of by-product gases from the mixtures. The dashed line shows the amount of milled AB. As shown in Fig. 1(a), the amount of NH_3 has a tendency to be low when χ_p becomes high value. AB-AlH_3 mixture almost suppressed the emission of NH_3. On the other hand, the amount of B_2H_6 has a tendency to be low when χ_p becomes low value as shown in Fig. 1 (b). AB-MH_n (M = Na, Li, Ca ($\chi_p \leq 1.0$)) mixtures completely suppressed B_2H_6. Only AB-MgH_2 mixture desorbed $B_3H_6N_3$ as shown in Fig. 1(c).

Diammoniate of diborane (DADB), $[(NH_3)_2BH_2]^+[BH_4]^-$, is known as an intermediate phase of AB before H_2 desorption occurs.[3] This DADB is important for considering the by-product gas emissions from AB. The sources of NH_3 and B_2H_6 emissions would be DADB. If NH_3 reacts with MH_n, NH_3 emission is suppressed. The previous study about ammonia absorption properties of metal halides and borohydrides indicated that the material with higher χ_p of cation showed lower plateau pressure on the ammonia absorption.[4] The similar trend would exist in case of MH_n. B_2H_6 emission is suppressed if the $[BH_4]^-$ of DADB reacts with M^{n+} of MH_n to form solid phase of $M(BH_4)_n$. The trend in the amount of B_2H_6 was similar to the thermal stability of $M(BH_4)_n$ system. The thermal stability can be described using χ_p and the equation means that the stability increases as χ_p decreases.[5] Thus, the key issues for NH_3 and B_2H_6 suppressions are NH_3 absorption properties of MH_n and the formation of stable $M(BH_4)_n$ phase, respectively.

In chapter 3, AB-$MAlH_4$ (M = Na, Li) mixtures were synthesized based on the factor proposed in chapter 2. The emissions of NH_3 and B_2H_6 were suppressed by combining with AlH_3 and NaH (LiH), respectively. From this result, it is expected that $MAlH_4$ (M = Na, Li) additives may suppress all the by-product gases from AB because $MAlH_4$ (M = Na, Li) is the compound consisting of AlH_3 and NaH (LiH). The mixtures were synthesized by hand-mixing and ball-milling methods. Hand-mixing was performed in an Ar purified glovebox. In case of hand-mixing, the violent exothermic H_2 desorption reaction occurred. By-product gases were not suppressed. Ball-milling under Ar atmosphere also showed a similar reaction as hand-mixing. On the other hand, ball-milling under H_2 atmosphere for 180 minutes can generate a novel hydrogen storage material of $Na[Al(NH_2BH_3)_4]$ in AB-$NaAlH_4$ system. The synthesized $Na[Al(NH_2BH_3)_4]$ desorbed about 8.3 mass% H_2 with a small amount of by-product gas emissions. The solid products after H_2 desorption are $NaBH_4$ and amorphous Al-N-B-H phases. Fig. 2 shows the TG-DTA-MS profiles of AB-$MAlH_4$ mixtures with a molar ratio of 1 : 1. Ball-milling time was only 5 minutes. Both mixtures effectively suppressed the by-product gas emissions as shown in MS profiles. Thus, $MAlH_4$ is effective to decrease the by-product gas emissions from AB.

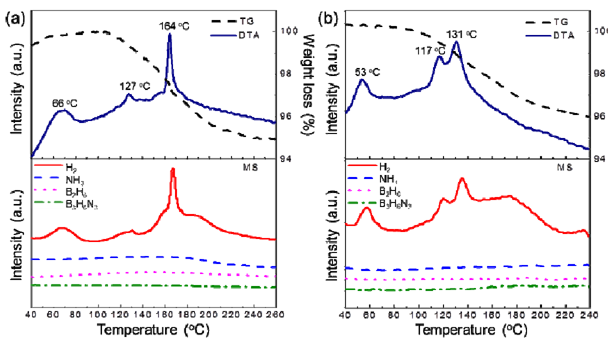

Fig. 2 TG-DTA-MS profiles of ball-milled AB-$MAlH_4$ (M = Na, Li) mixtures; (a) AB-$NaAlH_4$, (b) AB-$LiAlH_4$ mixture. The heating rate was 5 °C min^{-1}.

Chapter 4 shows general discussions and conclusions. The strategy for synthesizing advanced AB-MH_n mixtures was proposed. AB-AlH_3 mixture should be considered as base material because it showed the highest hydrogen amount among the investigated mixtures. By combining alkali metal hydride and $FeCl_2$ ($CuCl_2$) with the mixture, it would be possible to synthesize the material with high hydrogen amounts, low desorption temperature and no by-product gas emissions.

Conclusions

The H_2 desorption properties of AB-MH_n mixtures were systematically investigated. From the investigation, the Pauling electronegativity of metal (χ_p) was proposed as an important factor to reduce H_2 desorption temperatures and amounts of by-product gas emissions. Based on the factor, advanced AB-$MAlH_4$ (M = Na, Li) mixtures were synthesized. Ball-milling under H_2 atmosphere can generate a novel hydrogen storage material of $Na[Al(NH_2BH_3)_4]$ in AB-$NaAlH_4$ system. The synthesized $Na[Al(NH_2BH_3)_4]$ desorbed about 8.3 mass% H_2 with a small amount of by-product gases. The solid products after H_2 desorption are $NaBH_4$ and amorphous Al-N-B-H phases. By-product gas emissions were effectively decreased in the mixtures. AB-$MAlH_4$ mixture with a molar ratio of 1 : 1 showed no by-product gas emissions. Thus, $MAlH_4$ is effective to decrease the by-product gas emissions from AB. To desorb a large amount of H_2 at low temperatures with no by-product gas emissions, AB-AlH_3 mixture with alkali metal hydride and $FeCl_2$ ($CuCl_2$) would be promising.

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