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Hydrogen desorption properties of $\text{NH}_3\text{BH}_3\text{-MH}_n$ mixtures: How to control by-product gases

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Abstract

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.

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 ($\text{B}_3\text{H}_6\text{N}_3$)) 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. However, systematic investigation on these mixtures has not been explored. In this study, various kinds of AB-MH_n ($M = \text{K, Na, Li, Ca, Mg, Al}$) 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 the following chapters, those issues were targeted on the basis of a series of experiments.

In chapter 2, the crystalline phases and H_2 desorption properties of AB-MH_n ($M = \text{K, Na, Li, Ca, Mg, Al}$) mixtures were investigated. 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 $\text{H}^{\delta-}$ of MH_n and $\text{H}^{\delta+}$ of AB would result in the temperature decrease. The amount of NH_3 has a tendency to be low when χ_p becomes high value. On the other hand, the amount of B_2H_6 has a tendency to be low when χ_p becomes low value. 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-MAIH₄ (M = Na, Li) mixtures were synthesized based on the factor proposed in chapter 2. 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 H₂ 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 H₂ atmosphere can generate a novel hydrogen storage material of NaAl(NH₂BH₃)₄ in AB-NaAlH₄ system. The synthesized NaAl(NH₂BH₃)₄ desorbed about 8.3 mass% H₂ with a small amount of by-product gas emissions. AB-MAIH₄ mixture with a molar ratio of 1 : 1 showed no by-product gas emissions. Thus, MAIH₄ is effective to decrease the by-product gas emissions from AB.

Chapter 4 shows general discussions and conclusions. The strategy for synthesizing advanced AB-MH_n mixtures was proposed. AB-AlH₃ mixture should be considered as base material because it showed the highest hydrogen amount among the investigated mixtures. By combining alkali metal hydride and FeCl₂ (CuCl₂) with the mixture, it would be possible to synthesize the material with high hydrogen amounts, low desorption temperature and no by-product gas emissions.

1. Introduction

1.1 Background of Hydrogen Storage

1.1.1 Hydrogen Energy

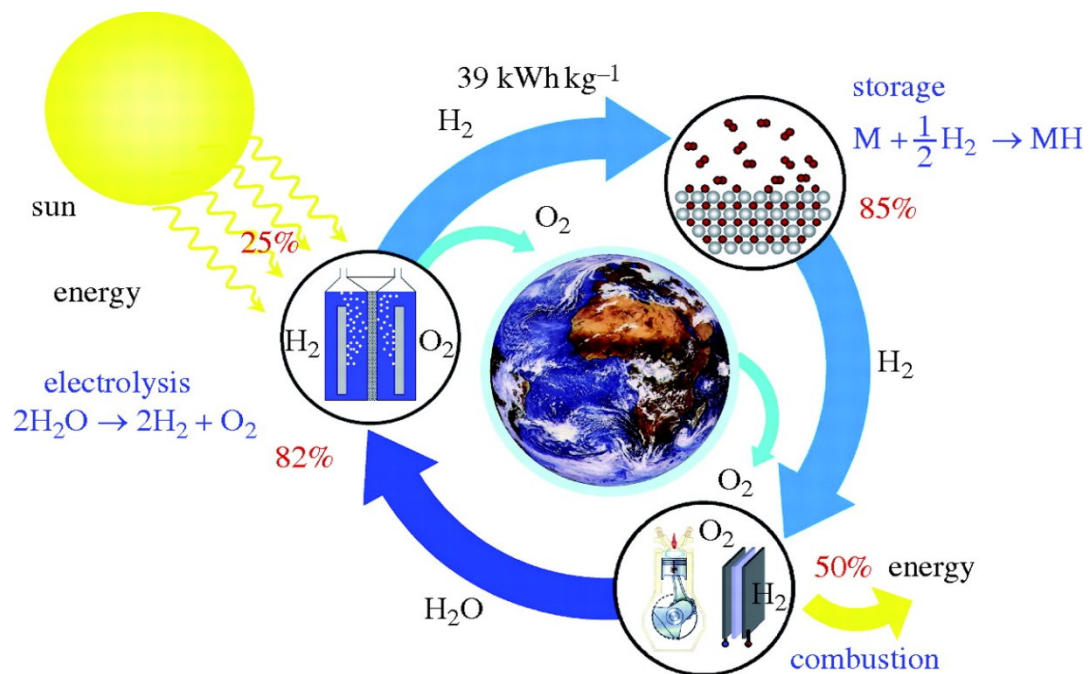


Fig. 1 Ideal hydrogen cycle (reprinted from ref. 1)

“Hydrogen” is a promising solution for a future energy society because it is the most abundant element in the universe, has the highest energy density per unit mass, and produces only water after burning. Hydrogen is a kind of secondary energy. Therefore, it needs to be produced from water or other organic compounds. Fig. 1 shows an ideal hydrogen cycle.¹ In this cycle, hydrogen is produced by splitting water through electrolysis. Then, produced hydrogen is stored in a solid material. To produce energy, hydrogen is desorbed from a solid material again and is used in a fuel cell. However, many difficulties make this cycle impossible. Key technologies for a hydrogen energy society are hydrogen production, transportation and storage. In the current situation, hydrogen is primarily produced from natural gas reforming. This method produces carbon dioxide. Therefore, carbon neutral hydrogen production is needed. Kawasaki Heavy Industries developed a new technology to produce hydrogen from brown coal. If the carbon dioxide capture and storage (CCS) is achieved, this technique will open a new avenue for applications.² Organic hydrides are promising for hydrogen transportation materials. Chiyoda corporation developed a novel organic hydride system for hydrogen transportation.³ In this system, gas hydrogen is changed to liquid methylcyclohexane by the reaction with toluene. Methylcyclohexane is liquid state at ambient temperature and pressure, therefore it is suitable as hydrogen carrier. Also, it is possible to desorb H₂ from methylcyclohexane by using platinum catalyst. This new technology is promising for hydrogen transportation. Recently, ammonia also attracts much attention as hydrogen carrier.⁴ Hydrogen storage is the difficult problem.⁵ Fig. 2 shows the various kinds of hydrogen storage techniques.⁶ Basically, hydrogen storage techniques are classified to physical- and material-based. In the current fuel cell vehicles, the compressed gas H₂ tank is utilized. For future hydrogen energy society, material-based storage will be needed because this technique has a potential to store hydrogen in a compact and light weight package.

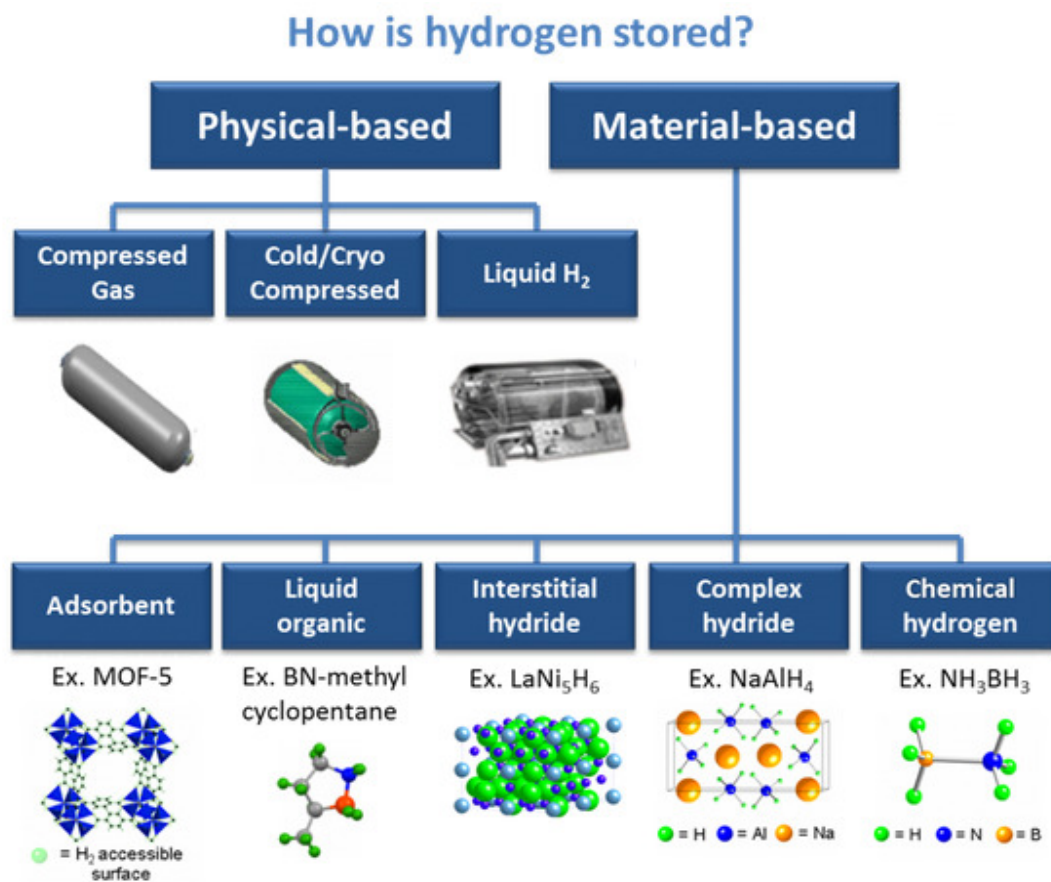


Fig. 2 Hydrogen storage techniques (reprinted from ref. 6).

1.1.2 Compressed Hydrogen Gas Tank

TOYOTA started the sales of their Fuel Cell Vehicle (FCV), MIRAI, on December 15th in 2014. Compressed hydrogen gas tank is utilized for this FCV. The pressure of compressed hydrogen in tanks is at 70 MPa and hydrogen capacity is 5.7 mass%. Fig. 3 shows the image of compressed hydrogen gas tank loaded into MIRAI.⁷ Two tanks are loaded into MIRAI. The wall of tank is made of 3 materials: plastic liner, carbon fiber reinforced plastic layer and glass fiber reinforced plastic layer. The technology of compressed hydrogen gas tank opened a new avenue for a hydrogen energy society. However, there are still some disadvantages. One is the danger of hydrogen leak or eruption. The tank contains hydrogen with high pressure. Once the hydrogen leaks to the environment, it would give rise to the dangerous situations. Furthermore, the

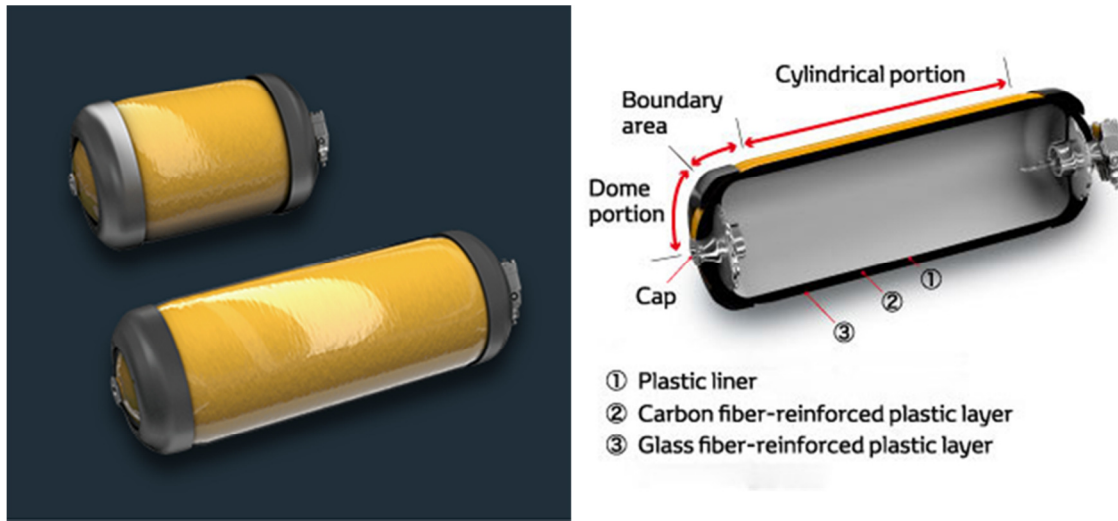


Fig. 3 The image of compressed hydrogen gas tank loaded with MIRAI (revised from ref. 7).

gravimetric and volumetric densities of hydrogen are not enough high. Therefore, more compact and lightweight storage of hydrogen is needed for future applications.

1.1.3 Liquid Hydrogen

Fig. 4 shows the first FCV, GM Electrovan in 1966, which was powered by a hydrogen fuel cell with alkaline electrolyte.⁸ Liquid hydrogen and liquid oxygen were stored in cryogenic vessels in this vehicle. Liquid hydrogen has a higher hydrogen density than that of gaseous hydrogen. However, boil-off is a big problem. Boiling point of liquid hydrogen is 20.4 K, which means very low storage temperatures are required to keep the hydrogen liquid. Boil-off takes place because of the unavoidable heat flow, which consists of three fractions: thermal conduction, convection and thermal radiation. Dominant parts are the thermal conduction through pipes to the inner vessel and the heat radiation from the environment to the cryogenic liquid. Ortho-para conversion also causes the boil-off.⁹

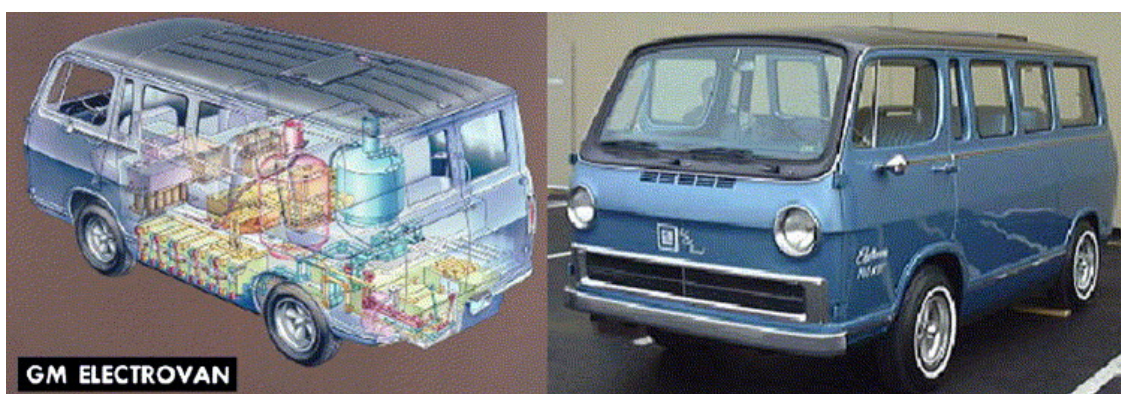


Fig. 4 GM Electrovan (1966), the first fuel cell vehicle, which was powered by a hydrogen fuel cell with alkaline electrolyte, liquid hydrogen and liquid oxygen were stored on-board in cryogenic vessels (reprinted from ref. 8).

1.1.4 Hydrogen Storage Materials

Hydrogen storage materials can store hydrogen in a compact package compared to compressed hydrogen gas tank and liquid hydrogen. The U.S. Department of Energy (DOE) introduced some technical targets for on-board hydrogen storage systems.¹⁰ Targets until 2017 for system gravimetric and volumetric capacities of hydrogen were 5.5 mass% and 40 g L⁻¹, respectively. The Japan New Energy and Industrial Technology Development Organization (NEDO) also set the technical targets.¹¹ Targets until 2020 were 6.0 mass% and 50 g L⁻¹ and those until 2030 were 7.5 mass% and 70 g L⁻¹. These values were based on the tank-system. Therefore, the values on materials-basis should be much larger than those on system-basis.¹²

Hydrogen storage materials can be classified into 5 categories: adsorbent, liquid organic, interstitial hydride, complex hydride and chemical hydride. Porous lightweight materials (carbon-based materials and metal-organic frameworks (MOFs)) are candidates for adsorbents. The interaction between hydrogen and most sorbents involves molecular hydrogen, which means hydrogen is physisorbed. Carbon- and MOF-based sorbents are attractive materials because they have high gravimetric densities. Nevertheless, all sorbents generally have one disadvantage, which is a too low operating temperature. The weak *Van der Waals* interaction between molecular

hydrogen and the sorbent needs the low temperature of near liquid nitrogen. Chemisorption system is also a promising way of hydrogen storage. Fig. 5 shows the map of potential hydrogen storage materials.¹³ Though interstitial hydrides have high volumetric capacities, gravimetric capacities are not enough to meet the targets. LaNi_5H_6 and Mg_2NiH_4 are typical interstitial hydrides. Complex hydrides, chemical hydrides and liquid organic hydrides have high gravimetric and volumetric densities to meet the targets. Therefore, these materials are promising for future applications. Complex hydrides are composed of metal cations and hydrogen-containing complex anions. Metal alanates ($\text{M}(\text{AlH}_4)_n$), borohydrides ($\text{M}(\text{BH}_4)_n$) and amides ($\text{M}(\text{NH}_2)_n$) are representatives. Chemical hydrides are synthesized by chemical reactions. NH_3BH_3 and

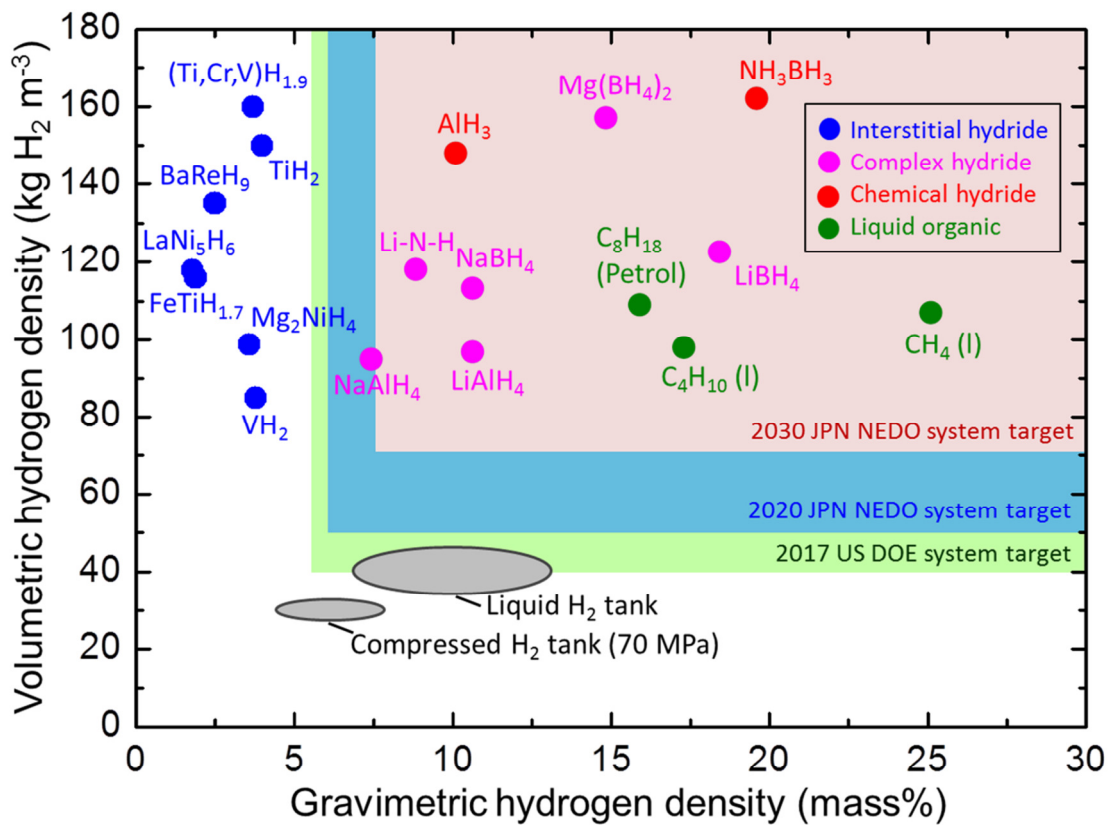


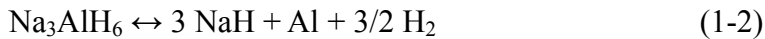
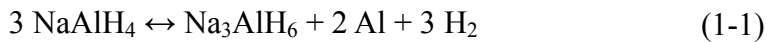
Fig. 5 The map of potential hydrogen storage materials versus the United States and Japan targets for hydrogen systems, liquid and compressed hydrogen tanks. The theoretical hydrogen capacity is indicated (revised from ref. 13).

AlH₃ are typical chemical hydrides. Some disadvantages of complex and chemical hydrides are their sluggish sorption kinetics and poor reversibility. Many scientists have focused on the studies of catalyst addition or thermodynamic tuning to improve these disadvantages.

1.2 Hydrogen Storage Materials

1.2.1 Complex Hydrides (Alanates and Borohydrides)

Alanates are generally formed from alkali or alkaline earth metals and [AlH₄][−] anion. Sodium alanate (NaAlH₄) is one of alanates, which consists of sodium ions surrounded by [AlH₄][−] tetrahedra. H₂ desorption reactions are described as follows.



Reaction (1-1) occurs at around 210 °C, releasing 3.7 mass% of hydrogen. An intermediate phase of Na₃AlH₆ is formed by this reaction. Reaction (1-2) occurs at around 250 °C, releasing 1.9 mass% of hydrogen. It was reported that Ti-catalyzed sodium alanate exhibited approximately twice the reversible capacity of any conventional metal hydrides.¹⁴ Except NaAlH₄ and Na₃AlH₆, a number of other alanates were reported such as LiAlH₄,^{15,16} Li₃AlH₆,^{15,16} Mg(AlH₄)₂,¹⁷ Ca(AlH₄)₂,¹⁷ Sr(AlH₄)₂,¹⁸ and Eu(AlH₄)₂.¹⁸

Borohydrides are generally formed from alkali or alkaline earth metals and [BH₄][−] anion. One of typical borohydrides is lithium borohydride (LiBH₄). LiBH₄ has high gravimetric and volumetric hydrogen densities (18.5 mass%, 121 g L^{−1}). LiBH₄ can release hydrogen up to ~13.5 mass% according to the following reaction.



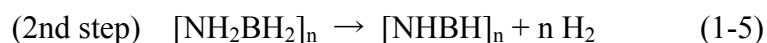
However, reaction (1-3) occurs at a high temperature region above 400 °C.¹⁹ The hydrogenation to LiBH₄ from LiH and B is possible at 600 °C under 35 MPa or at 690 °C under 20 MPa.²⁰ It means the hydrogenation under moderate conditions is difficult. Alkaline earth and transition metal borohydrides (Mg(BH₄)₂,²¹ Ca(BH₄)₂,²² Zn(BH₄)₂²³) have been also reported.

Some complex hydrides have attracted much attention as solid electrolyte materials. For instance, it was experimentally verified that the hexagonal phase of LiBH₄ exhibited lithium fast ionic conduction.²⁴ Sodium ionic conduction in complex hydrides with [BH₄][−] and [NH₂][−] was also clarified.²⁵ These findings will open a new application route of complex hydrides.

1.2.2 Ammonia Borane and Metal Amidoborane

Ammonia borane (NH₃BH₃, AB) is a promising hydrogen storage material because of its high hydrogen capacities (19.6 mass%, 145 g L^{−1}) and relatively low H₂ desorption temperature (~13 mass% of H₂ below 200 °C).²⁶ The molecular structure of AB is similar with that of ethane (C₂H₆). AB exists as solid at standard conditions, which is different from ethane as gas. The stability is attributed to a dihydrogen bonding network. The solid state AB exhibits shorter BH...HN intermolecular distance than the *Van der Waals* distance.²⁷⁻²⁹ The melting point of AB is in the range of 110-114 °C.³⁰

AB consists of nitrogen, boron and hydrogen. It doesn't contain any metals. Therefore, H₂ desorption mechanism of AB is very different from the well-known metal hydrides. The H₂ desorption reaction of AB takes place in three steps as shown below.³¹⁻³³



The 1st and 2nd steps occur at the temperature range of 70-120 °C and 120-200 °C, respectively. The 3rd step occurs in a high temperature region above 500 °C, which is

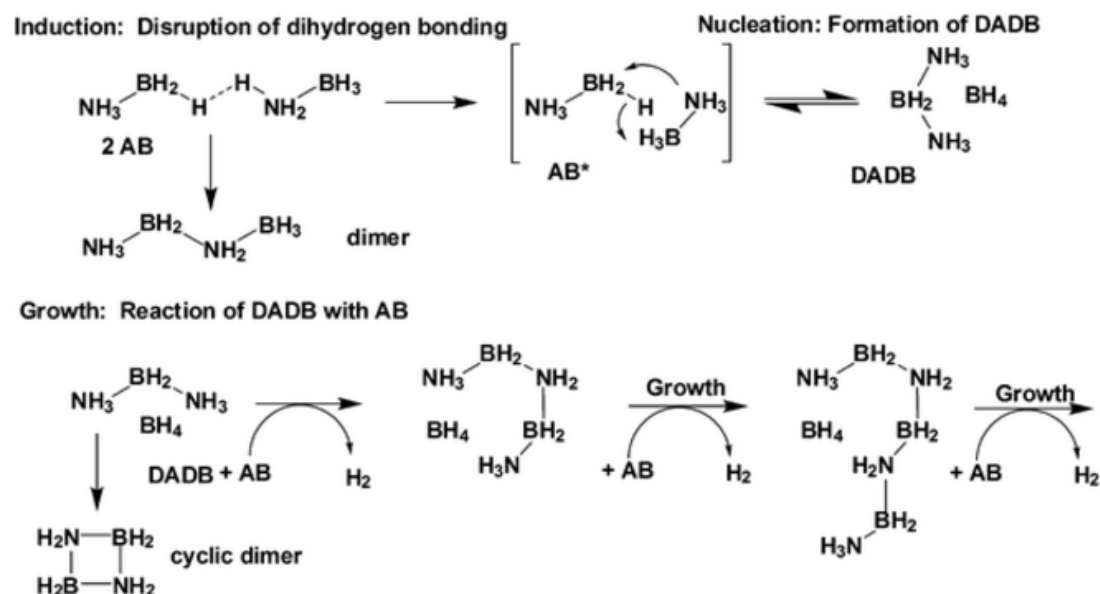
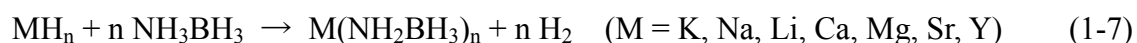


Fig. 6 The proposed H_2 desorption mechanism of ammonia borane (reprinted from ref. 31).

not suitable for practical applications. Basically, metal hydrides desorb H_2 in endothermic reactions. However, AB desorbs H_2 in exothermic reactions in the 1st and 2nd steps (Reaction (1-4) and (1-5)). The reaction enthalpy (ΔH) was $-21 \text{ kJ/mol } H_2$.³³ Only the 3rd step (Reaction (1-6)) desorbs hydrogen in an endothermic reaction. Therefore, entire rehydrogenation of decomposed AB is thermodynamically difficult. Chemical regeneration route of AB has been developed, which is promising for future applications.³⁴ In this method, AB can regenerate by nearly 24 hours-treatment with hydrazine in liquid ammonia at 40°C in sealed pressure vessel. The H_2 desorption mechanism of AB was clarified *via in situ* solid state MAS-NMR techniques. Fig. 6 shows the proposed H_2 desorption mechanism of AB.³⁵ During the induction period, the dihydrogen bonding network is disrupted to form a more mobile phase (AB^*). The detailed study of mobile phase was described in ref. 36. The mobile phase converts to yield diammoniate of diborane (DADB), $[(NH_3)_2BH_2]^+[BH_4]^-$, an ionic isomer of AB. After the DADB formation, AB molecule reacts with DADB to release hydrogen. Thus, DADB is an important phase to cause the H_2 desorption from AB. Except DADB, other

two BH_2N_2 species of linear ($\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$) and cyclic dimer ($(\text{NH}_2\text{BH}_2)_2$) of aminoborane are also observed. Except the poor reversibility, the disadvantages for its applications are sluggish kinetics below 100 °C and the emission of by-product gases. AB desorbs not only hydrogen but also by-product gases such as ammonia (NH_3), diborane (B_2H_6) and borazine ($\text{B}_3\text{H}_6\text{N}_3$). For instance, release of ammonia causes the damage to the fuel cell performance even at ppm levels.³⁷ Also, ammonia and diborane are toxic gases for living creatures.^{38,39}

To overcome these disadvantages, several approaches, such as infusion of AB in nanoscaffolds,⁴⁰ doping with transition metals as catalysts,⁴¹ have been developed. One of the effective approaches is the chemical modification of AB by replacing one of H atoms with an alkali or alkaline earth metal to form metal amidoborane. The formation reaction can be described by using AB and metal hydride (MH) as shown below.⁴²⁻⁴⁹



Metal amidoboranes have been synthesized by solid phase method (ball milling) or liquid phase method. The way of synthesis was different from each other. For example, KNH_2BH_3 was synthesized by liquid phase method, whereas solid phase method was not possible.⁴⁵ The synthesis of $\text{Mg}(\text{NH}_2\text{BH}_3)_2$ was a mystery because it was impossible to synthesize by solid and liquid phase methods. However, recent study showed that ball-milling AB with MgH_2 followed by heating the mixture to 80 °C formed the $\text{Mg}(\text{NH}_2\text{BH}_3)_2$.⁴⁷ MgH_2 would react with the mobile phase of AB (AB^*), which is formed by keeping the sample to 80 °C. In this way, the synthesis route was different according to metal species. Basically, metal amidoborane shows superior properties than AB from the viewpoint of H_2 desorption temperature and the amount of by-product gas emissions. Fig. 7 shows the H_2 and borazine mass spectra of AB, LiNH_2BH_3 and NaNH_2BH_3 . LiNH_2BH_3 and NaNH_2BH_3 showed the lower H_2 desorption temperature and the suppression of borazine.⁴² Recently, mixed-metal amidoborane was also synthesized such as $\text{NaLi}(\text{NH}_2\text{BH}_3)_2$ ⁵⁰ and $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$.⁵¹ Fig. 8 shows the TG-DSC-MS profile of $\text{NaLi}(\text{NH}_2\text{BH}_3)_2$.⁵⁰ Not only H_2 but also by-product gases of

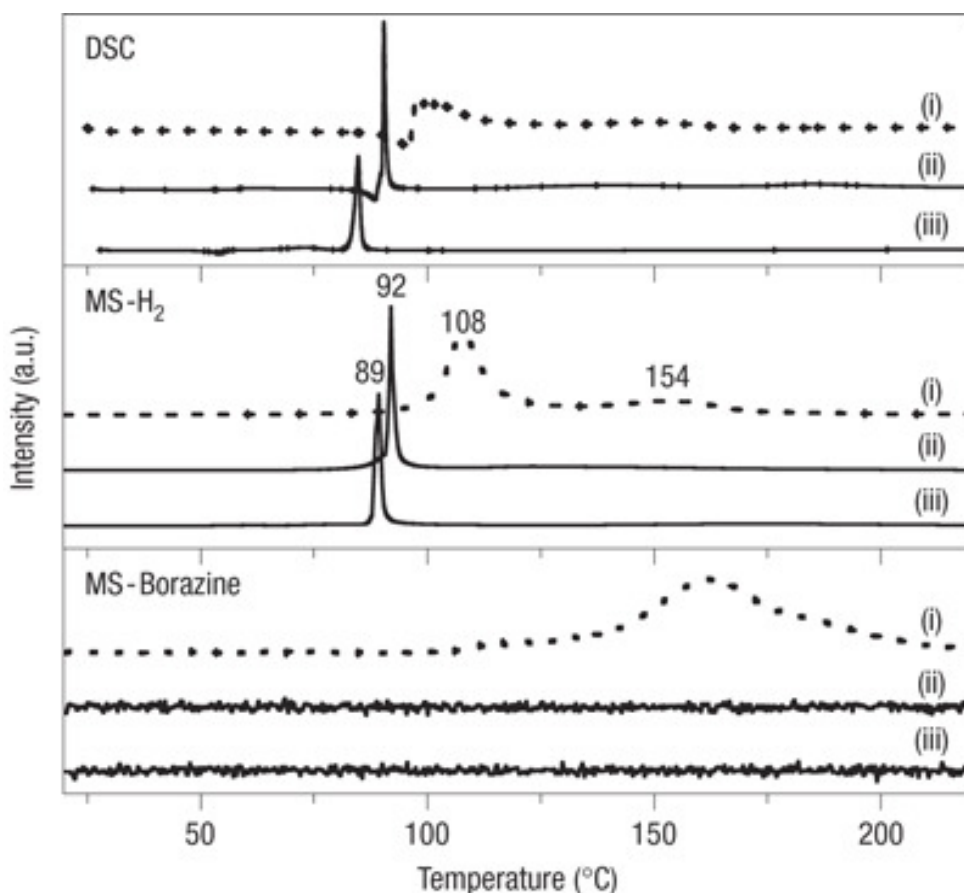


Fig. 7 DSC profiles, hydrogen and borazine desorption curves of (i) NH_3BH_3 , (ii) LiNH_2BH_3 and (iii) NaNH_2BH_3 (reprinted from ref. 42).

NH_3 and NH_2BH_3 were desorbed.

AB-complex hydride systems also have been explored such as AB-LiNH_2 ,⁵² AB-LiBH_4 ,⁵³ $\text{AB-Mg(BH}_4)_2$,⁵⁴ and $\text{AB-Li}_3\text{AlH}_6$.⁵⁵ As shown in Fig. 9, AB-LiNH_2 mixture showed the H_2 desorption as low as 60 °C.⁵² Hydrogen of 11.9 mass% were released up to 250 °C in this system. $\text{AB-Li}_3\text{AlH}_6$ mixture effectively suppressed the emission of by-product gases as shown in Fig. 10.⁵⁵ Furthermore, the chemical regeneration of this system was partially achieved. In this system, the formation of mixed-metal (Li, Al) amidoborane was suggested. However, the crystalline structure of this phase has not been determined.

In this way, a number of metal amidoborane or AB-complex hydride systems have been reported. Basically, these mixtures showed the lower H_2 desorption temperature

and small amounts of by-product gases compared with AB. However, the poor reversibility is a disadvantage for applications. Another disadvantage is a decreased hydrogen capacity by the substitution of H to M.

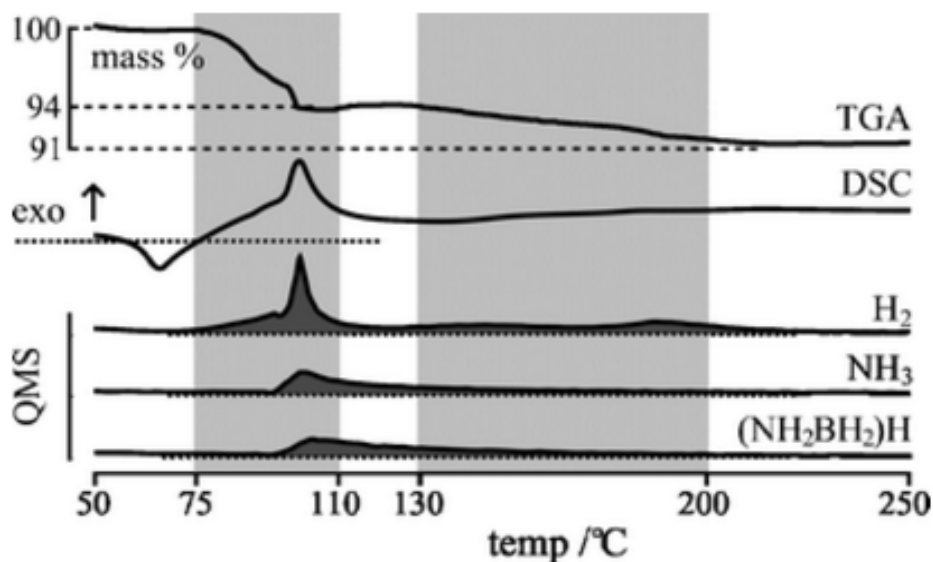


Fig. 8 TG-DSC-MS profile of Na[Li(NH₂BH₃)₂]. The first and second broad steps of decomposition are marked with gray fields. The heating rate was 10 °C min⁻¹ (reprinted from ref. 50).

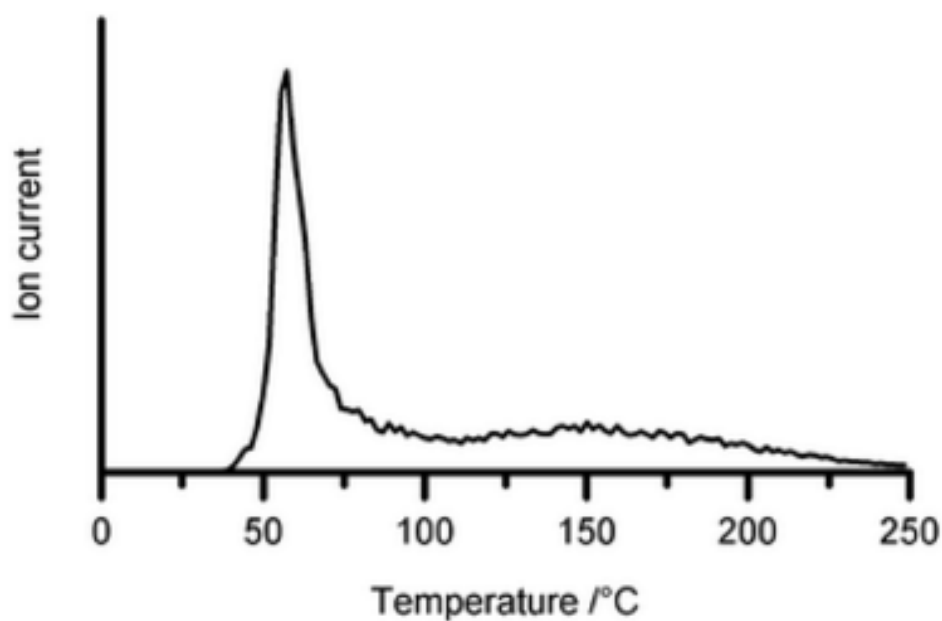


Fig. 9 Hydrogen desorption curve of AB-LiNH₂ mixture. The heating rate was 1 °C min⁻¹ (reprinted from ref. 52).

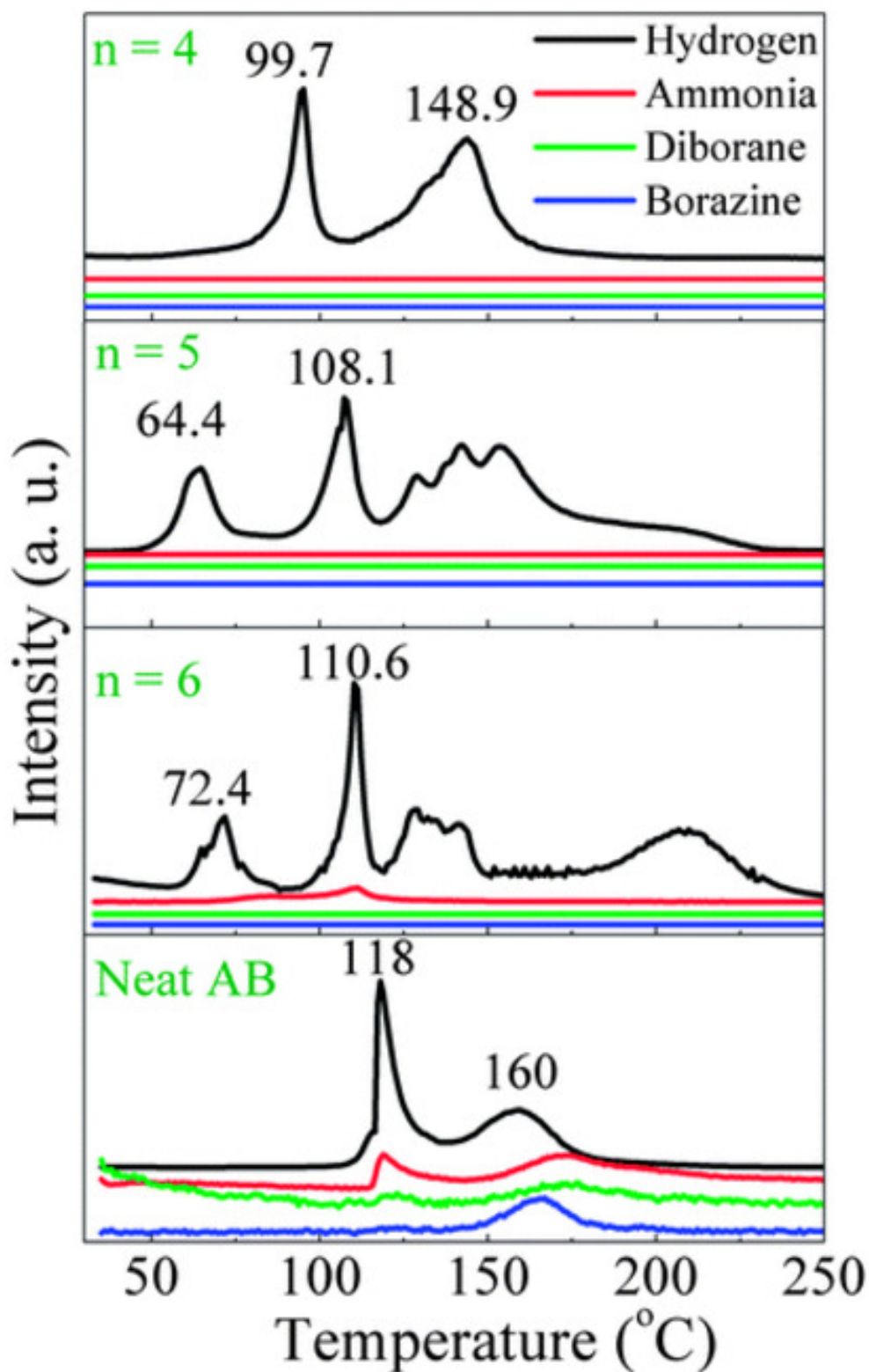


Fig. 10 MS spectra of nAB-Li₃AlH₆ mixtures and neat AB. The heating rate was 2 °C min⁻¹ (reprinted from ref. 55).

In 2014, Korean research group demonstrated to drive an unmanned aerial vehicle (UAV) powered by AB.⁵⁶ This was the first case in the world to use AB-based power pack. The ability of power-pack to drive a UAV for 57 min with fast load-following ability and rapid response time was verified. Fig. 11 shows the image of UAV platform.⁵⁶ Pure hydrogen is generated from AB by using the reactor filled with tetraethylene glycol dimethylether (T4EGDE), a liquid promoter. Thus, the application of AB to UAV may be promising.

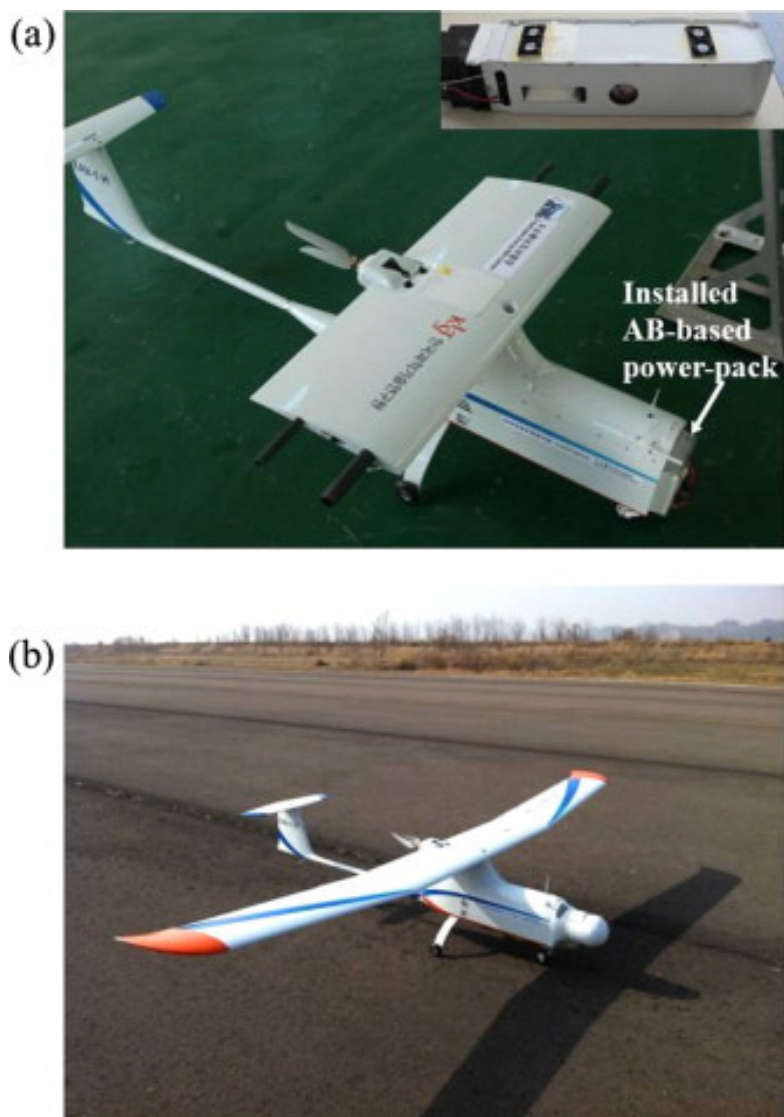


Fig. 11 The UAV platform; (a) installation of as-developed power pack into the UAB and the AB power pack (inset), (b) fully-assembled UAV before the test flight (reprinted from ref. 56).

1.3 Strategies for the Improvements in Complex Hydrides

1.3.1 Hydride Destabilization

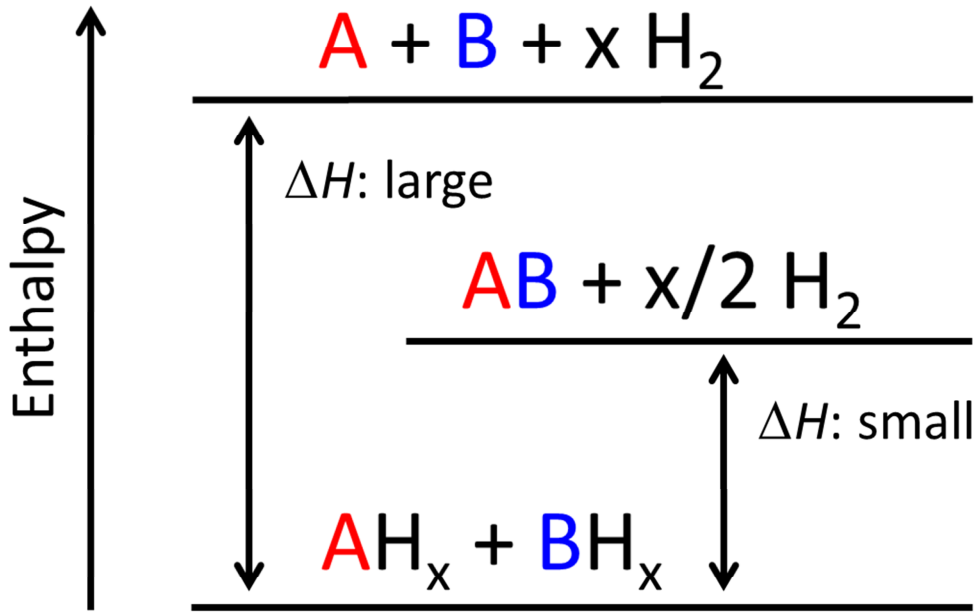


Fig. 12 The concept of hydride destabilization.

A promising approach for controlling the H_2 desorption thermodynamics is to react two or more hydrogen storage materials during the release of hydrogen.¹⁴ The simplified scheme is described in Fig. 12. The overall reaction is destabilized to form more stable compounds ($AH_x + BH_x \rightarrow AB + x H_2$) rather than the elements ($AH_x + BH_x \rightarrow A + B + x H_2$). This concept has been utilized for various kinds of hydrogen storage systems.

In 2002, P. Chen *et al.* discovered the reversible hydrogen release and storage of lithium amide hydride ($LiNH_2$ - LiH) system according to the reactions as follows.⁵⁷

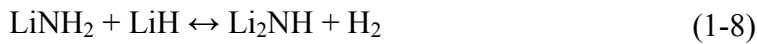


Fig. 13 shows the weight variations during H_2 absorption and desorption processes over Li_3N samples.⁵⁷ As shown in Fig. 13, reaction (1-8) occurs in the temperature range of

170-210 °C. Reaction (1-8) is reversible at moderate conditions with a hydrogen capacity of 6.5 mass% and an enthalpy change of 66 kJ mol⁻¹ H₂, which is promising for practical applications.⁵⁸ On the other hand, dehydrogenation reaction of lithium imide (reaction (1-9)) requires high vacuum and temperatures above 320 °C, which is not suitable for practical applications. The reaction process based on Li⁺ migration between LiNH₂ and LiH was proposed about reaction (1-8).⁵⁹ The addition of LiTi₂O₄ catalyst showed the improvement of H₂ desorption properties, which was correlated with the increasing of lithium ion mobility in the system.⁶⁰

J.J. Vajo *et al.* discovered the reversible hydrogen storage in destabilized LiBH₄ by the addition of MgH₂.⁶¹ The dehydrogenation reaction is described as follows.

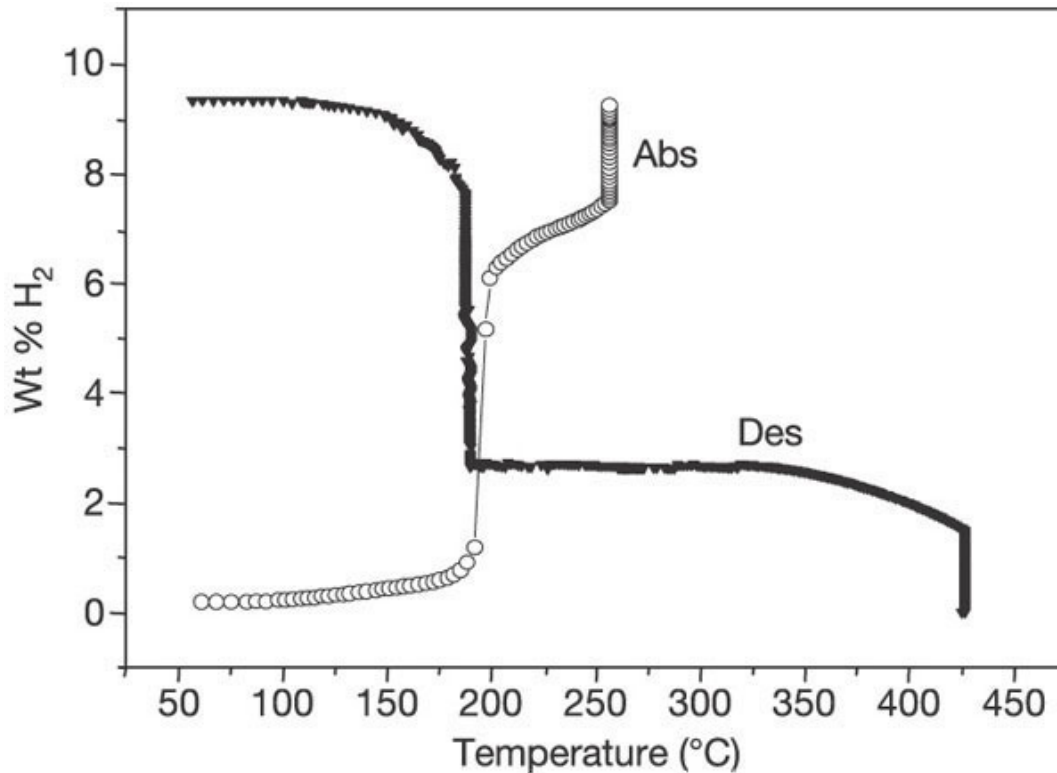
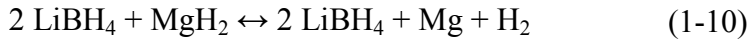


Fig. 13 Weight variations during hydrogen absorption and desorption processes over Li₃N samples (reprinted from ref. 57).

In this system, the addition of MgH_2 lowered the de/hydrogenation enthalpy by $25 \text{ kJ mol}^{-1}\text{H}_2$ compared with pure LiBH_4 .⁶¹ The hydrogenation occurred at the hydrogen pressure of 50 bar and in the temperature range of 250-300 °C, which is more favorable condition than that of LiBH_4 .⁶² Furthermore, H-D exchange reaction between LiBH_4 and MgD_2 was observed in $\text{LiBH}_4\text{-MgD}_2$ system.⁶³ This interesting phenomenon was observed even in the solid phases. The hydrogen desorption temperature was increased by the H-D exchange effect. By the H-D exchange, the entropy change of hydrogen desorption (ΔS) would be decreased. Though the concept in Fig. 12 can be considered as ΔH (the enthalpy change of hydrogen desorption) control, the H-D exchange may open a strategy for ΔS control.

1.3.2 Electronegativity of Metal as Important Factor for Thermodynamic Tuning

Electronegativity of metal is an important factor to predict the thermodynamic stabilities of complex hydrides. The thermodynamic stabilities of $\text{M}(\text{BH}_4)_n$ have been systematically investigated by first-principle calculations. The heat of formation of the $\text{M}(\text{BH}_4)_n$ can be described by using Pauling electronegativity of metal (χ_p) as follows.⁶⁴

$$\Delta H_{\text{boro}} = 248.7 \chi_p - 390.8 \text{ (kJ/(mol of BH}_4\text{))} \quad (1-12)$$

Thus, the stability depends linearly on χ_p . This relationship was also experimentally verified. Fig. 14 shows the correlation between Pauling electronegativity of metal (χ_p) and H_2 desorption temperature of $\text{M}(\text{BH}_4)_n$ derived from the experiments.⁶⁵ The desorption temperature has a tendency to be low as χ_p increases. The desorbed gas for $\text{M} = \text{Ca, Sc, Ti, V and Cr}$ ($\chi_p \leq 1.5$) is hydrogen only, while gases for $\text{M} = \text{Mn, Zn and Al}$ ($\chi_p \geq 1.5$) contain diborane and hydrogen.⁶⁵ The experimental results are consistent with the simulation results. The same correlation was observed between desorption temperature and the averaged χ_p of MM' in $\text{MM}'(\text{BH}_4)_n$ system.⁶⁶

In addition, similar correlation between χ_p and desorption temperature is observed in

M_3AlH_6 system. Fig. 15 shows the correlation between χ_p and sorption reaction enthalpy (ΔH) in M_3AlH_6 system.¹⁴ It is clear that the correlation exists between χ_p and ΔH . For the bimetal alanates ($M_2M'AlH_6$), the averaged χ_p is used. χ_p is a good indicator not only for single cation system but also double cation system. In this way, the thermodynamic tuning by cation substitution would be possible for metal borohydrides and alanates.

χ_p is also an important factor for predicting the decomposition temperatures of metal borohydride ammoniates, $M(BH_4)_m \cdot nNH_3$. Metal borohydride ammoniates have recently attracted much attention because of its high hydrogen capacities and lower H_2 desorption temperatures compared to metal borohydrides. Fig. 16 shows the decomposition temperatures for selected metal borohydrides and metal borohydride ammoniates.⁶⁷ As shown in Fig. 16, metal borohydrides with low χ_p are destabilized by ammoniate formation while those with high χ_p are stabilized. For example, Co-catalyzed $Li(NH_3)_{4/3}BH_4$ releases ca. 17.8 mass% of H_2 in the temperature range of 135-250 °C, in contrast to $LiBH_4$ which release H_2 around 400 °C.⁶⁸ $Al(BH_4)_3$, which has the highest capacity (16.9 mass%) among the borohydrides, is unstable and volatile. However, $Al(BH_4)_3 \cdot 6NH_3$ is stable and releases 11.8 mass% of H_2 around 168 °C.⁶⁹ According to ref. 67, metals with low χ_p tend to release NH_3 during heating in open systems and those with high χ_p coordinate more strongly to NH_3 causing a collapse of the structure and release H_2 in the temperature range of 100-200 °C. Thus, electronegativity of metal is an important factor to predict the H_2 desorption temperature of complex hydride system.

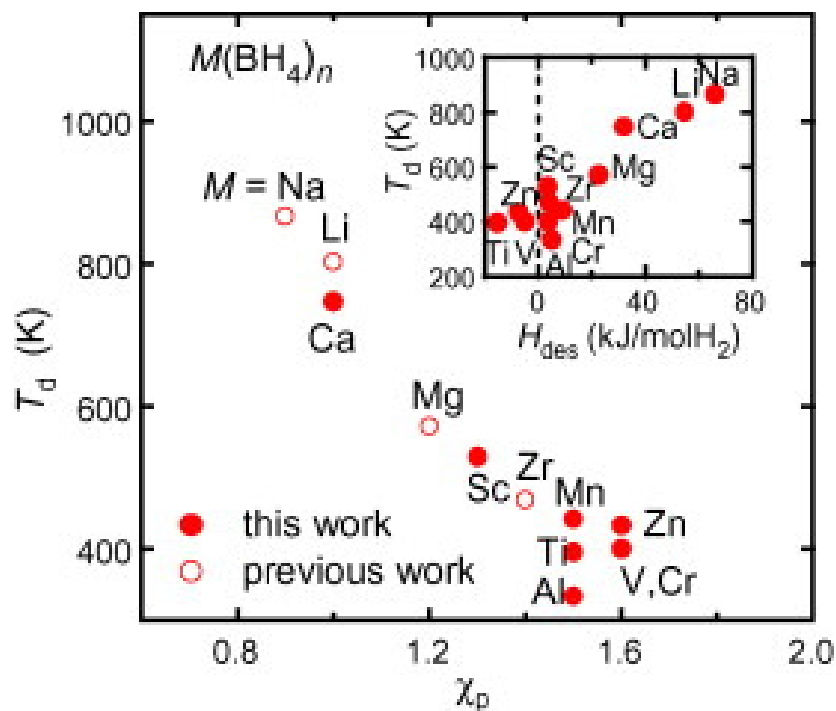


Fig. 14 The correlation between the Pauling electronegativity of metal (χ_p) and the H_2 desorption temperature in $M(BH_4)_n$ system (reprinted from ref. 65).

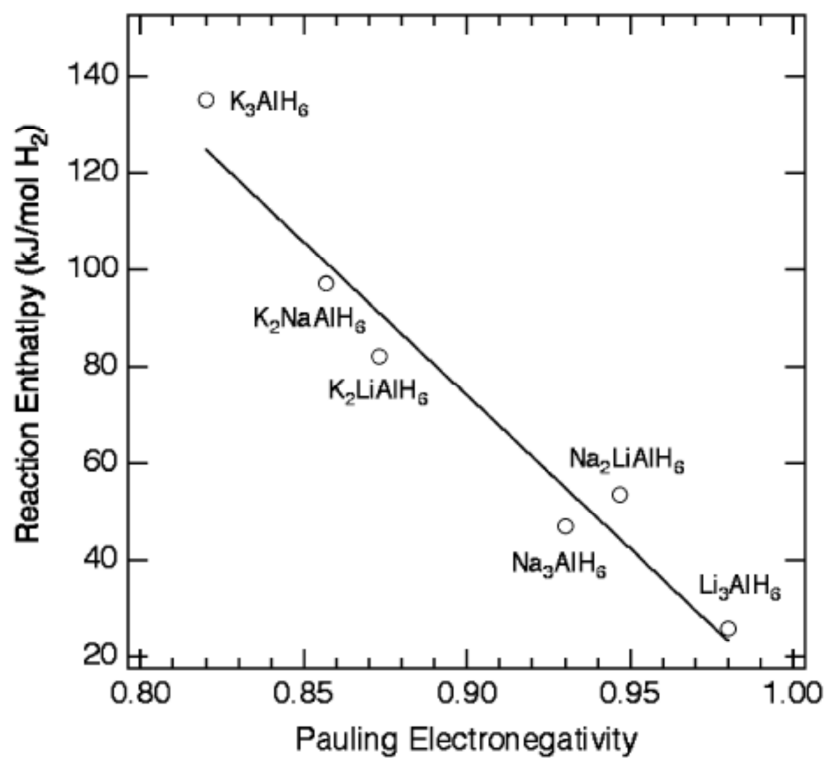


Fig. 15 The correlation between the Pauling electronegativity of metal (χ_p) and the H_2 desorption reaction enthalpy in M_3AlH_6 system (reprinted from ref. 14).

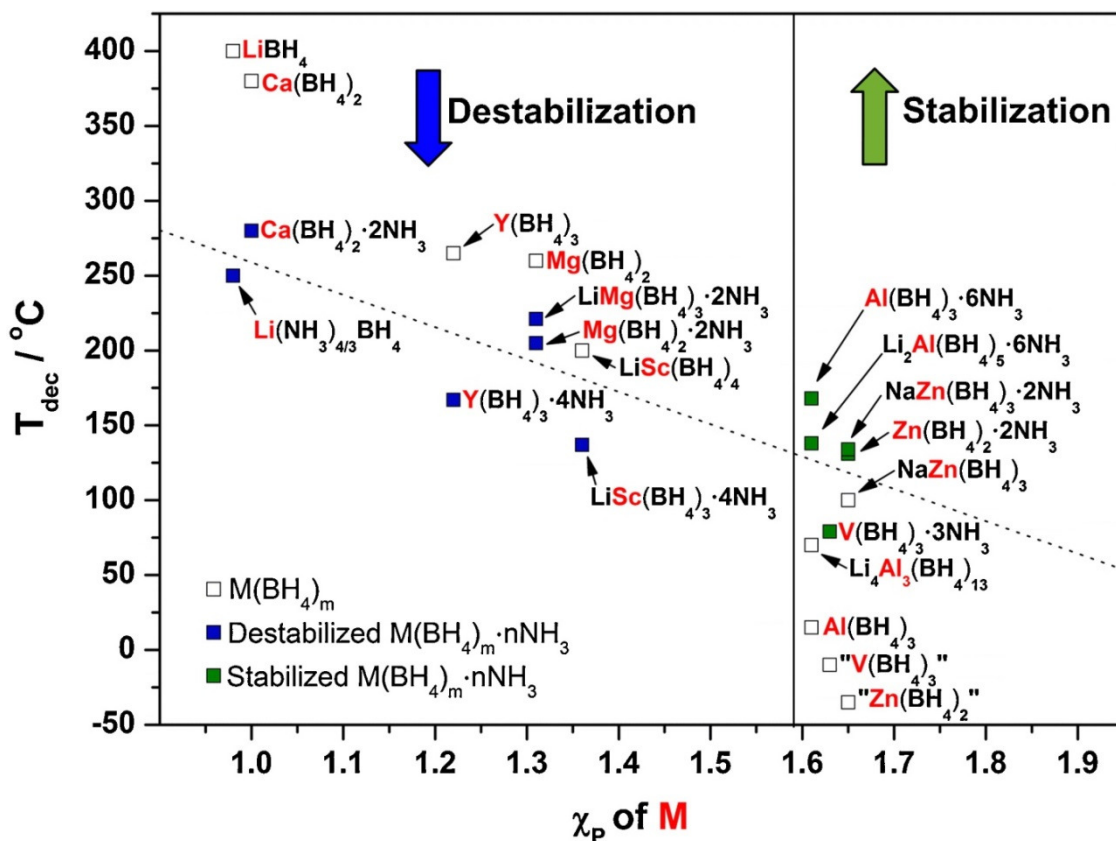


Fig. 16 The decomposition temperatures for selected metal borohydrides and metal borohydride ammoniates plotted as a function of the electronegativity of metal, χ_p . The dashed line indicates a correlation between decomposition temperatures and χ_p for metal borohydride ammoniates. (reprinted from ref. 67).

1.4 Objective

The study about hydrogen storage materials were started in 1960s and many scientists have explored their properties. However, there are no materials fulfilling all the targets for applications up to now. Therefore, developing novel hydrogen storage materials are needed. Recently, hydrogen storage materials consisting of light elements attract much attention from the standpoint of their high hydrogen densities. Ammonia borane (NH_3BH_3 , AB) is a promising hydrogen storage material because of its high hydrogen capacities (19.6 mass%, 145 g L⁻¹). Nevertheless, its poor reversibility, sluggish kinetics and by-product gas emissions prohibited its applications. To overcome these disadvantages, ammonia borane - metal hydride (AB-MH_n) mixtures have been extensively studied. However, systematic investigation on these mixtures has not been explored. Some important factors are needed for the improvements of H₂ desorption properties in AB-MH_n mixtures. In this thesis, various kinds of AB-MH_n mixtures were synthesized and their H₂ desorption properties were investigated. Basically, the mixtures were synthesized by ball-milling method because this method may cause the novel phase formation by mechanochemical reactions. The objective of the thesis lies in the following points.

- (1) Exploring important factors for the improvements of H₂ desorption properties of AB-MH_n mixtures from the systematic investigation on the H₂ desorption properties
- (2) Synthesizing advanced AB-MH_n mixtures based on the proposed factors and investigating H₂ desorption properties in detail
- (3) Investigating the H₂ desorption processes of the advanced AB-MH_n mixtures

In the following chapters, those issues will be targeted on the basis of a series of experiments. The conclusion will be carefully shown after discussions.

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2. Hydrogen desorption properties of $\text{NH}_3\text{BH}_3\text{-MH}_n$ system

2.1 Background and purpose

The H_2 desorption properties of AB-MH_n mixtures have been extensively studied such as AB-LiH ,¹ AB-NaH ,¹ AB-KH ,² AB-MgH_2 ,³ and AB-LiNH_2 .⁴ However, systematic investigation on AB-MH mixtures has not been explored. Some important factors are needed for improving the disadvantages of AB . Therefore, the objective in this chapter is to explore important factors to predict crystalline phases, decrease H_2 desorption temperatures and by-product gas emissions in AB-MH_n mixtures.

2.2 Experimental procedures

Six kinds of metal hydrides (KH , NaH , LiH , CaH_2 , MgH_2 , AlH_3) were ball-milled with AB . NH_3BH_3 , NaH , LiH , CaH_2 (purity 97 %, 55-65% (moistened with oil), 95 %, 99.99 %, respectively) were purchased from Sigma Aldrich Co. Ltd. KH was synthesized according to ref. 5. AlH_3 was synthesized by the chemical reaction between LiAlH_4 and AlCl_3 in ether solution.⁶ Ball-milling was performed under 0.1 MPa Ar with 400 rpm for 30 min, using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with

20 stainless steel balls and 300 mg samples (ball : powder ratio = 70 : 1, by mass). The crystalline phase analysis was conducted by powder X-ray diffraction (XRD, PANalytical, X'Pert Pro with Cu K α radiation). The H₂ desorption properties were examined by thermal desorption mass spectrometry (TDMS, ULVAC, BGM-102) combined with thermogravimetry and differential thermal analysis (TG-DTA, Bruker, 2000SA). The heating rate was 2 °C min⁻¹ and helium gas flow rate was 300 mL min⁻¹. The amounts of hydrogen and by-product gases were defined by integrating the peaks of mass spectra. The value of integral for by-product gases was normalized by that for hydrogen. The mass loss of each gas was estimated by using these integral values and the total mass loss obtained from TG results. Transmission electron microscopy (TEM) observations were performed with 200 kV of accelerating voltage (JEOL, JEM-2010). The samples were dispersed on molybdenum micromesh grids. All samples were handled in a glovebox filled with Ar.

2.3 Results and discussions

2.3.1 Crystalline phase analysis

Fig. 2-1 shows the XRD profiles of each AB-MH_n mixture after milling and heating to 200 °C. Broad diffraction peaks around 20° and 27° in all profiles originate from the polyimide film and grease to prevent the sample oxidation. A phase of (NH₂BH₂)₄ was observed in milled AB. This phase was an impurity in as-received AB. After heating, AB became amorphous state. In AB-NaH mixture, peaks were consistent with sodium amidoborane (NaNH₂BH₃), which was discovered by Xiong *et al.*¹ After heating, NaBH₄ was observed, which was different from the experimental results of previous reports.^{7,8} One of the possibilities of NaBH₄ formation would come from the different milling condition. There are some cases that non-equilibrium phases appear by mechanical ball-milling.⁹ As described in ref. 7, the formation of [BH₄]⁻ ions may occur under the milling condition. In AB-LiH mixture, peaks were consistent with

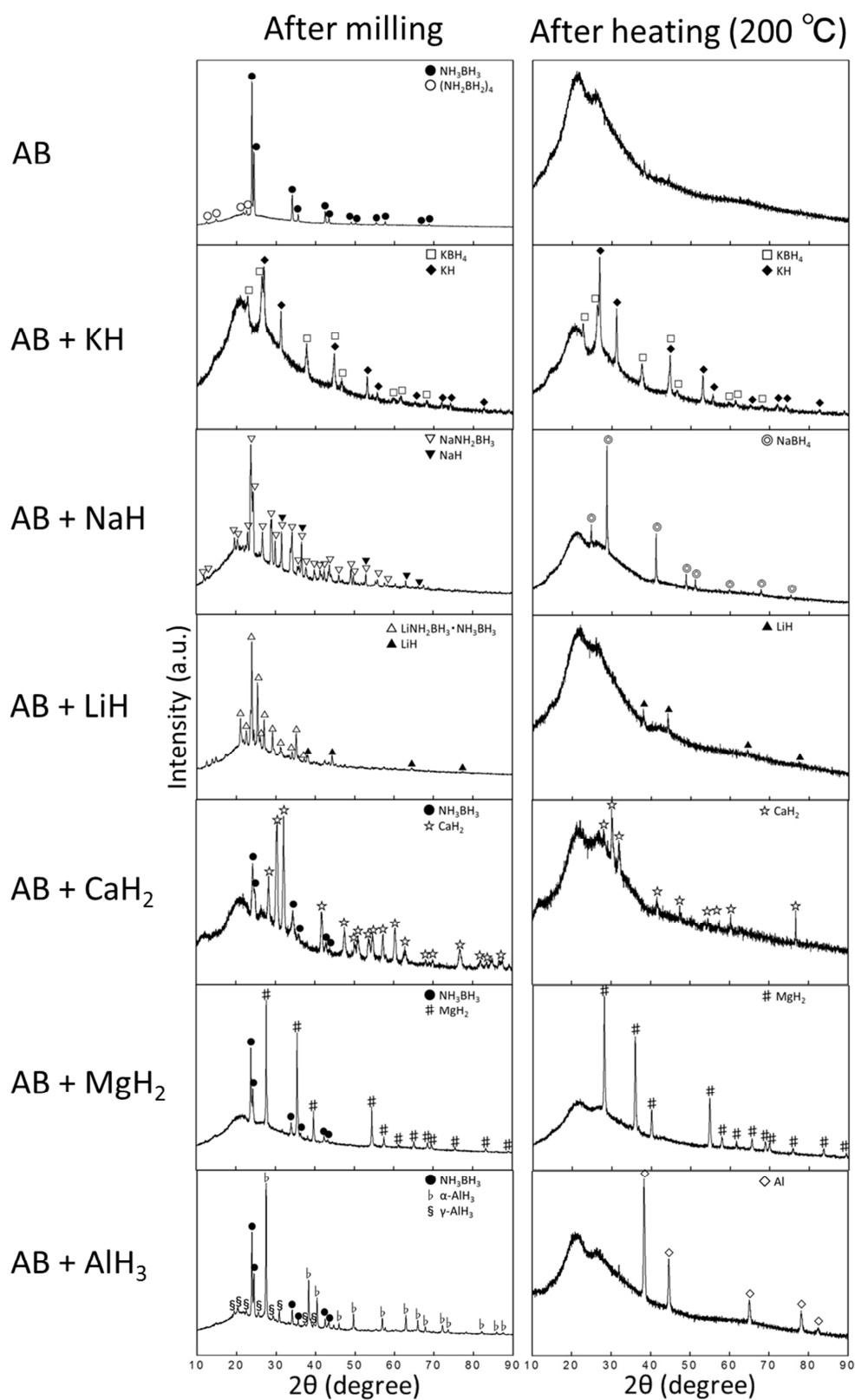


Fig. 2-1 Powder X-ray diffraction (XRD) profiles of AB-MH_n (M = K, Na, Li, Ca, Mg, Al) mixtures and AB after milling and heating to 200 °C.

lithium amidoborane-ammonia borane ($\text{LiNH}_2\text{BH}_3 \cdot \text{NH}_3\text{BH}_3$). This phase is the intermediate phase during the synthesis of LiNH_2BH_3 .¹⁰ Thus, metal amidoborane (MNH_2BH_3 , $\text{M} = \text{Na, Li}$) was observed after milling for $\text{M} = \text{Na, Li}$. In AB-KH mixture, KBH_4 was observed instead of KNH_2BH_3 after milling. In case of AB- CaH_2 , AB- MgH_2 and AB- AlH_3 systems, no new compounds were observed after milling. Only AB and each MH_n phase were observed. According to ref. 11, more than 6 hours milling by using a shaker mill can generate $\text{Ca}(\text{NH}_2\text{BH}_3)_2$. Though the synthesis of $\text{Mg}(\text{NH}_2\text{BH}_3)_2$ was unsuccessful by ball-milling, the synthesis was successfully achieved by aging treatment of the post-milled AB- MgH_2 mixture.¹² After heating, only each MH_n phase was observed for $\text{M} = \text{Mg, Ca}$. These results are in good agreement with previous reports.^{3,13} In AB- AlH_3 mixture, Al was observed after heating, which indicated AlH_3 desorbed hydrogen below 200 °C. The major crystalline phases observed in Fig. 2-1 were summarized in Table 2-1. The crystalline phases were arranged in order of the Pauling electronegativity of M, χ_p . As shown in Table 2-1, MBH_4 was formed for $\text{M} = \text{K, Na}$ ($\chi_p \leq 0.9$), MNH_2BH_3 was formed for $\text{M} = \text{Na, Li}$ ($0.9 \leq \chi_p \leq 1.0$) and no new compounds were formed for $\text{M} = \text{Ca, Mg, Al}$ ($1.0 \leq \chi_p$). Thus, it was experimentally revealed that χ_p is an important factor to predict the crystalline phases of AB- MH_n mixtures.

Table 2-1 Major crystalline phases of AB-MH_n mixtures classified by the Pauling electronegativity of M.

MH	KH	NaH	LiH	CaH ₂	MgH ₂	AlH ₃
Pauling electronegativity χ_p of M	0.82	0.93	0.98	1.00	1.31	1.61
Crystalline phases after milling	KBH ₄ , KH	NaNH ₂ BH ₃	LiNH ₂ BH ₃ • NH ₃ BH ₃	NH ₃ BH ₃ , CaH ₂	NH ₃ BH ₃ , MgH ₂	NH ₃ BH ₃ , AlH ₃
Crystalline phases after heating (200 °C)	KBH ₄ , KH	NaBH ₄	LiH	CaH ₂	MgH ₂	Al

2.3.2 H₂ desorption temperature

Fig. 2-2 shows the MS profiles of milled AB and AB-MH_n mixtures. The results of AB-KH mixture were not plotted because it didn't desorb any gases during heating below 200 °C. Fig. 2-3 shows the H₂ desorption peak temperatures of AB-MH_n mixtures below 200 °C. The temperatures of the 1st and 2nd H₂ desorption peaks in mass spectra are plotted in Fig.2-3(a) and (b), respectively. In case of AB-NaH and AB-LiH mixtures, the strongest two peaks were selected. The dashed line shows the temperature of H₂ desorption peak from milled AB. Though it is difficult to compare the whole results of temperatures because crystalline phases are different from those for M = Na, Li (MNH₂BH₃) and those for M = Ca, Mg, Al (no new compounds), the correlation between desorption temperature and χ_p was observed for each system as shown in Fig. 2-3. In case of M = Na, Li, H₂ desorption from MNH₂BH₃ was observed. According to the first-principles calculations, the thermodynamic stability of MNH₂BH₃ increases with decreasing χ_p .¹⁴ This result is consistent with the experimental results. In case of M = Ca, Mg, Al, MH_n and AB were observed from the XRD profiles after milling. After heating, only MH_n was observed. The H₂ desorption from AB-MH_n mixture would be promoted by the Coulombic attraction between the H^{δ-} in MH_n and H^{δ+} in the NH₃ group of AB. This interaction would affect the intramolecular N-H, B-H and B-N chemical bonds and intermolecular dihydrogen bond. In case of AB-MgH₂ mixture, MgH₂ additive exerted considerable influence on the chemical bonding state of AB.³ The similar influence was also reported in case of AB-AlH₃ mixture.¹⁵

Fig. 2-4 shows the DTA profiles of AB and AB-MH_n (M = Ca, Mg, Al) mixtures. AB showed an endothermic reaction around 103 °C, which corresponds to the melting of AB. After the melting, exothermic H₂ desorption reaction around 108 °C occurred. On the other hand, AB-MH_n (M = Ca, Mg, Al) mixtures showed no endothermic reactions, which suggests AB didn't melt in AB-MH_n mixtures. Only exothermic reactions were observed. These exothermic peaks correspond to the H₂ desorption peaks from MS profiles. Because of the Coulombic attraction between MH_n and AB, H₂ desorption

from AB would occur before the melting of AB occurs.

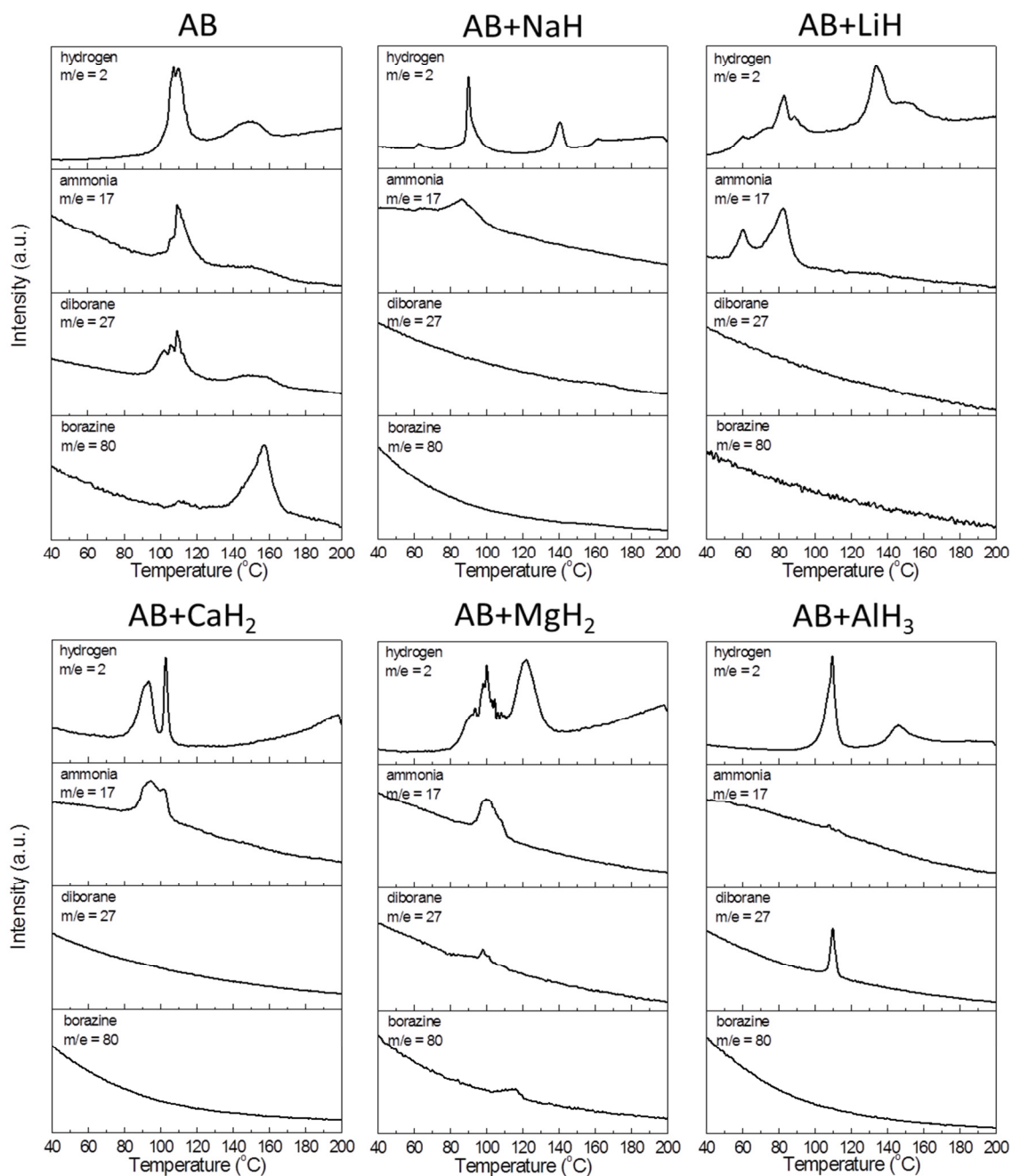


Fig. 2-2 MS profiles of milled AB and AB-MH_n mixtures below 200 °C. The heating rate was 2 °C min⁻¹.

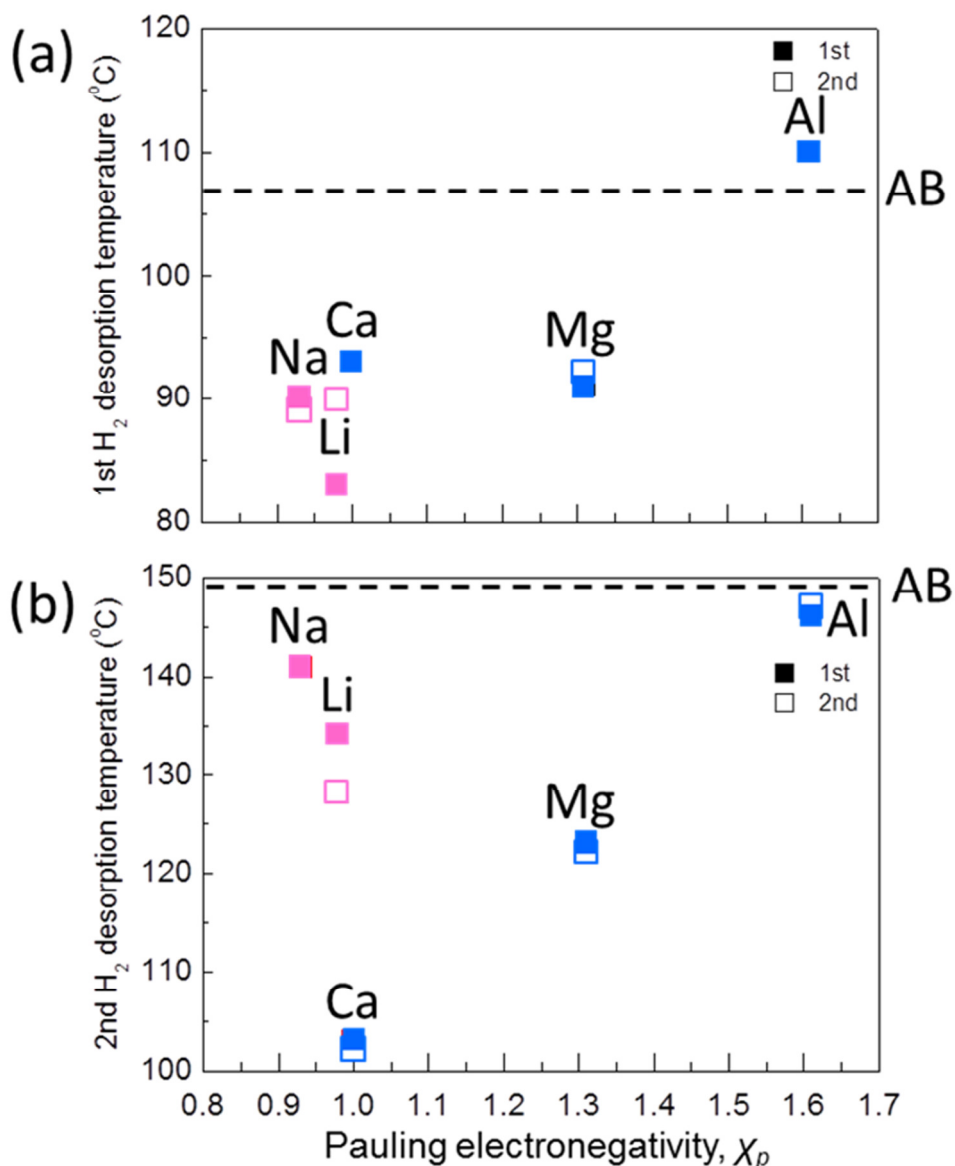


Fig. 2-3 H₂ desorption temperatures of AB-MH_n (M = Na, Li, Ca, Mg, Al) mixtures classified by the Pauling electronegativity of M; (a) 1st peak temperatures and (b) 2nd peak temperatures. Pink square shows MNH₂BH₃ and blue square shows MH_n and AB phases. The measurements were conducted twice. The filled square symbols show the results of 1st measurement and the white square symbols show those of the 2nd measurement. The heating rate was 2 °C min⁻¹.

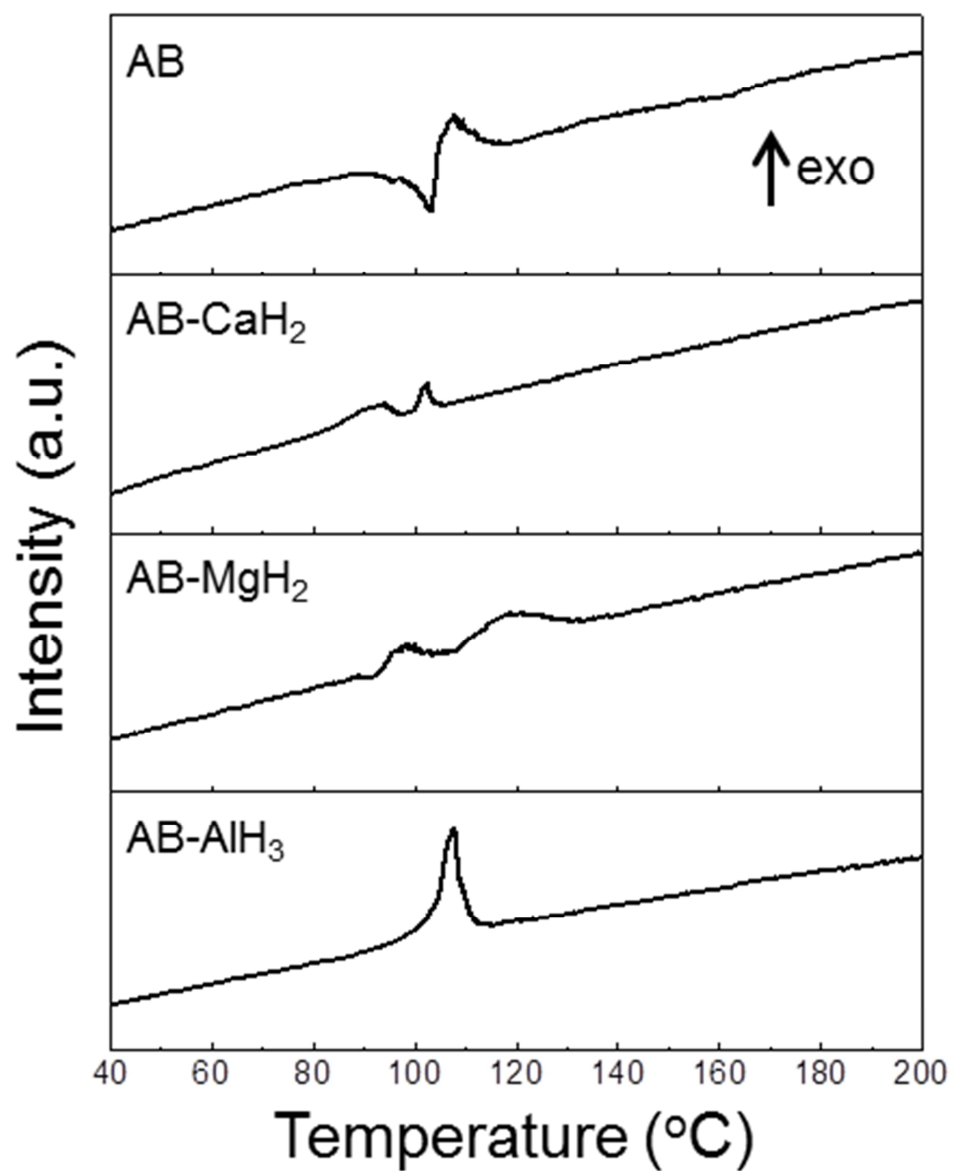


Fig. 2-4 DTA profiles of milled AB and AB-MH_n (M = Ca, Mg, Al) mixtures below 200 °C. The heating rate was 2 °C min⁻¹.

2.3.3 Amounts of by-product gases

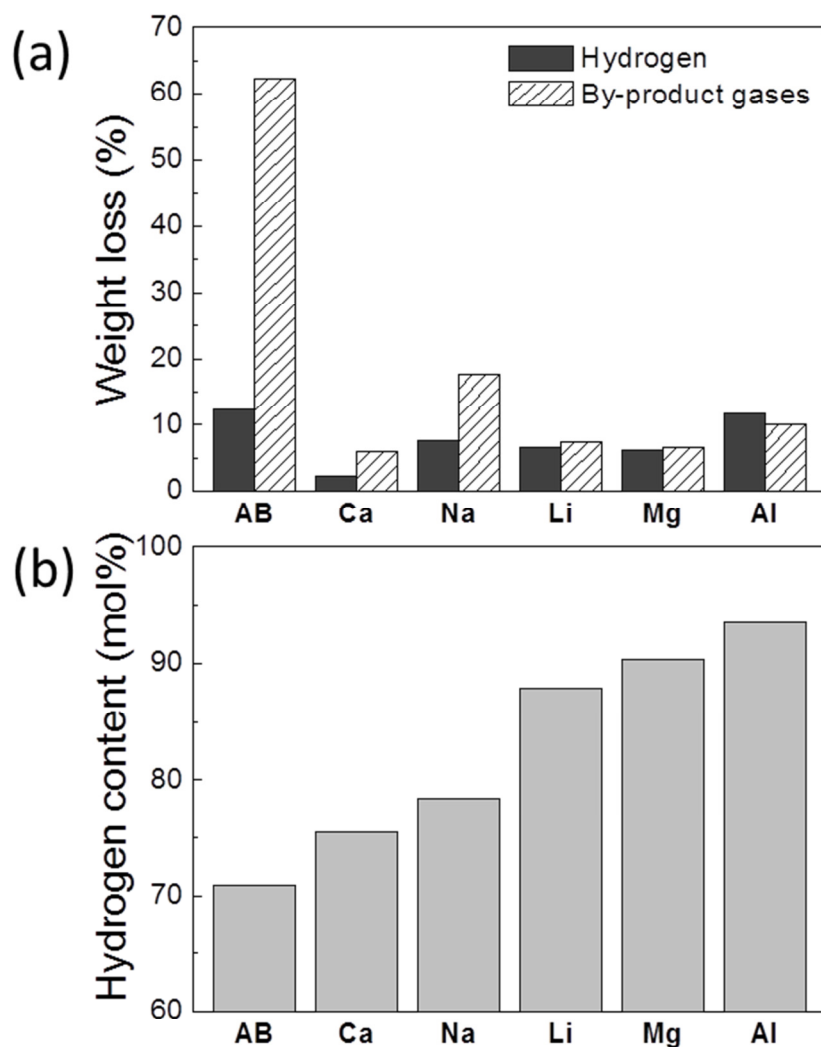


Fig. 2-5 (a) Weight losses of hydrogen and by-product gases and (b) hydrogen contents of AB-MH_n mixtures below 200 °C. The heating rate was 2 °C min⁻¹.

The amounts of hydrogen and by-product gases from AB-MH_n mixtures were estimated by using TG-MS results. Fig. 2-5(a) shows the 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_n mixtures showed by-product gas emission of 6-18 %, indicating that the by-product gas emissions were significantly decreased. AB-AlH₃ mixture showed the largest H₂ amount

among all the mixtures. AlH_3 is a typical chemical hydride with a gravimetric hydrogen density of 10.1 mass% and it desorbs H_2 around 100-200 °C.¹⁶ Therefore, H_2 desorption from both AB and AlH_3 would result in a large amount of desorbed H_2 from AB- AlH_3 mixture. Fig. 2-5(b) shows the hydrogen contents of AB- MH_n mixtures. The content for $\text{M} = \text{Li}, \text{Mg}, \text{Al}$ was about 90 %, whereas the content for $\text{M} = \text{Na}, \text{Ca}$ was only less than 80 %. AB- AlH_3 mixture showed the largest H_2 content among all the mixtures.

The composition of by-product gases was further estimated. Fig. 2-6 shows the amounts of by-product gases of AB- MH_n mixtures. NH_3 , B_2H_6 and $\text{B}_3\text{H}_6\text{N}_3$ were analyzed by mass spectrometry. The dashed line shows the amount of milled AB. As shown in Fig. 2-6(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. 2-6(b). AB- MH_n ($\text{M} = \text{Na}, \text{Li}, \text{Ca}$ ($\chi_p \leq 1.0$)) mixtures completely suppressed B_2H_6 . Fig. 2-6(c) shows that only AB- MgH_2 mixture desorbed $\text{B}_3\text{H}_6\text{N}_3$. Comparing the results of Fig. 2-6, it was found that the low hydrogen content for $\text{M} = \text{Na}, \text{Ca}$ in Fig. 2-5(b) was ascribed to a large amount of NH_3 emission. The result for $\text{M} = \text{Na}$ is in good agreement with the previous report.⁷ The $\text{B}_3\text{H}_6\text{N}_3$ emission from AB- MgH_2 mixture could be ascribed to the reaction between NH_3 and B_2H_6 . $\text{B}_3\text{H}_6\text{N}_3$ can be generated by the reaction between NH_3 and B_2H_6 with a molar ratio of 2 : 1.¹⁷ Only AB- MgH_2 system desorbed both NH_3 and B_2H_6 . In the other mixtures, emission of either NH_3 or B_2H_6 was suppressed, which would result in the suppression of $\text{B}_3\text{H}_6\text{N}_3$ emission. As a result, χ_p is an important factor to decrease the H_2 desorption temperatures and the amount of by-product gas emissions.

The amounts of hydrogen below 200 °C *versus* H_2 desorption temperatures is plotted in Fig. 2-7. AB- CaH_2 system showed the lowest H_2 desorption temperature and AB- AlH_3 system showed the largest amount of hydrogen among all the systems. However, there were no materials fulfilling large amounts of hydrogen desorbed at low temperatures. In order to accomplish these requirements, other systems should be explored.

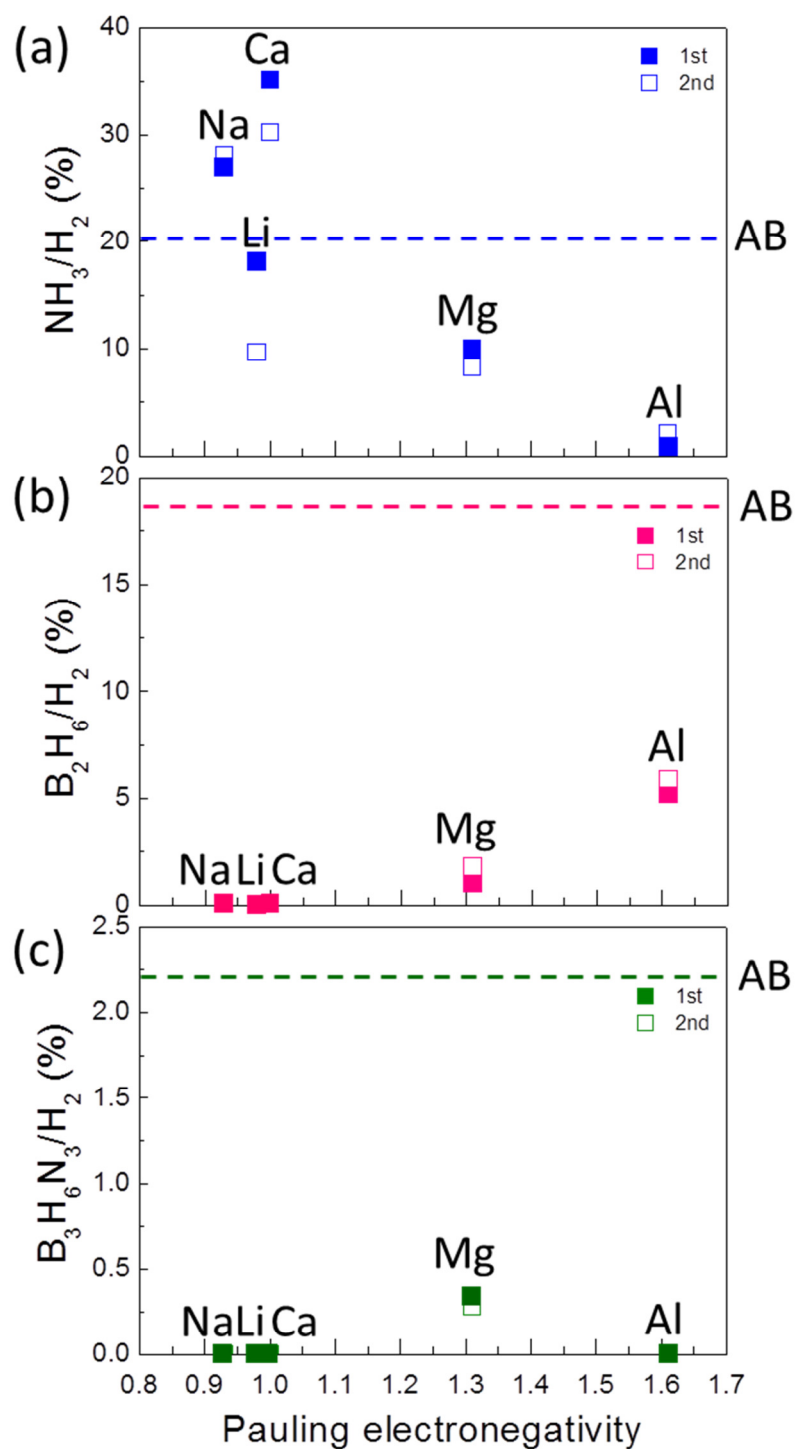


Fig. 2-6 The amounts of by-product gases desorbed from AB-MH_n mixtures classified by the Pauling electronegativity of M; (a) ammonia (NH₃), (b) diborane (B₂H₆) and (c) borazine (B₃H₆N₃). The heating rate was 2 °C min⁻¹. The filled squares show the results of 1st measurement and the white square shows the results of 2nd measurement.

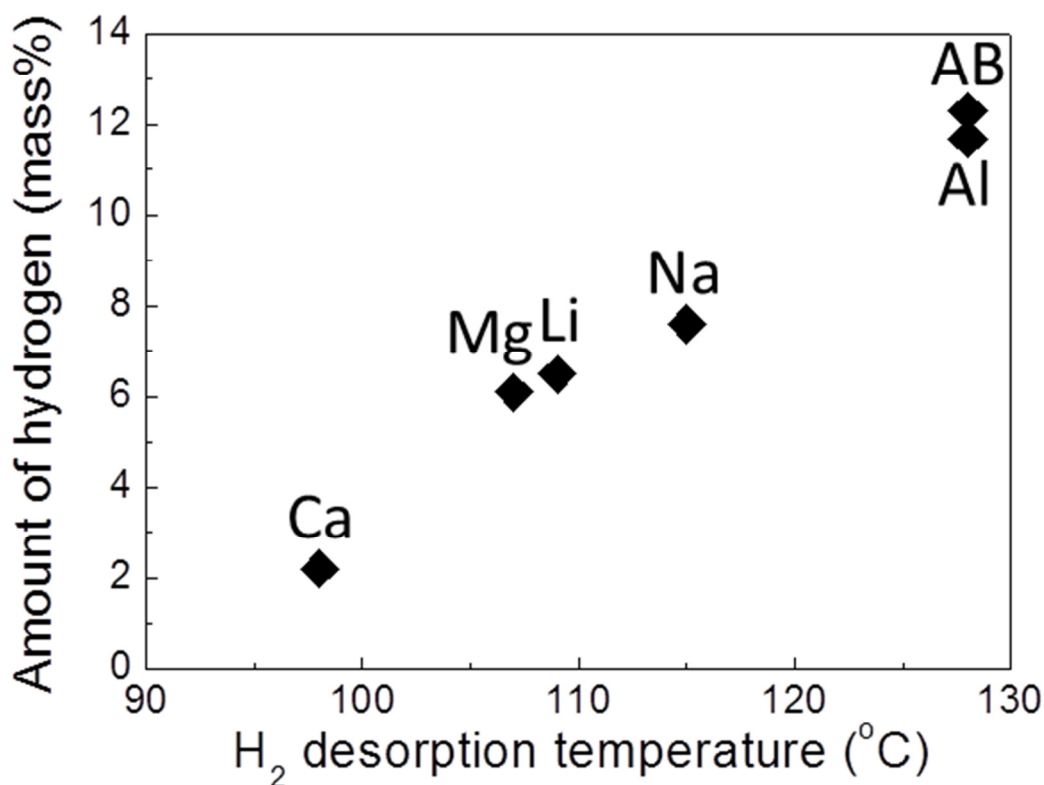


Fig. 2-7 The amounts of hydrogen desorbed from AB-MH_n mixtures below 200 °C versus H₂ desorption temperatures. The average temperatures between 1st and 2nd temperatures were plotted. The heating rate was 2 °C min⁻¹.

2.3.4 Discussion about the suppression of NH₃ and B₂H₆

As shown in Fig. 2-6, NH₃ emission was almost suppressed in AB-AlH₃ mixture and B₂H₆ emission was suppressed in AB-NaH, LiH, CaH₂ mixtures. The mechanism of the suppression is discussed in this section. In chapter 1, Diammoniate of diborane (DADB), [(NH₃)₂BH₂]⁺[BH₄]⁻, is introduced as an intermediate phase of AB before H₂ desorption occurs. This DADB would be a key phase for considering by-product gas emissions.

First, NH₃ suppression mechanism is discussed. The source of NH₃ emission would be DADB. If NH₃ reacts with MH_n, NH₃ emission is suppressed. Fig. 2-8 shows TEM

bright field image of AB-AlH₃ mixtures after heating to 200 °C. EDS results (Table 2-2) showed that nitrogen was detected in the place aluminum was detected. This suggested that nitrogen was trapped to aluminum in the solid state. Fig 2-9 shows the XRD profiles of AB-AlH₃ mixture after heating to 800 °C. AlN, AlB₂ and BN phases were

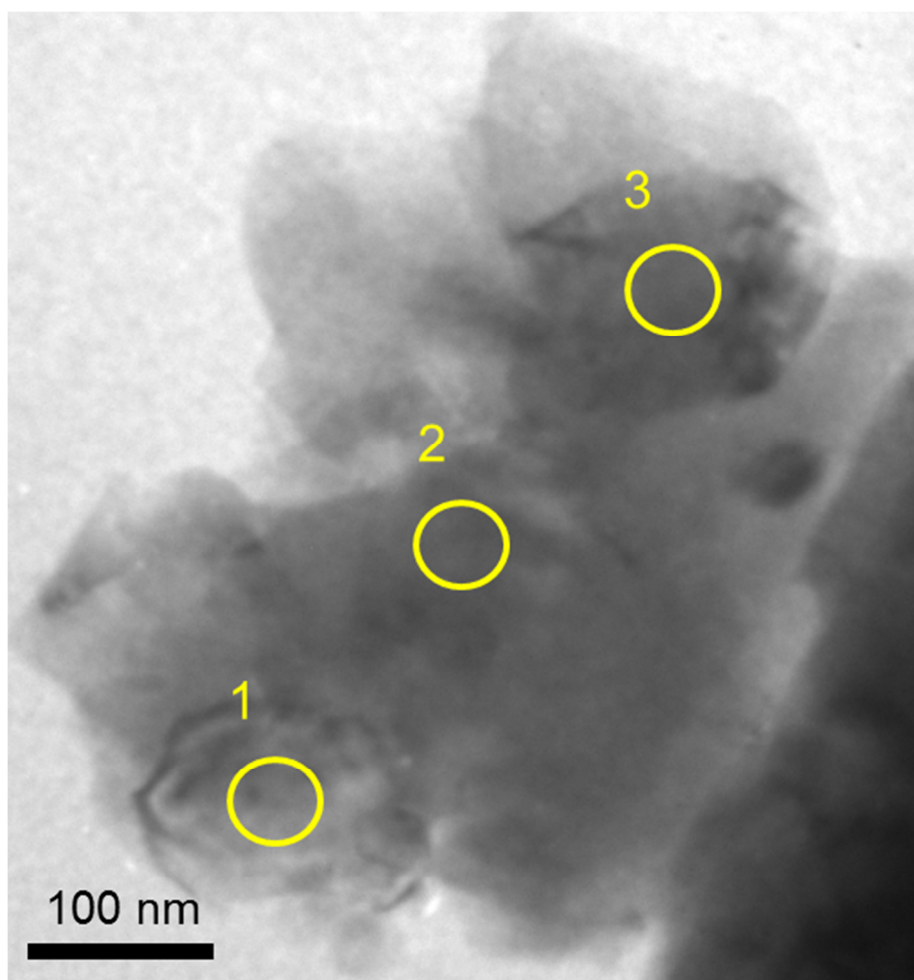


Fig. 2-8 TEM bright field image of AB-AlH₃ mixture after heating to 200 °C. EDS results are shown in Table 2-2.

Table 2-2 EDS results for AB-AlH₃ mixture after heating to 200 °C (Fig. 2-8).

	B	N	Al	O	
1	0	37	18	45	
2	0	35	17	48	
3	0	30	20	50	(at%)

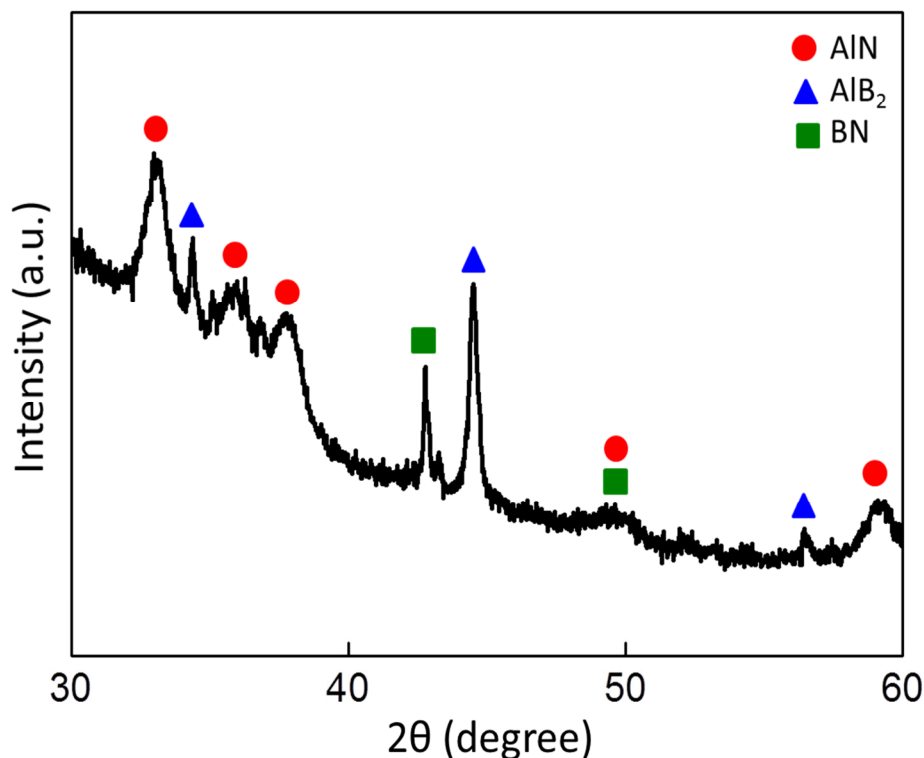


Fig. 2-9 XRD profile of AB-AlH₃ mixture after heating to 800 °C.

observed. Recent study showed that the Coulombic attraction between the $H^{\delta-}$ in AlH₃ and the $H^{\delta+}$ in the NH₃ group of AB caused the mutual dehydrogenation enhancement in AB-AlH₃ mixture.¹⁵ In this way, nitrogen was trapped in not only boron but also aluminum to form BN and AlN, which resulted in the NH₃ suppression. Furthermore, the study about ammonia absorption properties of metal halides and borohydrides indicated that the material with higher electronegativity of the cation showed lower plateau pressure on the ammonia absorption.¹⁸ The similar trend would exist in case of MH_n. The MH_n with high χ_p would absorb NH₃ immediately after it is desorbed.

Secondly, B₂H₆ suppression mechanism is discussed. The source of B₂H₆ emission would be also DADB. Therefore, if the [BH₄]⁻ of DADB reacts with Mⁿ⁺ of MH_n, B₂H₆ emission is suppressed. The trend in the amount of B₂H₆ was similar to the thermal stability of metal borohydride (M(BH₄)_n) system. The thermal stability of M(BH₄)_n can be described using χ_p and the equation means that the stability increases as χ_p

decreases.¹⁹ As shown in Table 2-1, KBH₄ and NaBH₄ were observed after ball-milling and after heating, respectively. Though M(BH₄)_n was not observed by XRD for M = Li, Ca, amorphous M(BH₄)_n would be formed. In this way, the suppression of B₂H₆ emission seemed to be correlated with the formation of M(BH₄)_n. M with low χ_p easily reacts with [BH₄]⁻ to form solid state M(BH₄)_n during heating, which would result in the suppression.

Fig. 2-10 summarizes the proposed reaction scheme between MH_n and DADB. When χ_p is low value, Mⁿ⁺ of MH_n and [BH₄]⁻ of DADB easily reacts to form M(BH₄)_n, which results in the B₂H₆ suppression. On the other hand, [(NH₃)₂BH₂]⁺ of DADB and H⁻ of MH_n reacts to form H₂ gas. At that time, NH₃ is desorbed. However, remaining MH_n immediately reacts with NH₃, which results in the NH₃ suppression. Thus, the key issue for NH₃ suppression is NH₃ absorption properties of MH_n. The plateau pressure on the ammonia absorption of MH_n would be correlated with χ_p . The previous reports also showed that MH_n such as LiH, NaH and KH can absorb NH₃.⁵ In case of B₂H₆ suppression, the key issue is the formation of stable M(BH₄)_n phase. Thermal stability of M(BH₄)_n is correlated with χ_p . Even though M(BH₄)_n phase is formed, unstable M(BH₄)_n like Al(BH₄)₃ desorbs B₂H₆.²⁰

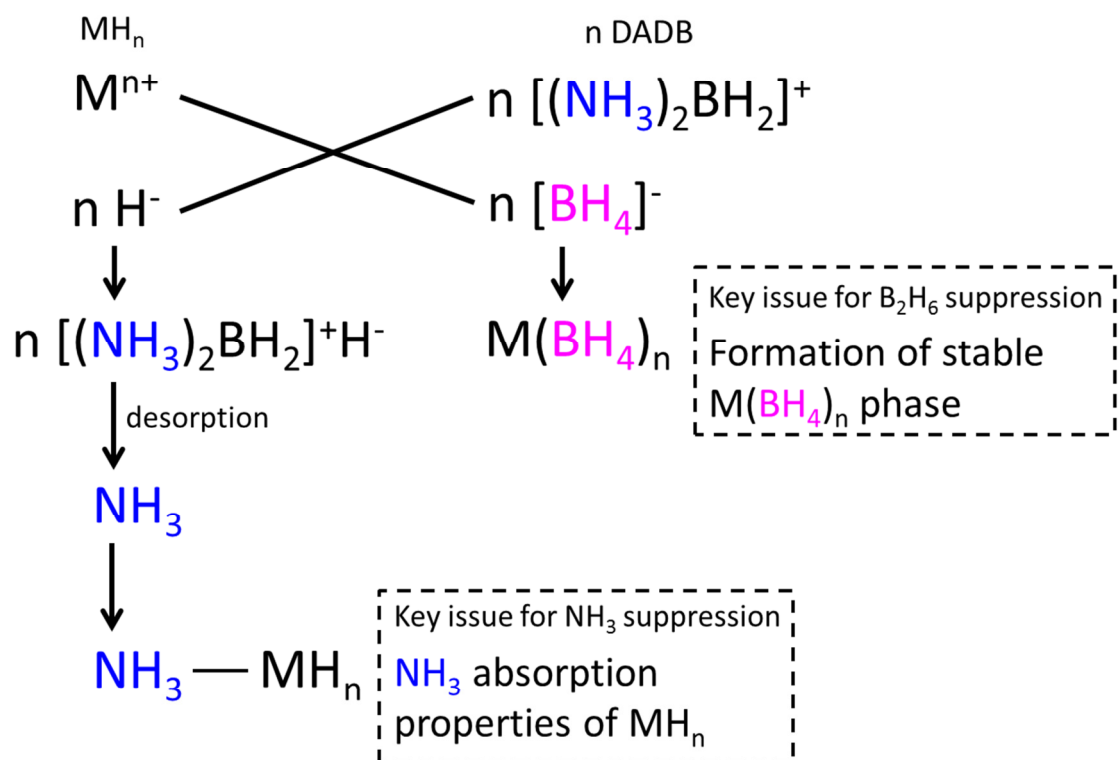


Fig. 2-10 The proposed reaction scheme between MH_n and DADB.

2.4 Conclusions

In this chapter, the crystalline phases and H₂ desorption properties of AB-MH_n mixtures were investigated. MBH₄ was formed for M = K, Na ($\chi_p \leq 0.9$), MNH₂BH₃ 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 correlation between H₂ desorption temperatures and χ_p was observed. Coulombic attraction between H ^{δ^-} of MH_n and H ^{δ^+} of AB would result in the temperature decrease. The amount of NH₃ has a tendency to be low as χ_p becomes high value. AB-AlH₃ mixture almost suppressed the NH₃ emission. On the other hand, the amount of B₂H₆ has a tendency to be low as χ_p becomes low value. AB-MH_n (M = Na, Li, Ca ($\chi_p \leq 1.0$)) mixtures suppressed the B₂H₆ emission. From these results, it was revealed that the Pauling electronegativity of M, χ_p , is an important factor to predict the phases of mixtures, H₂ desorption temperatures and the amount of by-product gas emissions (NH₃ and B₂H₆). B₃H₆N₃ emission was observed only for M = Mg. The emission could be attributed to the reaction between the desorbed NH₃ and B₂H₆. The key issues for NH₃ and B₂H₆ suppressions are the NH₃ absorption properties of MH_n and the formation of stable M(BH₄)_n phase, respectively. As χ_p becomes high value, MH_n would easily absorb NH₃. As χ_p becomes low value, Mⁿ⁺ of MH_n easily react to [BH₄]⁻ to form solid state M(BH₄)_n. AB-AlH₃ mixture would be a promising material because it showed the largest H₂ amount and content among all the investigated mixtures.

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3. Hydrogen desorption processes of $\text{NH}_3\text{BH}_3\text{-MAlH}_4$ (M = Na, Li) systems

3.1 Background and purpose

In chapter 2, hydrogen desorption properties of AB-MH_n mixtures were investigated. The emissions of NH₃ and B₂H₆ were suppressed by combining with AlH₃ and NaH (LiH), respectively. From this result, it is expected that MAlH₄ (M = Na, Li) additives may suppress all the by-product gases from AB because MAlH₄ (M = Na, Li) is the compound consisting of AlH₃ and NaH (LiH). In this chapter, AB-MAlH₄ (M = Na, Li) mixtures were synthesized by hand-mixing and ball-milling methods and their hydrogen desorption processes were investigated in detail.

3.2 Experimental procedures

The starting materials NH₃BH₃, NaAlH₄, LiAlH₄ (purity 97 %, 90 %, 95 %, respectively) were purchased from Sigma Aldrich Co. Ltd. These materials were used as-received. Hand-mixed mixtures were prepared by mixing AB and MAlH₄ in an agate mortar in an Ar-purified glove box for 90-120 seconds. Ball-milling was performed using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls

and 300 mg samples (ball : powder ratio = 70 : 1, by mass). The rotation speed was 300 rpm. The H₂ desorption properties were examined by thermal desorption mass spectrometry (TDMS, ULVAC, BGM-102) with thermogravimetry and differential thermal analysis (TG-DTA, Bruker, 2000SA). The heating rate was 5 °C min⁻¹ and the helium gas flow rate was 300 mL min⁻¹. The amounts of hydrogen and by-product gases were defined by integrating the peaks of mass spectra. The value of integral for by-product gases was normalized by that for hydrogen. The mass loss of each gas was estimated by using these integral values and the total mass loss obtained from TG results. Powder X-ray diffraction (XRD, PANalytical, X'Pert Pro with Cu K α radiation) were performed to observe crystalline phases of mixtures. Solid-state ¹¹B and ²⁷Al magic angle spinning - nuclear magnetic resonance (MAS-NMR) spectra were recorded on a JNM-ECA600 spectrometer (JEOL) at a magnetic field of 14.1 T with the ¹¹B resonant frequency of 192.6 MHz. All the samples were spun at 15 kHz, using 4 mm ZrO₂ rotors filled in argon atmosphere. Chemical shifts were referenced to saturated H₃BO₃ aqueous solution at 19.49 ppm for ¹¹B and AlCl₃ aqueous solution at -0.10 ppm for ²⁷Al. Single-pulse excitations of 2.0-3.0 μ s and relaxation delays of 2.0-11.0 s for ¹¹B and 1.5-10.0 s for ²⁷Al were employed. Fourier transform infrared spectrometry (FTIR, Spectrum One, Perkin-Elmer) measurements were performed using a diffuse reflection cell to investigate chemical bonds in the mixtures. All the samples were diluted with KBr to a mass ratio of 5 : 95 (sample : KBr).

3.3 Results and discussions

3.3.1 Starting materials

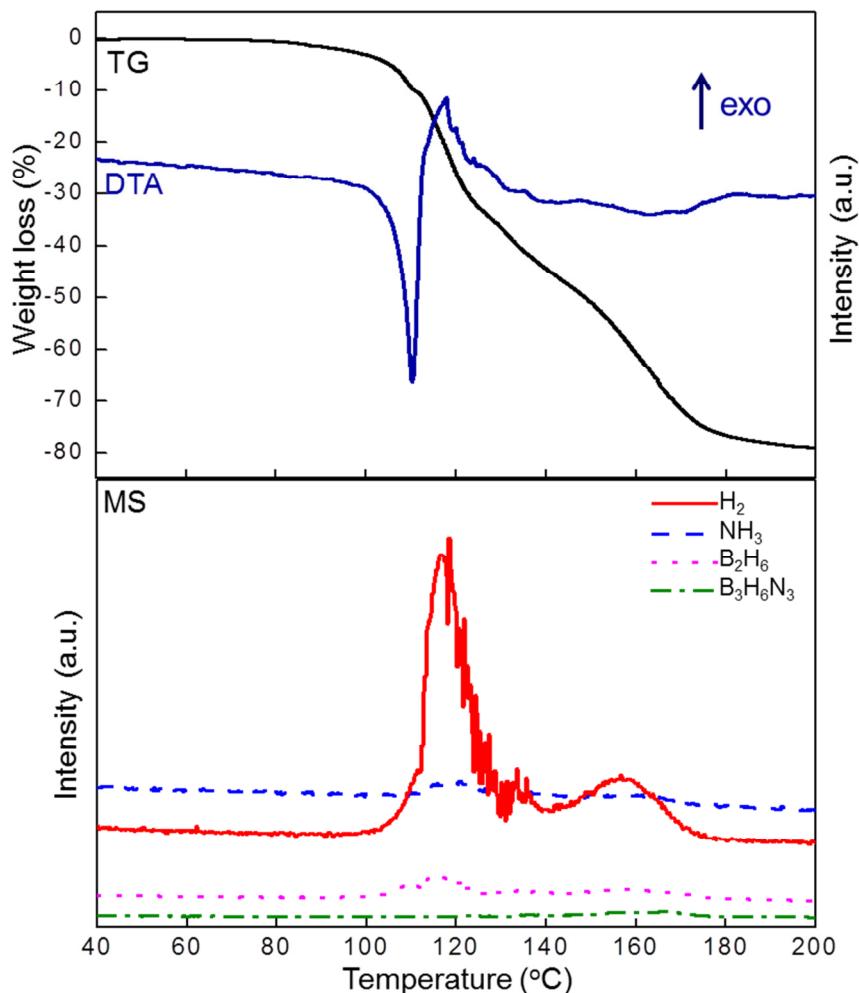


Fig. 3-1 TG-DTA-MS profiles of as-received AB. The heating rate was 5 °C min⁻¹.

Before synthesizing the mixtures, H₂ desorption properties of starting materials (AB, NaAlH₄ and LiAlH₄) were analyzed. Fig. 3-1 shows TG-DTA-MS profiles of as-received AB. As shown in the DTA profile, melting of AB at 110 °C (endothermic reaction) followed by the 1st step exothermic H₂ desorption around 120 °C occurred. Then, the 2nd step H₂ desorption occurred around 160 °C. From the TG profile, the total mass loss was about 78 mass%, indicating the emission of by-product gases. From the MS profile, NH₃, B₂H₆ and B₃H₆N₃ emissions were observed. These results were

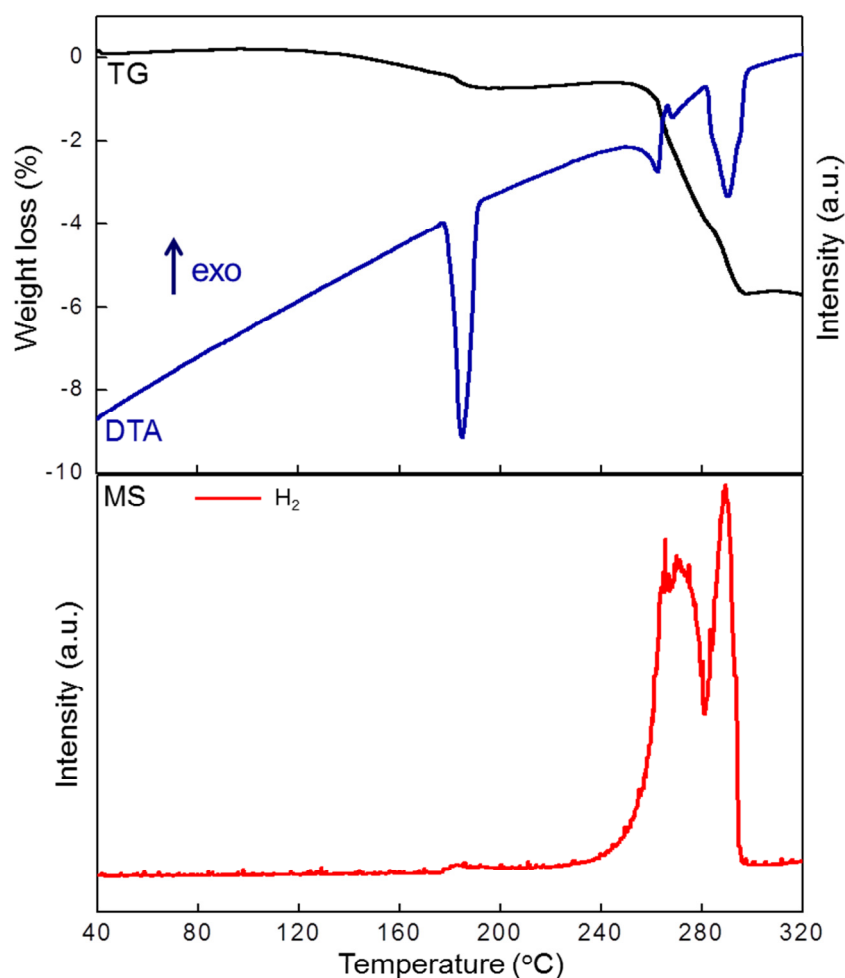
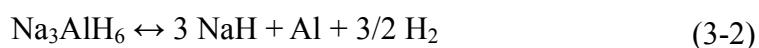
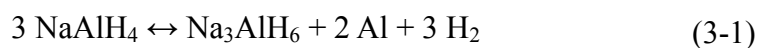


Fig. 3-2 TG-DTA-MS profiles of as-received NaAlH₄. The heating rate was 5 °C min⁻¹.

consistent with the previous report.¹

Fig. 3-2 shows TG-DTA-MS profiles of as-received NaAlH₄. An endothermic peak at 185 °C is ascribed to the melting of NaAlH₄. After the melting, two endothermic peaks (262 °C, 290 °C) were observed. These two peaks corresponds to the H₂ desorption reactions in MS profile. The H₂ desorption reactions are described as follows.



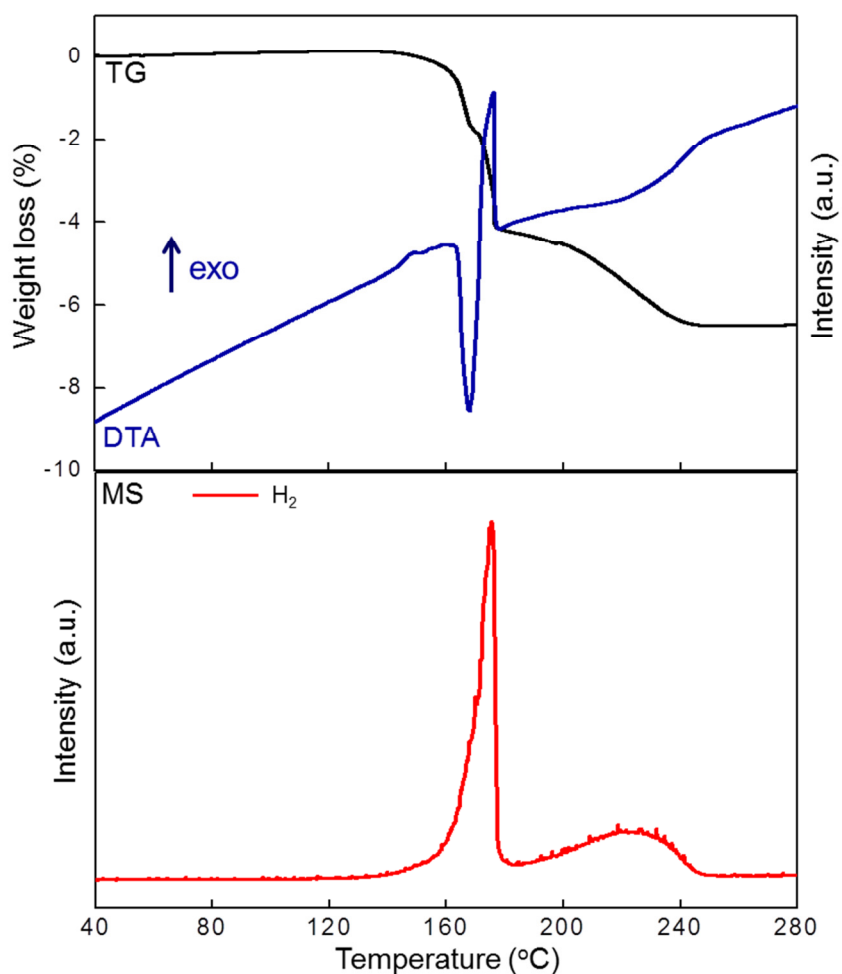
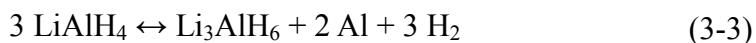


Fig. 3-3 TG-DTA-MS profiles of as-received LiAlH_4 . The heating rate was $5\text{ }^\circ\text{C min}^{-1}$.

The amount of H_2 from the TG profile was 5.9 mass%, similar with the theoretical H_2 loss of 5.6 mass%.

Fig. 3-3 shows TG-DTA-MS profiles of as-received LiAlH_4 . An endothermic peak at $168\text{ }^\circ\text{C}$ is ascribed to the melting of LiAlH_4 . After the melting, an exothermic H_2 desorption at $176\text{ }^\circ\text{C}$ occurs. Then, an endothermic H_2 desorption around $230\text{ }^\circ\text{C}$ occurs. The H_2 desorption reactions are described as follows.



The reactions are similar as NaAlH_4 . The amount of H_2 from the TG profile was 6.5 mass%, smaller than the theoretical H_2 loss of 8.0 mass%. The decomposition during the sample storage would result in the decrease of H_2 amount. The H_2 desorption temperature of LiAlH_4 was lower than that of NaAlH_4 , which is consistent with the previous report.² From the next section, AB- MAlH_4 mixtures ($\text{M} = \text{Na}, \text{Li}$) were synthesized and their H_2 desorption properties and processes were investigated.

3.3.2 Hand-mixed mixtures

Though hand-mixing was performed in a glovebox filled with Ar atmosphere, hand-mixing AB with MAlH_4 ($\text{M} = \text{Na}, \text{Li}$) over 120 seconds often caused the gas eruptions as shown in Fig. 3-4. To clarify what reaction happens in the eruption, the mixtures hand-mixed for 90 seconds (before gas eruption occurs) were investigated. Fig. 3-5 shows TG-DTA-MS profiles of the mixtures. Sharp exothermic peaks were



Fig. 3-4 Images of hand-mixing AB with LiAlH_4 in an argon glovebox; (a) in the beginning of the hand-mixing (before eruption), (b) After 120 seconds (gas eruption occurs.).

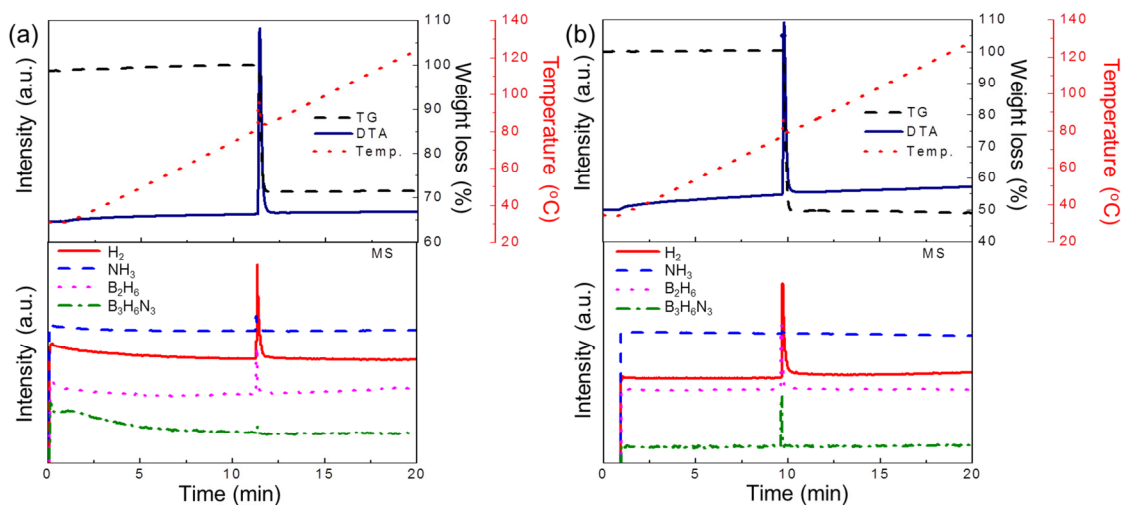


Fig. 3-5 TG-DTA-MS profiles of hand-mixed AB-MAIH₄ mixtures; (a) AB-NaAlH₄, (b) AB-LiAlH₄ mixture. The heating rate was 5 °C min⁻¹.

observed at 90 °C (AB-NaAlH₄) and 84 °C (AB-LiAlH₄) in DTA profiles. The mass losses of about 30 mass% (AB-NaAlH₄) and 50 mass% (AB-LiAlH₄) were also observed. From the mass spectra, H₂, NH₃, B₂H₆ and B₃H₆N₃ peaks were observed in both mixtures. Except this exothermic reaction, any reactions were not observed up to 260 °C. Fig. 3-6 shows the XRD profiles of hand-mixed mixtures before and after heating to 260 °C. Before heating, only starting materials, AB and MAIH₄ (M = Na, Li), were observed. However, after heating, NaBH₄ was observed in AB-NaAlH₄ mixture. The reaction observed in the hand-mixed mixture was quite similar to the solid state reaction between MAIH₄ (M = Na, Li) and NH₄Cl.³ By the ion-exchange reaction between two solid phases, MCl and [H₄Al·NH₄] is formed and soon [H₄Al·NH₄] decomposes to [HAlNH] and H₂, accompanied by a large exothermic heat.³ The previous study showed diammoniate of diborane (DADB), [(NH₃)₂BH₂]⁺[BH₄]⁻, an ionic isomer of AB, is formed during the induction period before H₂ desorption occurs.⁴ MAIH₄ was also confirmed to be an ionic compound, consisting of M⁺ cation and [AlH₄]⁻ anion.⁵ Considering the reaction between DADB and NaAlH₄, the ion-exchange reaction between [BH₄]⁻ anion of DADB and Na⁺ cation of NaAlH₄ would cause the formation of NaBH₄. On the one hand, the reaction between [(NH₃)₂BH₂]⁺ and [AlH₄]⁻

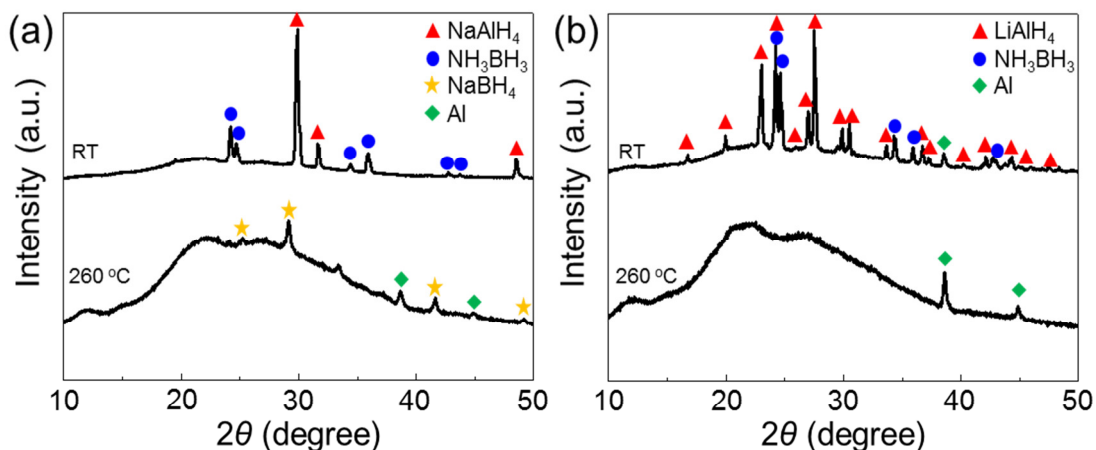


Fig. 3-6 XRD profiles of hand-mixed AB-MAlH₄ mixtures at RT an after heating to 260 °C; (a) AB-NaAlH₄, (b) AB-LiAlH₄ mixture.

would cause the formation of H₂ gas and amorphous Al-N-B-H phase. Thus, by-product gas emissions were not suppressed in the hand-mixed mixtures.

3.3.3 Ball-milled mixtures (Long milling time)

Fig. 3-7 shows XRD profiles of AB-NaAlH₄ mixtures milled under different atmospheres. Under Ar atmosphere, the reaction was similar as hand-mixed mixture.

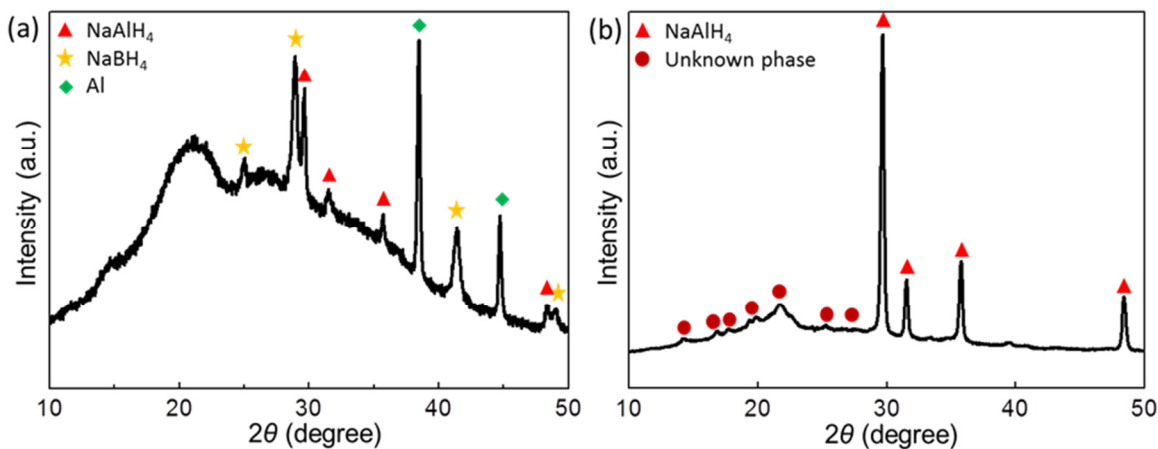


Fig. 3-7 XRD profiles of AB-NaAlH₄ mixtures ball-milled for 20 minutes under different atmosphere; (a) 0.1 MPa Ar atmosphere, (b) 0.1 MPa H₂ atmosphere.

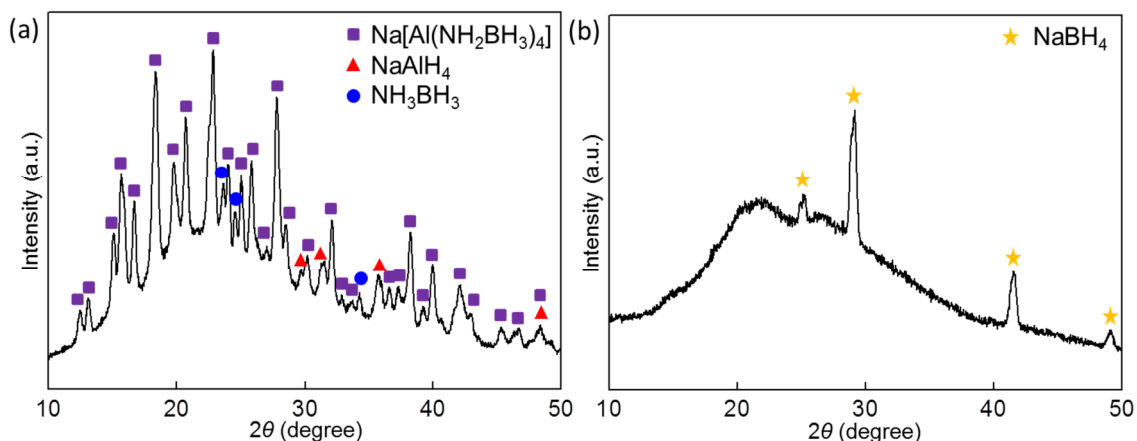


Fig. 3-8 XRD profiles of 4AB-NaAlH₄ mixtures ball-milled for 180 minutes under H₂ atmosphere; (a) after milling, (b) after heating to 260 °C.

NaBH₄ and Al phases were observed as shown in Fig. 3-7(a). Decomposition during ball-milling would occur. However, ball-milling was performed under H₂ atmosphere, the situation was changed. As shown in Fig. 3-7(b), unknown phases were observed. From this result, it was suggested that H₂ atmosphere is needed to form unknown phases.

To obtain a large amount of unknown phases, the molar ratio between AB and NaAlH₄ was changed. Fig. 3-8 shows the XRD profiles of 4AB-NaAlH₄ mixtures. After milling, most of starting materials (NaAlH₄ and AB) were disappeared. Instead of them, Na[Al(NH₂BH₃)₄] phase was observed. This phase was discovered by Dovgaliuk *et al* in 2015.⁶ Thus, the milling atmosphere is important in this system. Though the decomposition during ball-milling occurred under Ar atmosphere, the formation of intermediate phase of Na[Al(NH₂BH₃)₄] occurred under H₂ atmosphere. During ball-milling, the pressure increase due to the H₂ release was observed. Other by-product gas emissions were not observed during the milling procedure. Therefore, the formation reaction of Na[Al(NH₂BH₃)₄] can be described as follows.



Fig. 3-9 shows TG-DTA-MS profiles of 4AB-NaAlH₄ mixtures. One endothermic reaction at 120 °C and two exothermic reactions at 125 °C and 160 °C were observed in

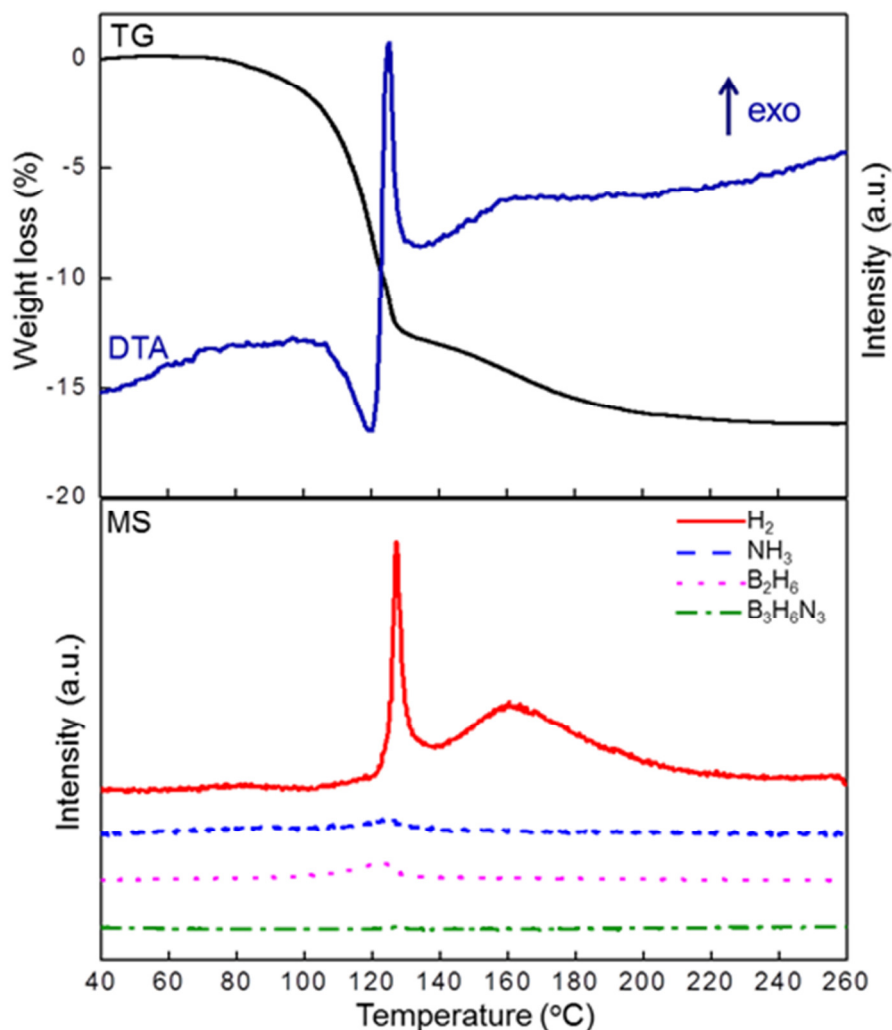


Fig. 3-9 TG-DTA-MS profiles of 4AB-NaAlH₄ mixtures ball-milled for 180 minutes under H₂ atmosphere. The heating rate was 5 °C min⁻¹.

DTA profiles. The endothermic reaction would be ascribed to the thermal decomposition of the mixture. During the reaction, a slight amount of NH₃ and B₂H₆ emission was observed from MS profile. The two exothermic reactions were ascribed to the H₂ desorption from Na[Al(NH₂BH₃)₄]. The mass loss of TG was about 16.7 mass% and the estimated value of H₂ was 8.3 mass%. As shown in Fig. 3-8(b), NaBH₄ was observed after heating to 260 °C. From the results of XRD and estimated amount of H₂, H₂ desorption reaction can be described as follows.



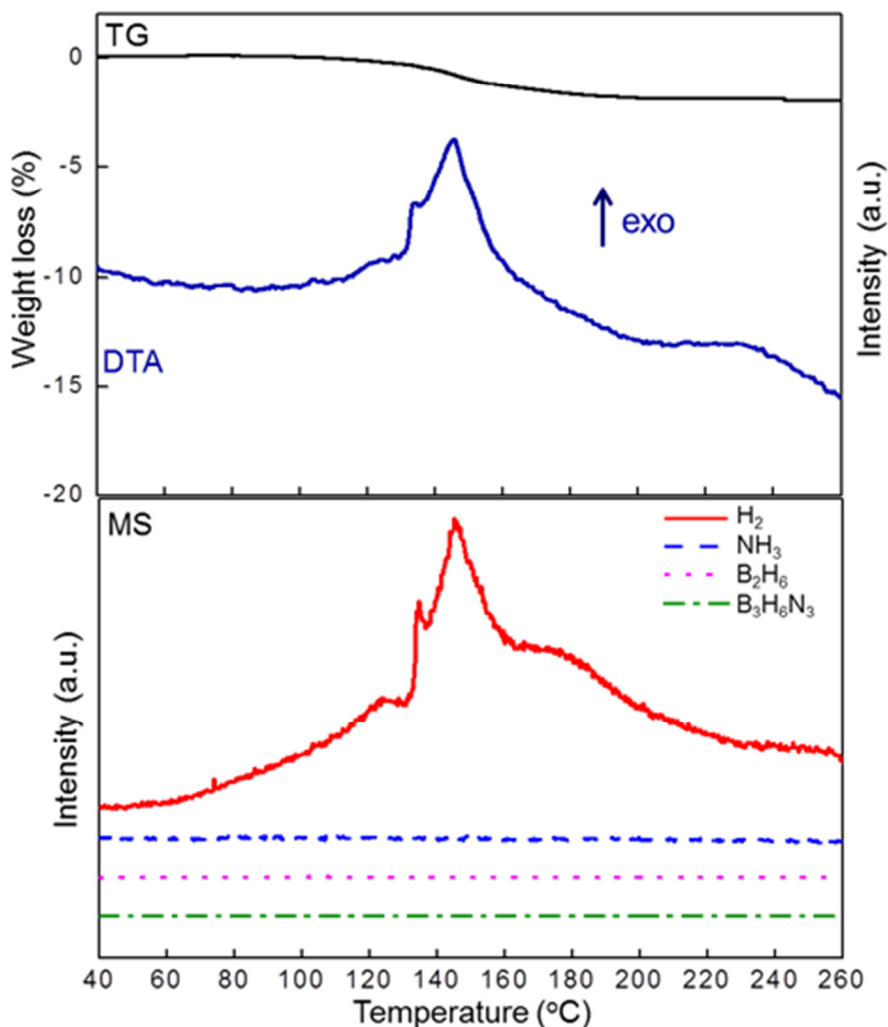


Fig. 3-10 TG-DTA-MS profiles of AB-NaAlH₄ mixtures ball-milled for 180 minutes under H₂ atmosphere. The heating rate was 5 °C min⁻¹.

The crystalline phase of AlN₄B₃H₂ was not reported, suggesting this phase exists as amorphous.

Though by-product gas emissions were not fully suppressed in Na[Al(NH₂BH₃)₄], AB-NaAlH₄ mixture with a molar ratio of 1 : 1 desorbed only H₂ as shown in Fig. 3-10. The amount of H₂ was about 2.0 mass%. Thus, NaAlH₄ additive is effective to suppress by-product gas emissions. However, a large amount of NaAlH₄ additive resulted in a small amount of desorbed H₂ in the system. Fig. 3-11 shows the XRD profiles of AB-NaAlH₄ mixtures. NaAlH₄ phase was observed after milling and NaBH₄ and Al

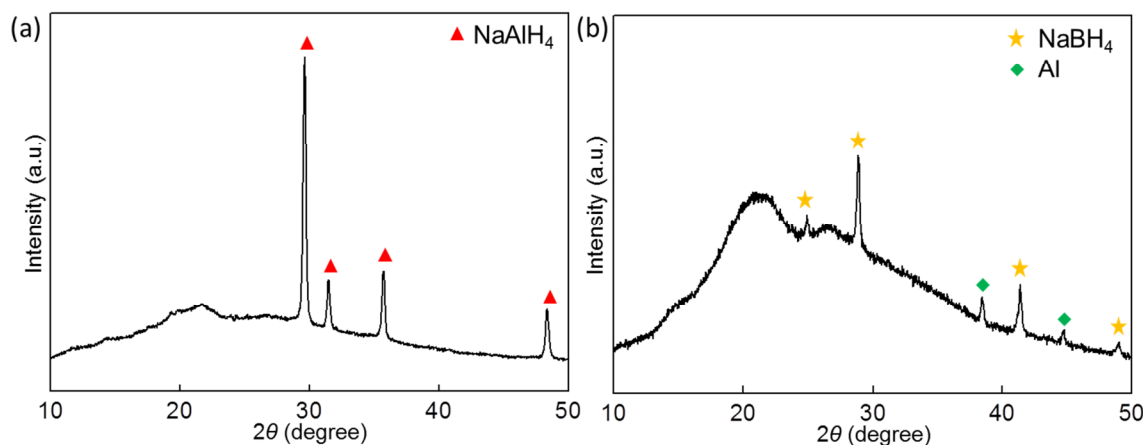


Fig. 3-11 XRD profiles of AB-NaAlH₄ mixtures ball-milled for 180 minutes under H₂ atmosphere; (a) after milling, (b) after heating to 260 °C.

phases were observed after heating. Al formation would be ascribed to the decomposition of remaining NaAlH₄.

To understand the reaction process in detail, ¹¹B and ²⁷Al MAS NMR spectra were obtained for 4AB-NaAlH₄ and AB-NaAlH₄ mixtures. Fig. 3-12 shows ¹¹B MAS NMR spectra of the mixtures and as-received AB. The peak position of as-received AB was -25.4 ppm. This peak is originated from a [NBH₃] environment from neat AB.⁷ The -24.8 and -24.9 ppm peaks were observed for AB-NaAlH₄ and 4AB-NaAlH₄ mixtures, respectively. The small chemical shift suggested the small difference in the chemical environment of the boron atom in NH₃BH₃ and Na[Al(NH₂BH₃)₄]. Fig. 3-13 shows the ²⁷Al NMR spectra of AB-NaAlH₄, 4AB-NaAlH₄ mixtures and as-received NaAlH₄. As-received NaAlH₄ showed two peaks at 94.0 ppm and 13.2 ppm. The 94.0 ppm peak is ascribed to NaAlH₄ phase.⁸ The small peak at 13.2 ppm is consistent with an octahedral coordinated aluminum oxide.⁹ The oxide would be formed during the transport the sample from the glovebox to the NMR apparatus. The 4AB-NaAlH₄ mixture showed two peaks at 110.0 ppm and 15.0 ppm. The peak at 15.0 ppm would be ascribed to the aluminum oxide similar as NaAlH₄ spectra. The peak at 110.0 ppm is similar to a [AlN₄] environment (115 ppm).¹⁰ Therefore, this peak would be attributed to Na[Al(NH₂BH₃)₄]. The substitution of H⁻ by [NH₂BH₃]⁻ induced substantial changes in

the electronic state of Al, which would result in a large chemical shift. In the AB-NaAlH₄ mixture, two peaks (109.1 ppm, 95.9 ppm) were observed. As shown in Fig. 3-11(a), NaAlH₄ was confirmed by XRD. Therefore, the peak at 95.9 ppm would be ascribed to NaAlH₄ phase. Though Na[Al(NH₂BH₃)₄] phase was not observed by XRD, the peak at 109.1 ppm suggested the formation of Na[Al(NH₂BH₃)₄]. This peak was broader than that observed in 4AB-NaAlH₄ mixture. This indicates Na[Al(NH₂BH₃)₄] is in amorphous state. Therefore, H₂ would be desorbed by the interaction between Na[Al(NH₂BH₃)₄] and NaAlH₄ in the AB-NaAlH₄ mixture.

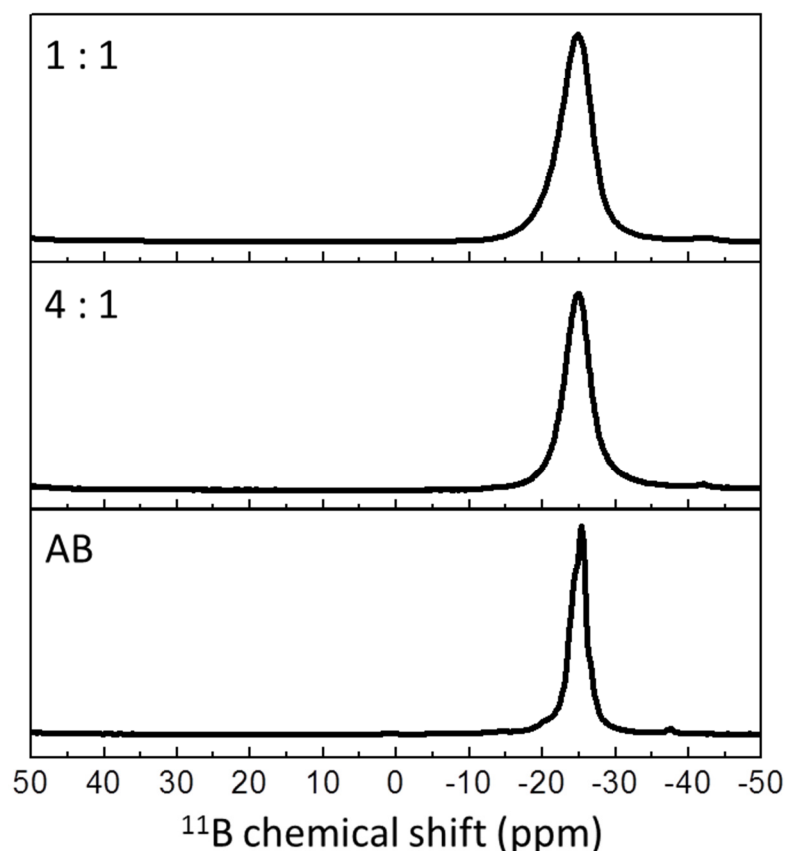


Fig. 3-12 ¹¹B MAS NMR spectra of AB-NaAlH₄, 4AB-NaAlH₄ mixtures after milling and as-received AB.

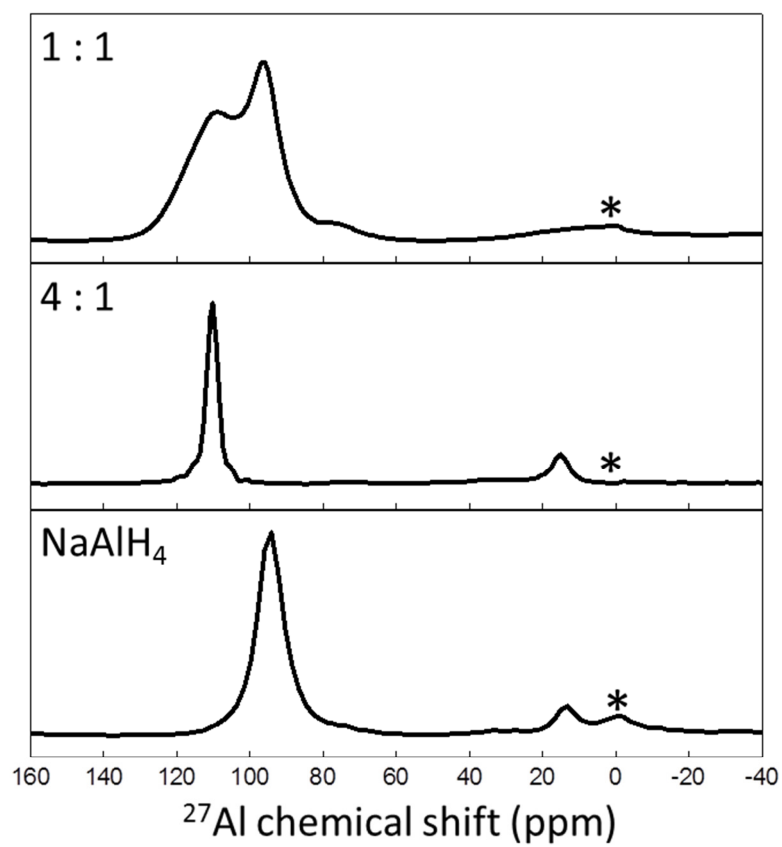


Fig. 3-13 ^{27}Al MAS NMR spectra of AB- NaAlH_4 , 4AB- NaAlH_4 mixtures after milling and as-received NaAlH_4 . Spinning sidebands are indicated by asterisks.

3.3.4 Ball-milled mixtures (Short milling time)

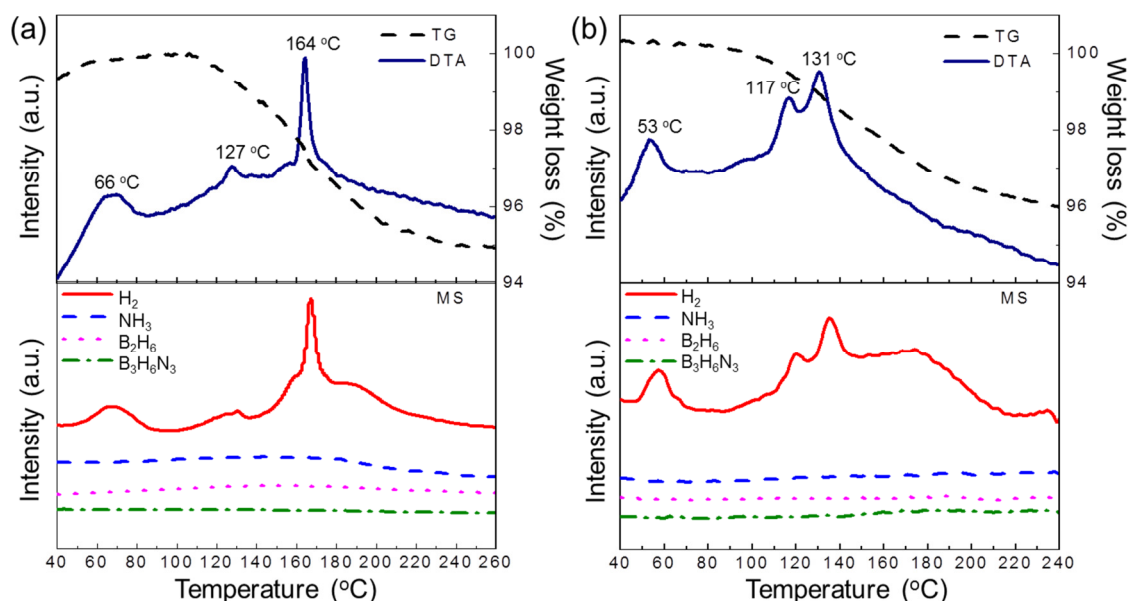


Fig. 3-14 TG-DTA-MS profiles of ball-milled AB-MAIH₄ (M = Na, Li) mixtures; (a) AB-NaAlH₄, (b) AB-LiAlH₄ mixture. The heating rate was 5 °C min⁻¹.

In the previous section, the ball-milling time was 180 min. In this section, the mixtures were ball-milled for short time and H₂ desorption properties were investigated. Fig. 3-14 shows TG-DTA-MS profiles of AB-MAIH₄ (M = Na, Li) mixtures ball-milled for 5 minutes. As shown in Fig. 3-14(a), exothermic peaks were observed at 66, 127 and 164 °C in DTA profile of AB-NaAlH₄ mixture. These peaks correspond to H₂ desorption peaks in MS profile. The emissions of NH₃, B₂H₆ and B₃H₆N₃ were not observed in MS profile, indicating the by-product gas emissions were effectively suppressed. The amount of desorbed H₂ was estimated at 5 mass% from TG profile. AB-LiAlH₄ mixture showed similar H₂ desorption properties as those of AB-NaAlH₄ mixture. As shown in Fig. 3-14(b), three exothermic peaks (53, 117 and 131 °C) were observed in DTA profile. The emissions of by-product gases were not observed in MS profile. The amount of desorbed H₂ was about 4 mass%. These results were quite different from the TG-DTA-MS results of AB (Fig. 3-1) or MAIH₄ (M = Na, Li) itself (Fig. 3-2, 3-3), suggesting the reactions between AB and MAIH₄ occurred during ball-milling and

heating. Theoretical hydrogen capacities of AB-NaAlH₄ and AB-LiAlH₄ systems are 11.9 mass% and 14.6 mass%, respectively. H₂ desorption during ball-milling and the formation of solid phase of MBH₄ during heating resulted in a reduction in the amount of desorbed H₂ (See below). Each exothermic peak of AB-LiAlH₄ mixture was lower than the corresponding peak of AB-NaAlH₄ mixture, arising from the lower thermal stability of LiAlH₄ than that of NaAlH₄ as shown in Fig. 3-2 and 3-3.

The pressure increase due to H₂ desorption was observed during ball-milling, which suggested M[Al(NH₂BH₃)₄] formed by the reaction between MAlH₄ (M = Na, Li) and AB. One of the driving forces for the reaction would be the affinity of H^{δ-} in MAlH₄ and H^{δ+} in NH₃ of AB. NH₃, B₂H₆ and B₃H₆N₃ desorption was not observed during ball-milling. Fig. 3-15 shows the XRD profiles of ball-milled AB-MAlH₄ (M = Na, Li)

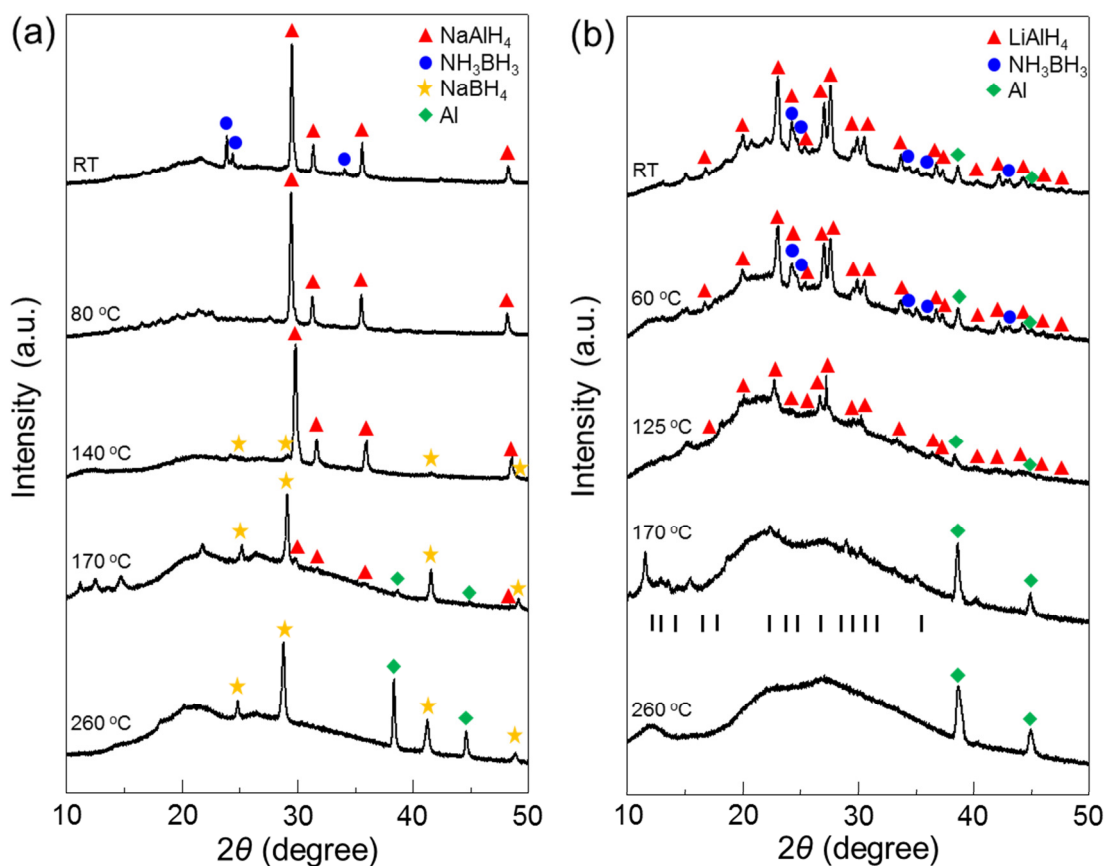


Fig. 3-15 XRD profiles of ball-milled AB-MAlH₄ mixtures after heating to each temperature; (a) AB-NaAlH₄, (b) AB-LiAlH₄ mixture.

mixtures after heating to each temperature. Broad diffraction peaks at around 20° and 27° in all profiles originate from the polyimide film and grease to prevent sample oxidation.

In AB-NaAlH₄ mixture, starting materials of AB and NaAlH₄ were observed at room temperature (RT). Besides, small unknown peaks appeared in the range of 10-30°. These peaks don't match with any diffraction patterns of decomposition products of starting materials or mono-metal amidoborane, suggesting the formation of Na[Al(NH₂BH₃)₄] during ball-milling. After heating to 80 °C, the peak intensities of unknown phases became stronger than those at RT. The reaction between AB and NaAlH₄ proceeded further to form Na[Al(NH₂BH₃)₄], resulting in the H₂ desorption at 66 °C as shown in Fig. 3-15(a). After heating to 140 °C, the unknown phases disappeared, indicating its decomposition. Also, NaBH₄ appeared at 140 °C. After heating to 170 °C, strong peak intensities of NaBH₄ were observed, while most of NaAlH₄ disappeared. Furthermore, a new set of peaks were observed in the range of 10-30°. This could be another mixed-metal (Na, Al) amidoborane formed by the reaction between Na₃AlH₆ and AB. After heating to 260 °C, this unknown phase decomposed and only NaBH₄ and Al phases were observed.

In case of AB-LiAlH₄ system, similar results were obtained as AB-NaAlH₄ system. At RT, unknown peaks were observed in the range of 10-25°. The unknown peaks could be Li[Al(NH₂BH₃)₄]. However, the crystal structure of this phase has not been determined yet. After heating to 170 °C, further new peaks were observed in the range of 10-40°, suggesting the formation of another mixed-metal (Li, Al) amidoborane between Li₃AlH₆ and AB. The peak positions of AB-Li₃AlH₆ mixtures reported by Xia *et al.* were also shown as reference in Fig. 3-15(b).¹¹ The positions of observed peaks were similar to the reference, suggesting the formation of mixed-metal (Li, Al) amidoborane. Though LiBH₄ phase was not observed in the XRD profiles of AB-LiAlH₄ mixture, the FTIR spectra (Fig. 3-17(b)) showed the strong B-H stretching. This suggested that the amorphous LiBH₄ formed during heating.

¹¹B MAS NMR spectra of AB and AB-NaAlH₄ mixtures are shown in Fig. 3-16. AB

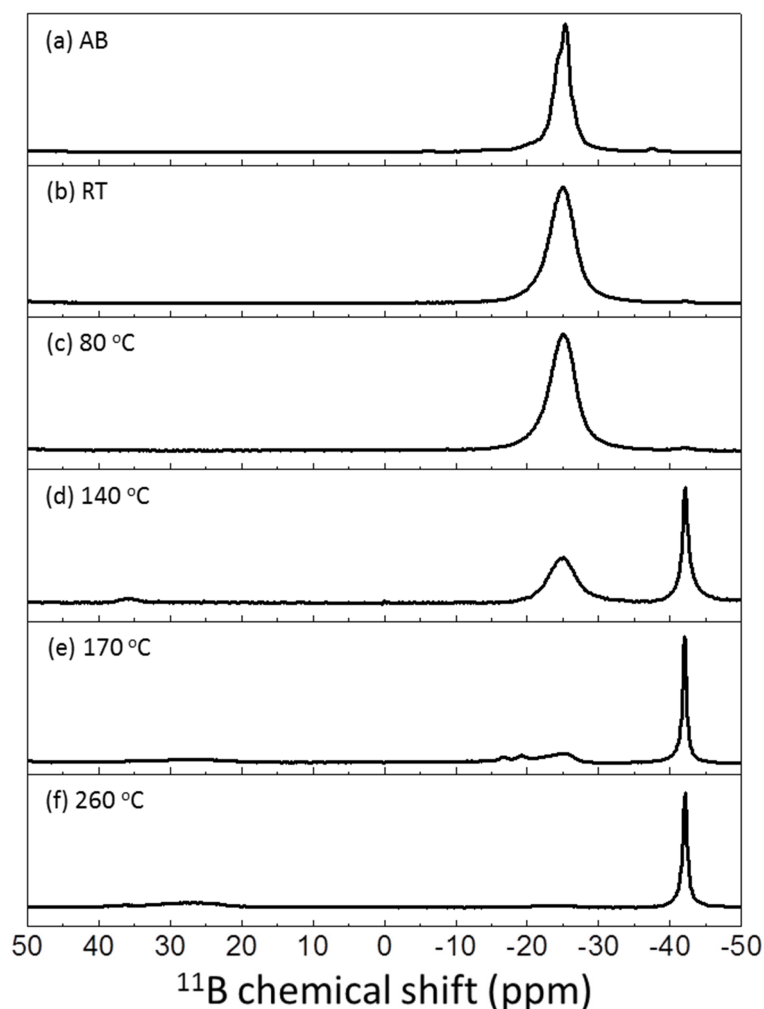


Fig. 3-16 ^{11}B MAS NMR spectra of (a) as-received AB and AB- NaAlH_4 mixture at (b) room temperature, (c) 80 °C, (d) 140 °C, (e) 170 °C and (f) 260 °C.

has a peak at -25.4 ppm at RT. This peak is originated from a $[\text{NBH}_3]$ environment from neat AB.⁷ AB- NaAlH_4 mixture showed a peak at -25.0 ppm at RT. The peak position was similar with that of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ (-24.9 ppm), suggesting the formation of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ in this mixture. The same peak position was observed at 80 °C, suggesting the unknown phases observed in Fig. 3-15(a) would be $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$. After heating to 140 °C, an additional peak was observed at -42.1 ppm. This peak can be assigned to BH_4 resonance in NaBH_4 phase. After heating to 170 °C and 260 °C, this peak still remained. This is consistent with the XRD results in

Fig. 3-15(a).

Fig. 3-17 shows the *in situ* FTIR spectra of ball-milled AB-MAlH₄ (M = Na, Li) mixtures during heating. The spectra of AB and MAlH₄ (M = Na, Li) at RT were also shown as references. Peak intensities corresponding to N-H stretching between 3150 and 3500 cm⁻¹ decreased as temperature increased, whereas peaks corresponding to B-H stretching between 2200 and 2400 cm⁻¹ were remained after heating to 260 °C in both mixtures. This phenomenon was also observed in other metal amidoboranes.¹¹⁻¹³ A new compound containing nitrogen would be formed during H₂ desorption.

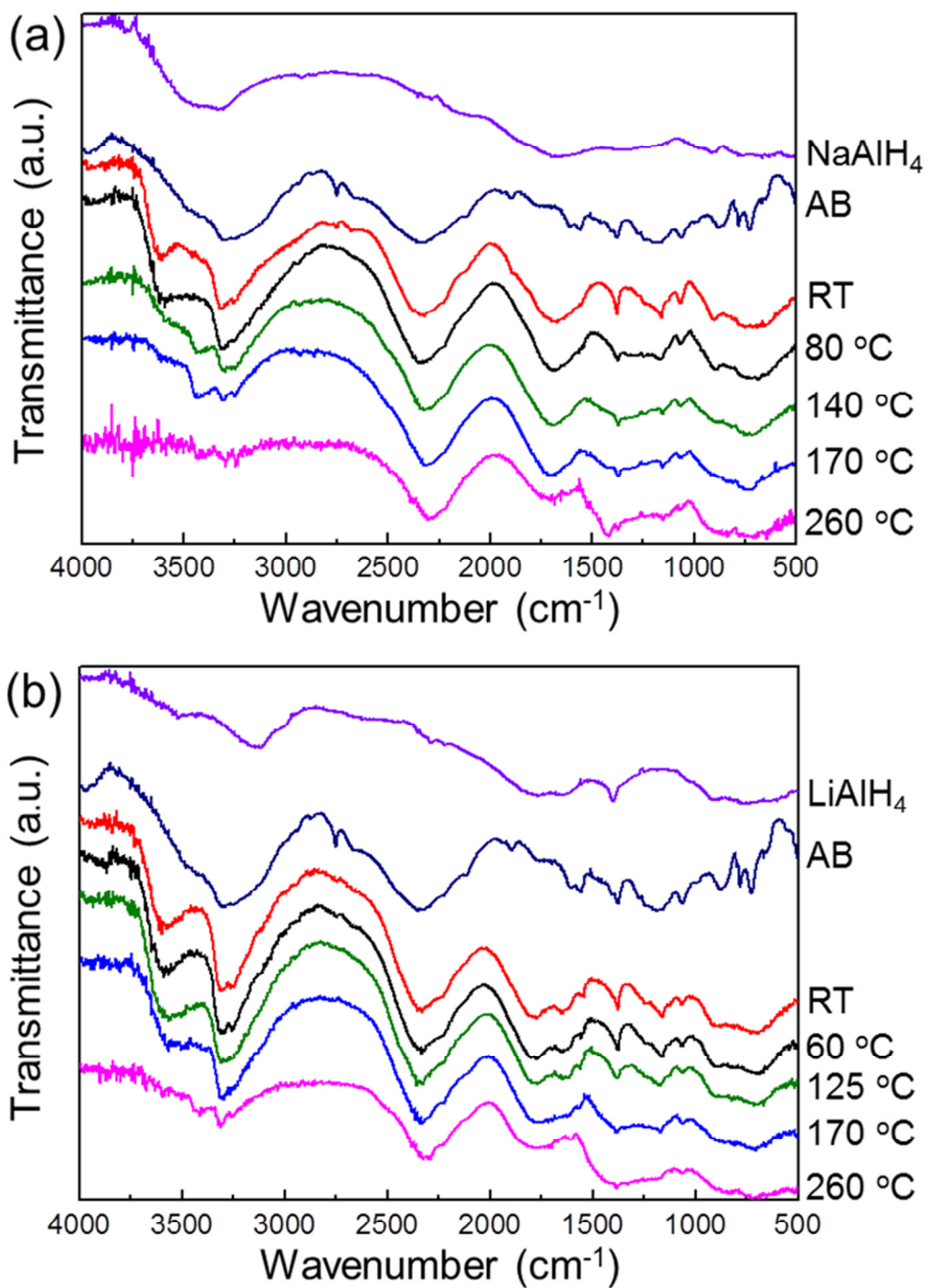


Fig. 3-17 *In situ* FTIR spectra of ball-milled AB-MAIH₄ mixtures at each temperature; (a) AB-NaAlH₄, (b) AB-LiAlH₄ mixture. AB and MAIH₄ (M = Na, Li) spectra was presented for comparison. The heating rate was 5 °C min⁻¹.

3.4 Conclusions

In this chapter, AB-MAIH₄ (M = Na, Li) mixtures were synthesized by hand-mixing and ball-milling and their H₂ desorption properties were investigated. In case of hand-mixing, ion-exchange reaction between DADB and MAIH₄ occurs to form MBH₄ and amorphous Al-N-B-H phase. The reaction is violent exothermic and by-product gas emissions are not suppressed. Ball-milling under Ar atmosphere also causes the reaction like hand-mixing. Fig. 3-18 summarizes the energy diagram of the phases of AB-NaAlH₄ system under Ar atmosphere. Most of the H₂ were desorbed during the

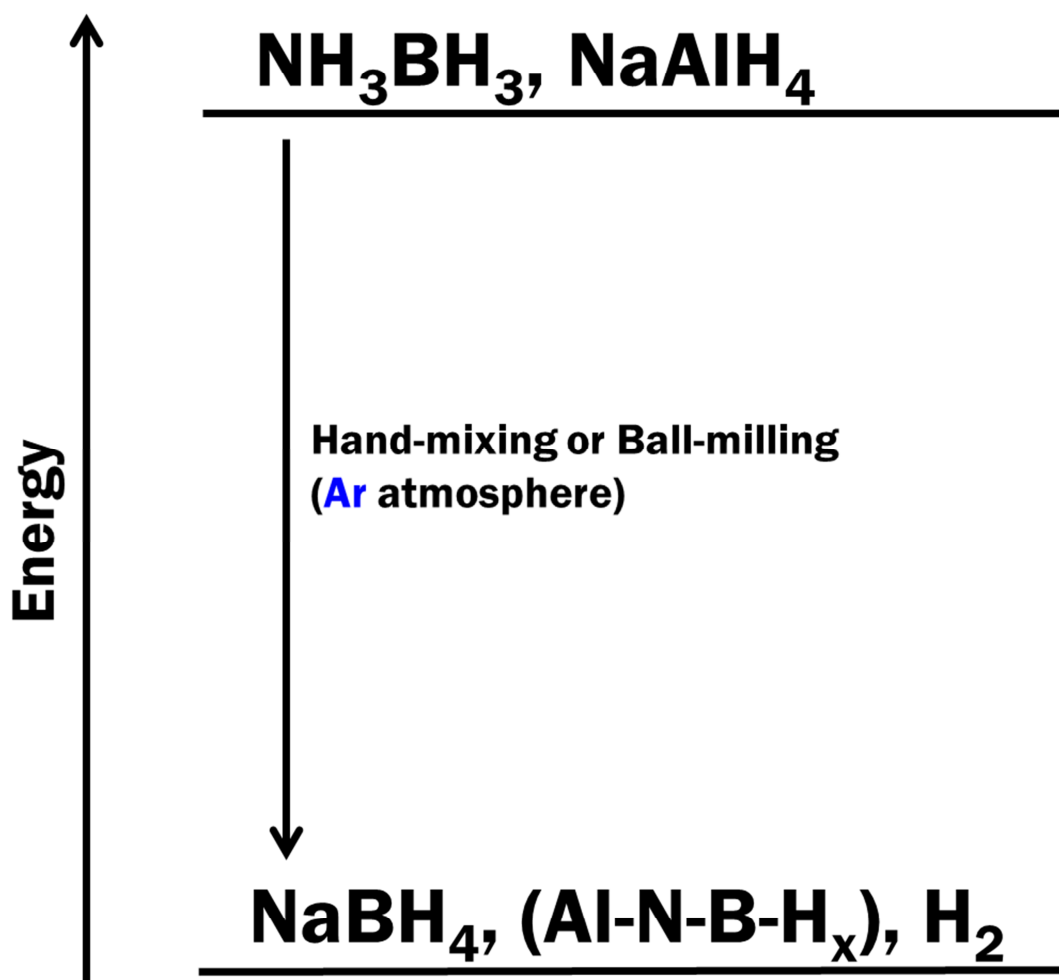


Fig. 3-18 Energy diagram of the phases of AB-NaAlH₄ system under Ar atmosphere.

procedure under Ar atmosphere. However, 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. Thus, ball-milling atmosphere is important in AB- $NaAlH_4$ system. Fig. 3-19 summarizes the energy diagram of the phases of AB- $NaAlH_4$ system under H_2 atmosphere. The solid products after H_2 desorption are $NaBH_4$ and amorphous Al-N-B-H phase, indicating these are basically same phases as in case of Ar atmosphere. In addition, AB- $MAIH_4$ mixture with a molar ratio of 1 : 1 showed no by-product gas emissions. $MAIH_4$ is effective to decrease the by-product gas emissions from AB.

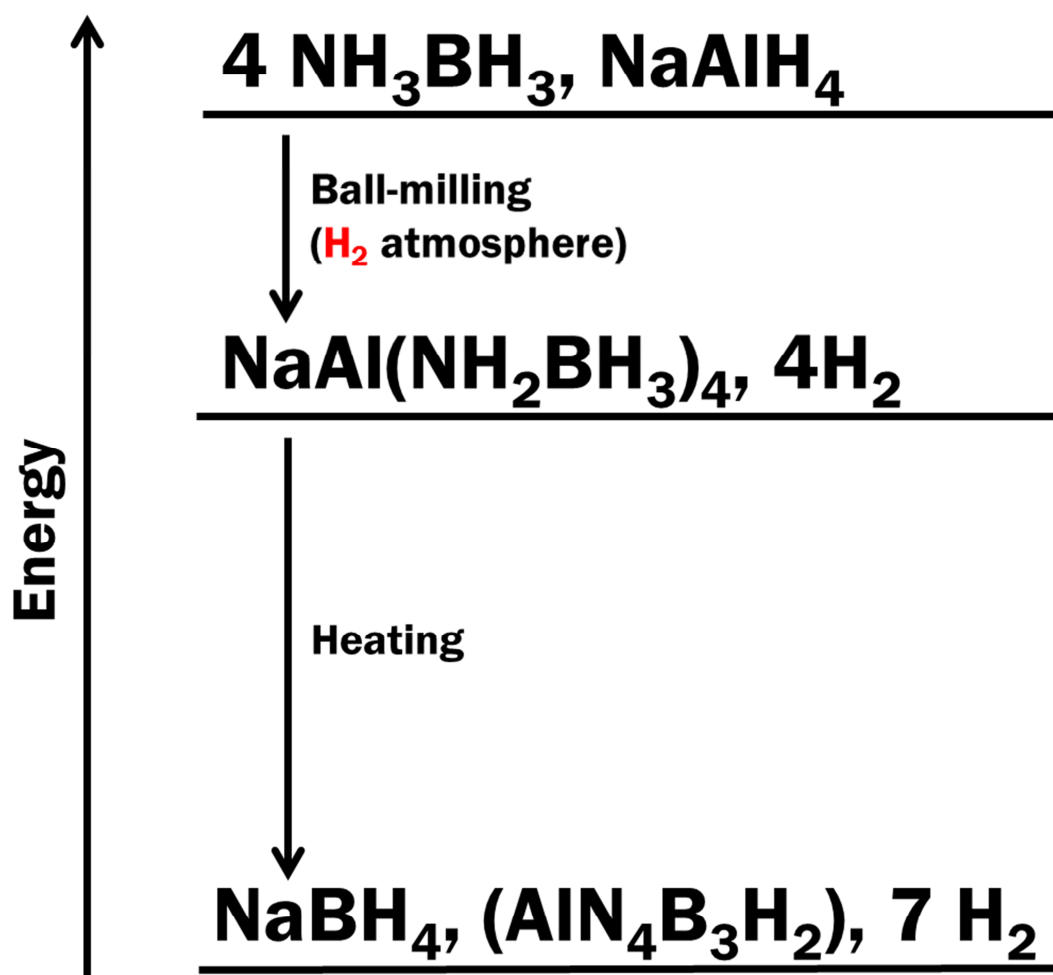


Fig. 3-19 Energy diagram of the phases of AB- $NaAlH_4$ system under H_2 atmosphere.

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4. General discussions and conclusions

4.1 Comparison with $\text{NH}_3\text{BH}_3\text{-M}$ system

In chapter 2 and 3, H_2 desorption properties of AB-MH_n mixtures were investigated. In this section, H_2 desorption properties and processes are compared with the system consisting of AB and pure metals. According to ref. 1, H_2 desorption properties of AB-M mixtures were investigated. Pure metals ($\text{M} = \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$ and Zn) were ball-milled with AB. The content of metal additive was 10 mol%. Fig. 4-1 shows H_2 MS profiles of milled AB and AB-M mixtures. The mixtures were arranged in order of the atomic number of metal, Z . The milled AB showed two H_2 desorption peaks in the temperature ranges of ca. 100-130 °C and 130-170 °C. The peak temperature of the 1st peak was 114 °C. All the mixtures showed similar profiles as that of milled AB. The 1st H_2 desorption temperatures of AB-M mixtures were plotted in Fig. 4-2. The dashed line shows the temperature from milled AB. All the samples showed almost same peak temperatures as compared with AB. Thus, it seemed that there was no interaction between pure metals and AB.

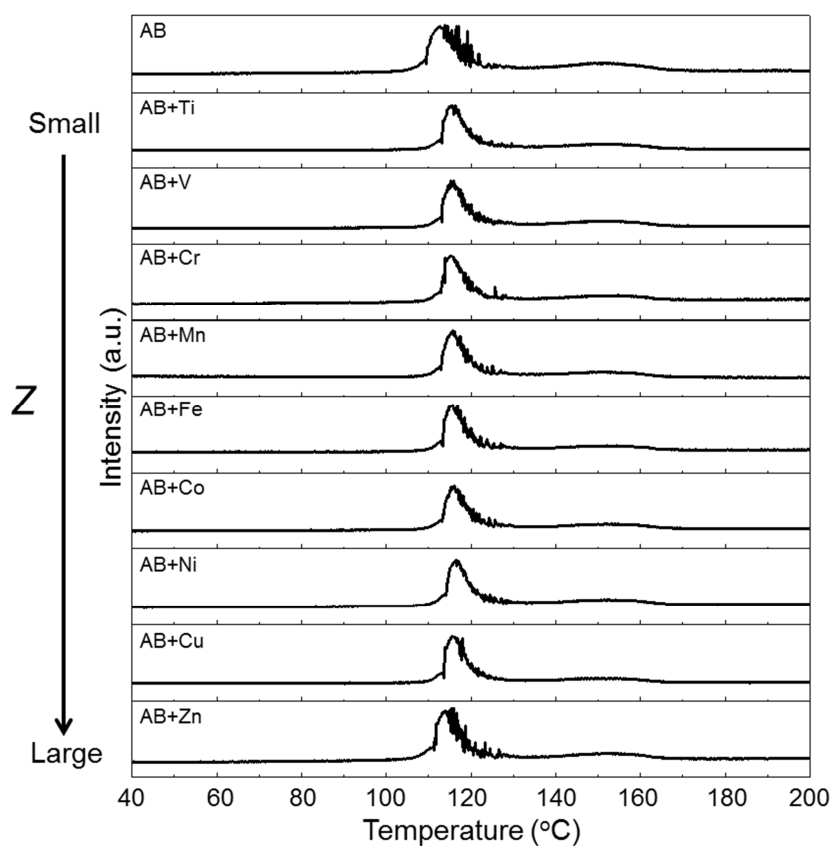


Fig. 4-1 H₂ MS profiles of AB-M mixtures. The heating rate was 3 °C min⁻¹. The mixtures were arranged in order of the atomic number of metal, Z. The data was referred from ref. 1.

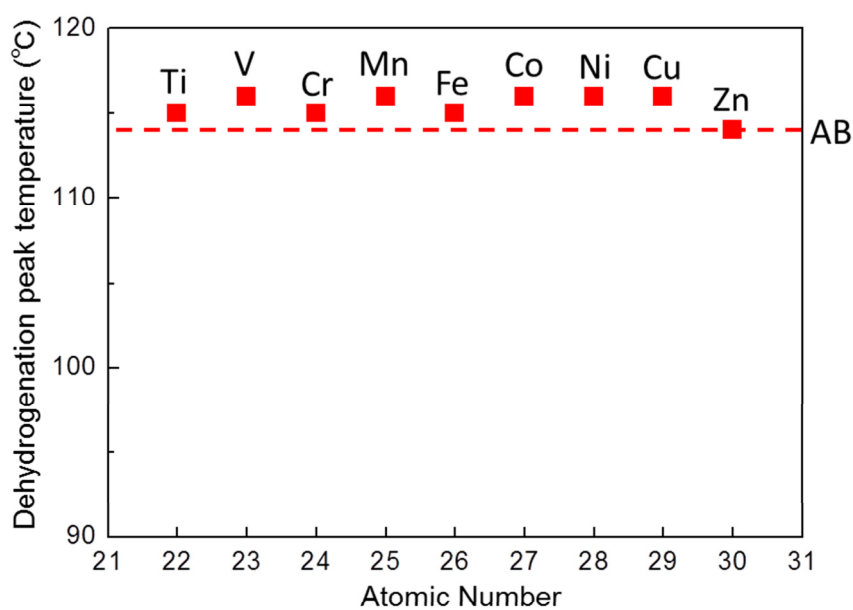


Fig. 4-2 H₂ desorption peak temperatures of AB-M mixtures. The heating rate was 3 °C min⁻¹. The data was referred from ref. 1.

4.2 Comparison with $\text{NH}_3\text{BH}_3\text{-MCl}_n$ system

Some metal chloride additives significantly affected the H_2 desorption properties of AB.¹⁻⁴ According to ref. 1, total of 17 metal chlorides were ball-milled with AB. The content of metal chloride additive was 10 mol%. Fig. 4-3 shows H_2 MS profiles of milled AB and AB- MCl_n mixtures. The mixtures were arranged in order of the Pauling electronegativity of metal, χ_p . The mixtures with low χ_p showed the similar profiles as that of milled AB, whereas the mixtures with high χ_p generally showed the lower H_2 desorption temperatures compared with milled AB. Especially, AB- FeCl_2 , AB- CoCl_2 , AB- CuCl_2 and AB- NiCl_2 mixtures showed the significantly low desorption temperatures below 100 °C.

Fig. 4-4 summarizes the 1st peak temperatures of AB- MCl_n mixtures. The dashed line shows the temperature from milled AB. The addition of MCl_n with $\chi_p \geq 1.6$ showed lower H_2 desorption temperature than that of AB. Thus, the correlation between χ_p and H_2 desorption temperature was observed. This tendency is consistent with the report by R. Benzouaa *et al.*⁵ Strong Lewis acids are known as initiators of H_2 desorption from AB.^{6,7} Our systematic data suggested that M^{n+} with high χ_p would act as a Lewis acid and initiate the AB dehydrocoupling by inducing changes in the electronic state of N. Since pure metals didn't exist as cations, they didn't work as Lewis acids, resulting in the almost no effect on H_2 desorption properties as shown in Figure 4-1. The tendency of AB- MCl_n system was different from that of AB- MH_n system. This would be ascribed to the difference of thermal stability between metal chloride and hydride. Though AB-MH (M = Na, Li) mixtures formed MNH_2BH_3 phases as shown in Table 2-1, these phases were not observed in AB-MCl (M = Na, Li) mixtures. The starting materials of AB and MCl_n were observed in XRD profiles. The formation reaction of MNH_2BH_3 did not occur because of the high thermal stability of MCl_n . Pure metal phases were observed after milling in the XRD profiles of AB- CuCl_2 and AB- AgCl mixtures. In AB- CuCl_2 mixture, the formation of $[\text{NH}_4]^+[\text{BCl}_4]^-$ phase was reported.⁸ In fact, as shown in Fig. 4-5, Cu phase was observed instead of CuCl_2 after milling in the XRD

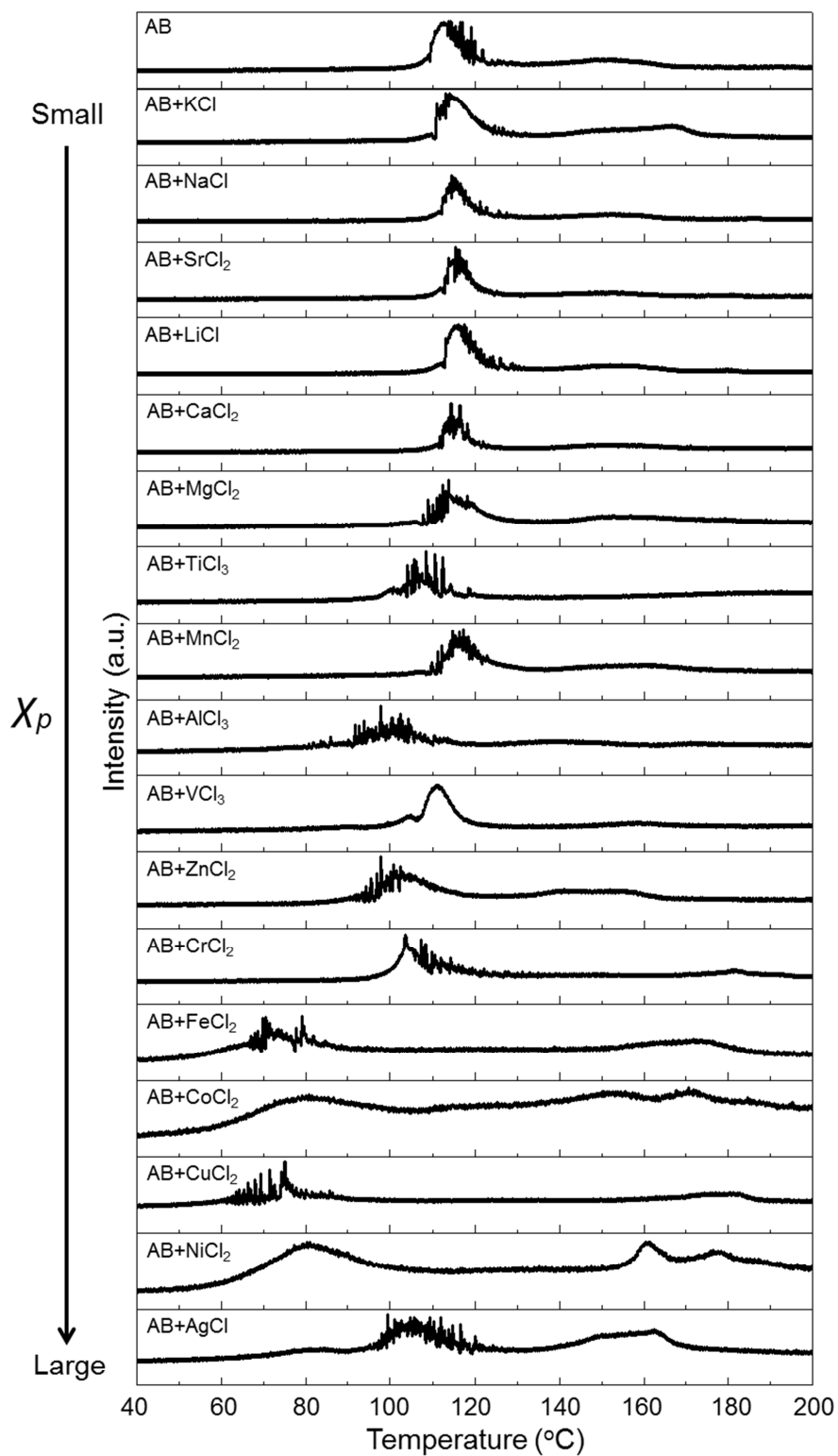


Fig. 4-3 H_2 MS profiles of AB-MCl_n mixtures. The heating rate was $3\text{ }^\circ\text{C min}^{-1}$. The mixtures were arranged in order of the Pauling electronegativity of metal, χ_p . The data was referred from ref. 1.

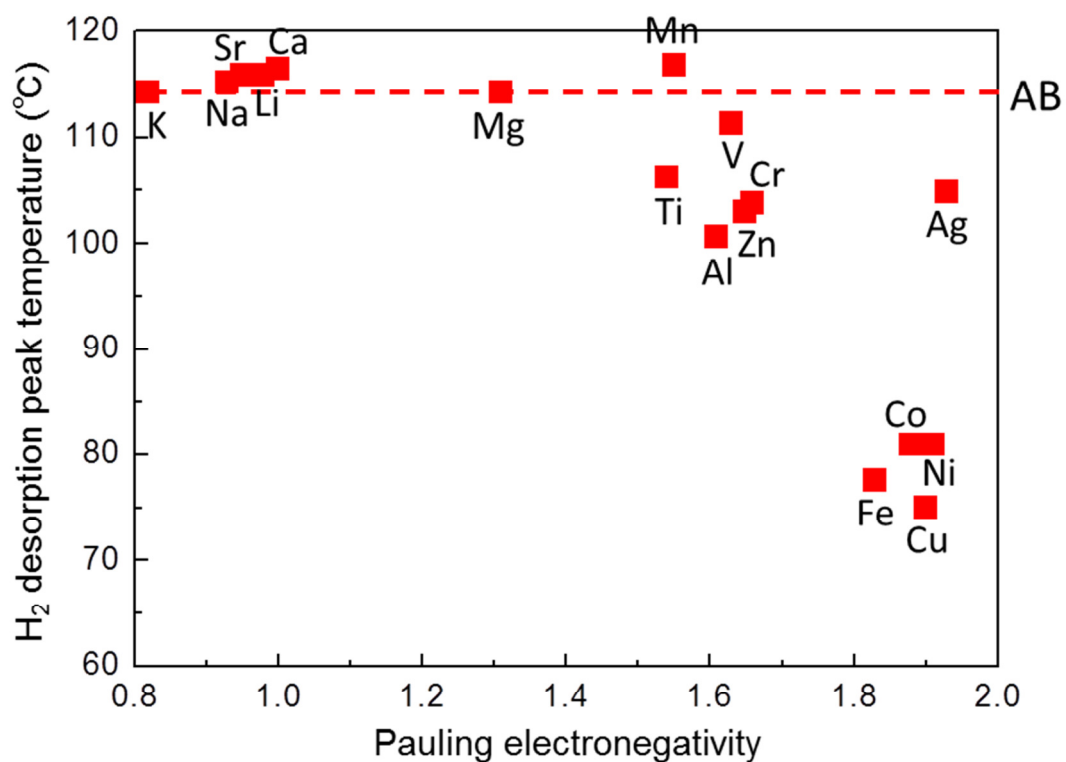


Fig. 4-4 H₂ desorption peak temperatures of AB-MCl_n mixtures classified by the Pauling electronegativity of M. The heating rate was 3 °C min⁻¹ (revised from ref. 1).

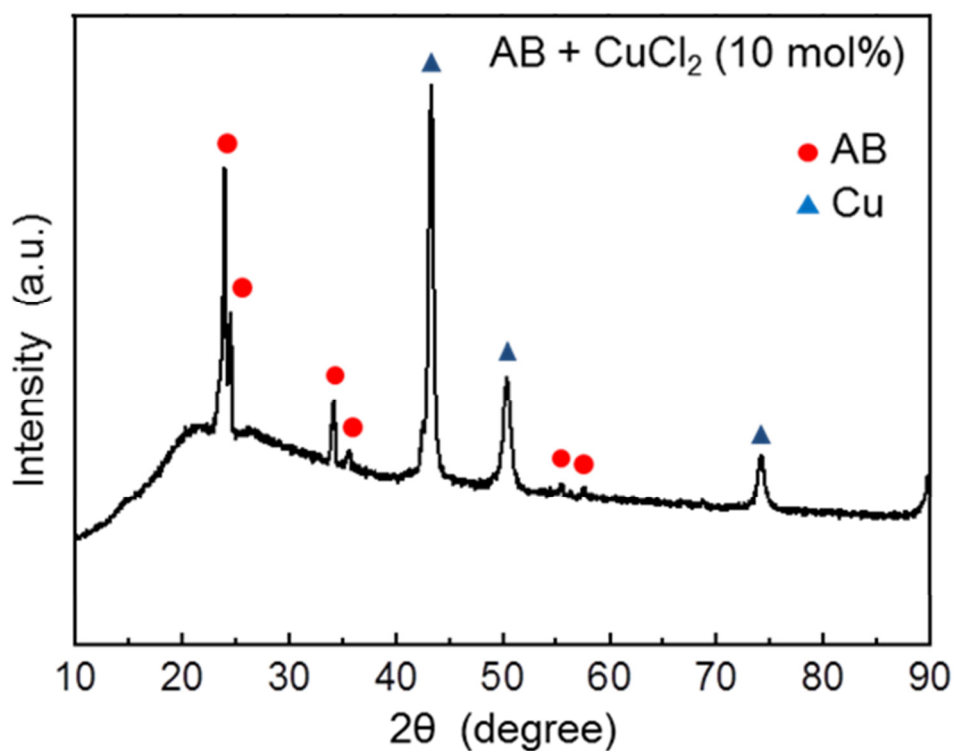


Fig. 4-5 The XRD profile of AB-CuCl₂ mixture after milling. The data was referred from ref. 1.

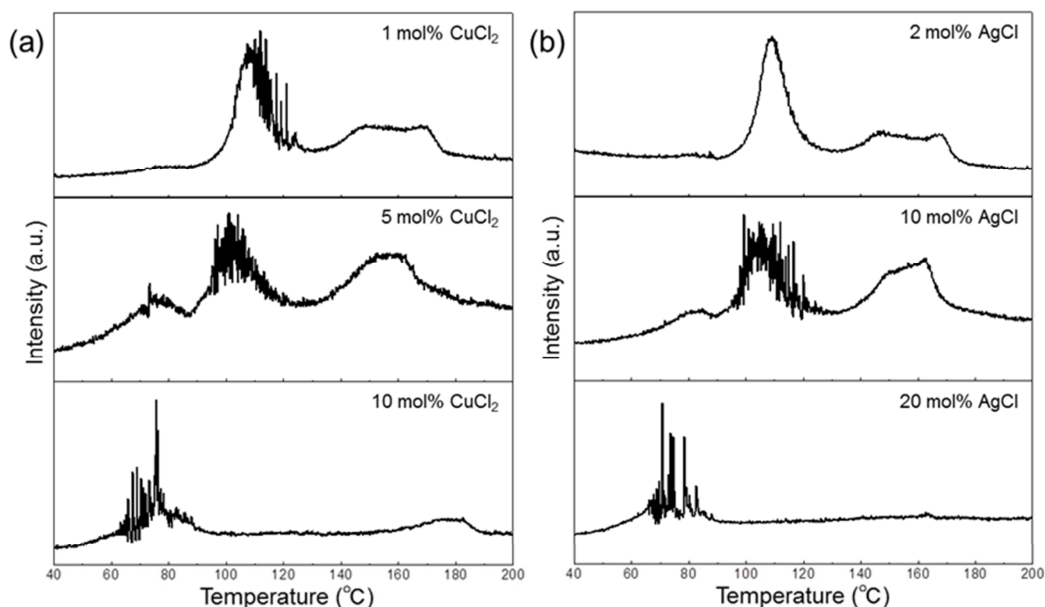


Fig. 4-6 H₂ MS profiles of (a) AB-CuCl₂ mixture prepared by hand mixing, (b) AB-AgCl mixture prepared by ball milling (BM). Heating rate was 3 °C min⁻¹. The data was referred from ref. 1.

profile of AB-CuCl₂ mixture, suggesting the formation of [NH₄]⁺[BCl₄]⁻ phase. AB was destabilized by the formation of this intermediate phase, which resulted in the lower H₂ desorption temperature.⁶ As shown in Fig. 4-4, the effect of AgCl addition was smaller than that of CuCl₂ in spite of almost same χ_p value. To investigate the effect of Cl⁻ amount, TG-DTA-MS profiles of AB-CuCl₂ mixture were compared with those of AB-AgCl mixture. Figure 4-6 shows the H₂ MS profiles of AB-CuCl₂ and AB-AgCl mixtures. Interestingly, both samples showed quite similar profiles when the amounts of Cl⁻ are the same values. For instance, H₂ MS profile of 5 mol% CuCl₂ mixture was quite similar with that of 10 mol% AgCl mixture. TG-DTA profiles and MS profiles of by-product gases were also similar. These results strongly suggest that the destabilization mechanism would be similar in AB-CuCl₂ and AB-AgCl systems. Therefore, the smaller effect of AgCl mixture would be ascribed to the small amount of Cl-containing phase.

Fig. 4-7 shows the amount of by-product gas emissions from AB-MCl_n mixtures. The amount of every by-product gas has a tendency to be low when χ_p becomes high value. The change of reaction pathway by the presence of Lewis acid site Mⁿ⁺ showed the small amounts of by-product gas emissions. MCl_n with low χ_p also showed the lower amount of NH₃ emission as shown in Figure 4-7 (a). In fact, it is well known that some metal chlorides are promising as NH₃ absorbing materials.⁹ The material with higher χ_p of the cation showed lower plateau pressure on the ammonia absorption.⁹ Thus, the MCl_n with high χ_p would absorb NH₃ immediately after it is desorbed. As a result, systematic investigation on H₂ desorption properties of AB-MCl_n indicated that addition of metal chlorides with high χ_p showed the improvements on H₂ desorption temperatures and by-product gas emissions.

From the viewpoint of gravimetric hydrogen capacity, the amounts of metal chloride additives should be small because most of the metals with $\chi_p \geq 1.6$ are heavy elements. Though the content of metal chloride additive was 10 mol% in this study, the MCl_n additives with small amounts also would be effective. For example, the addition of 2.0 mol% nanosized CoCl₂ or NiCl₂ decreased the H₂ desorption temperature as low as 59 °C and suppressed the borazine emission.¹⁰

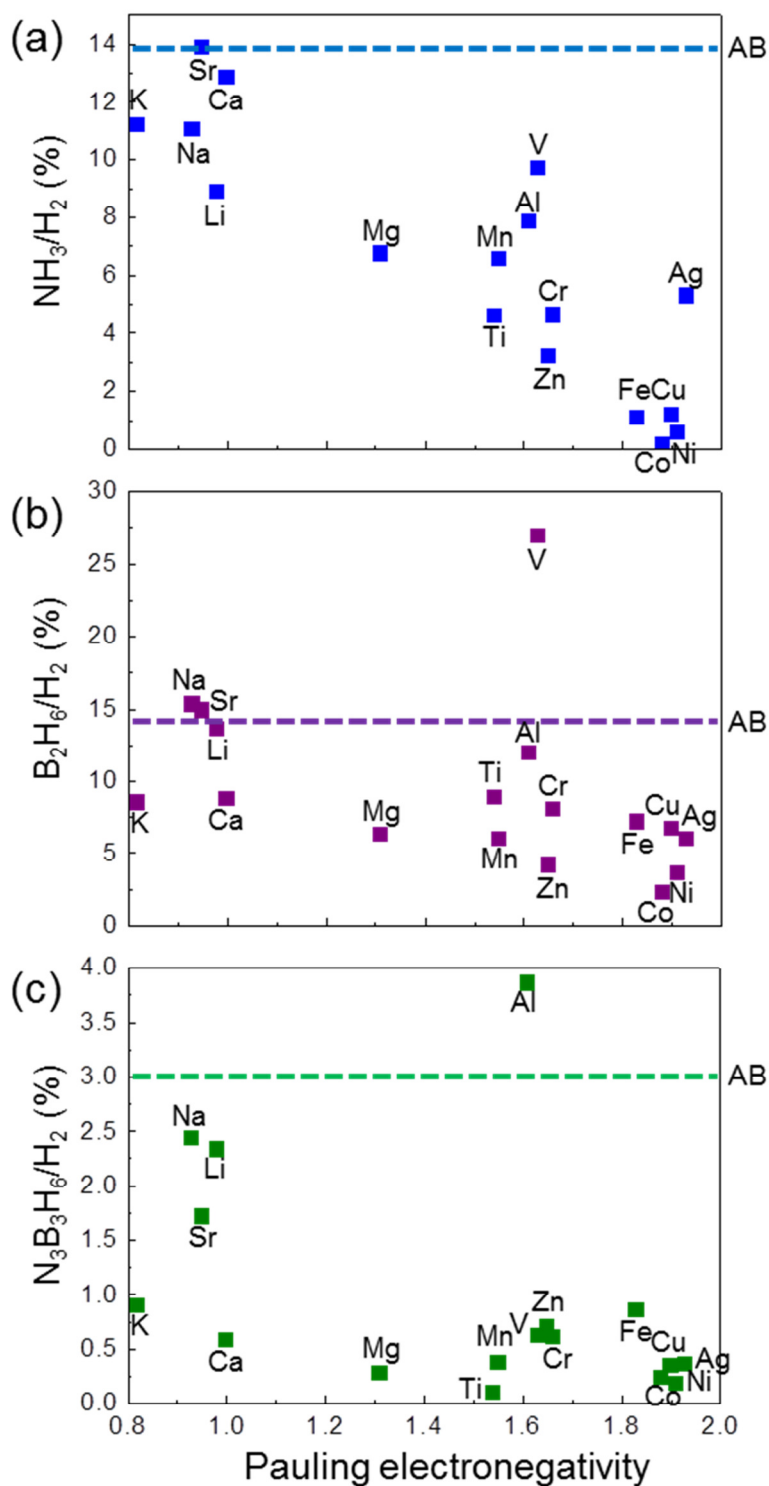


Fig. 4-7 The amounts of by-product gases desorbed from AB-MCl_n mixtures classified by the Pauling electronegativity of metal; (a) ammonia (NH₃), (b) diborane (B₂H₆), and (c) borazine (B₃H₆N₃). The heating rate was 3 °C min⁻¹ (revised from ref. 1).

4.3 Strategy for advanced materials

Chapter 2 and 3 focused on how to control by-product gases from AB. Various kinds of AB-MH_n mixtures were synthesized and investigated. From the results, Pauling electronegativity of metal, χ_p was proposed as an important factor. Then, AB-MAlH₄ (M = Na, Li) mixtures were synthesized. However, hydrogen amount from the mixture was not large. Therefore, another point of view should be added. It is how to release a large amount of H₂ at low temperatures from the system. From the viewpoint of hydrogen amount, AB-AlH₃ mixture is attractive. The mixture showed the highest H₂ amount among the mixtures investigated in this study. Estimated amount of H₂ was 13.5 mass%. The problems are B₂H₆ emissions and a little high H₂ desorption temperature. Fig. 4-8 shows a proposed strategy for more advanced materials. Base material should be AB-AlH₃ mixture because it has high hydrogen capacities. To suppress by-product gas emissions, LiH or NaH should be added according to the results of chapter 2. In addition, FeCl₂ or CuCl₂ should be added to reduce H₂ desorption temperatures according to the results of section 4.2. Then, a large amount of hydrogen can be released at a low temperature range with no by-product gas emissions.

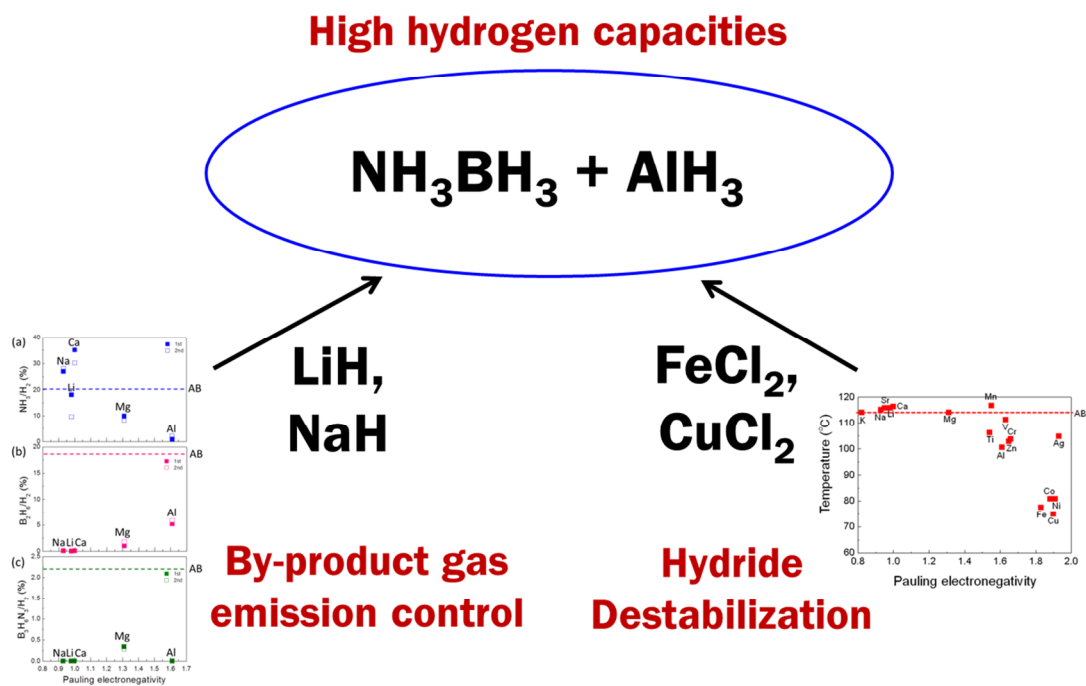


Fig. 4-8 Proposed strategy for more advanced materials.

4.4 Conclusions

4.4.1 Overview

In this thesis, the H₂ desorption properties of AB-MH_n mixtures were systematically investigated. From the investigation, electronegativity of metal (χ_p) was proposed as an important factor to reduce H₂ desorption temperatures and amounts of by-product gas emissions. Based on the factor, advanced AB-MAlH₄ (M = Na, Li) mixtures were synthesized. By-product gas emissions were effectively decreased in the mixtures. To desorb a large amount of H₂ at low temperatures with no by-product gas emissions, AB-AlH₃ mixture with alkali metal hydride and FeCl₂ (CuCl₂) would be promising. The detailed results and conclusions were summarized in the following.

4.4.2 NH₃BH₃-MH_n system

NH₃BH₃-MH_n (M = K, Na, Li, Ca, Mg, Al) mixtures were synthesized by ball-milling. The crystalline phases and H₂ desorption properties were investigated. Pauling electronegativity of metal (χ_p) was proposed as an important factor.

1) The crystalline phases of mixtures can be predicted by using χ_p . MBH₄ was formed for M = K, Na ($\chi_p \leq 0.9$), MNH₂BH₃ 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 ($1.0 \leq \chi_p$).

2) The correlation between H₂ desorption temperatures and χ_p was observed. Coulombic attraction between H^{δ-} of MH_n and H^{δ+} of NH₃ group of AB would result in the temperature decrease.

3) The amount of NH₃ has a tendency to be low as χ_p becomes high. On the other hand, the amount of B₂H₆ has a tendency to be low as χ_p becomes low. AB-AlH₃ mixture almost suppressed the NH₃ emission. AB-MH_n (M = Na, Li, Ca ($\chi_p \leq 1.0$)) mixtures suppressed the B₂H₆ emission.

4) The key issues for NH_3 and B_2H_6 suppressions are the NH_3 absorption properties of MH_n and the formation of stable $\text{M}(\text{BH}_4)_n$ phase, respectively. As χ_p becomes high value, MH_n would easily absorb NH_3 . As χ_p becomes low value, M^{n+} of MH_n easily react to $[\text{BH}_4]^-$ to form solid state $\text{M}(\text{BH}_4)_n$.

4.4.3 $\text{NH}_3\text{BH}_3\text{-MAIH}_4$ ($\text{M} = \text{Na, Li}$) system

AB-MAIH_4 ($\text{M} = \text{Na, Li}$) mixtures were synthesized by hand-mixing and ball-milling. The H_2 desorption properties and processes were investigated in detail.

1) In hand-mixing, ion-exchange reaction between $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$ (DADB) and MAIH_4 occurs to form MBH_4 and amorphous Al-N-B-H phase. The reaction is violent exothermic and by-product gas emissions are not suppressed.

2) Ball-milling under Ar atmosphere also causes the reaction similar as hand-mixing. Decomposition during the milling occurs to form MBH_4 and amorphous Al-N-B-H phases.

3) Ball-milling under H_2 atmosphere can generate a novel hydrogen storage material of $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ in AB-NaAlH_4 system. The synthesized $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$ 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 phase, indicating basically same as in case of Ar atmosphere.

4) AB-MAIH_4 mixture with a molar ratio of 1 : 1 showed no by-product gas emissions. Thus, MAIH_4 is effective to decrease the by-product gas emissions from AB.

4.4.4 Prospects of future work

As described in this thesis, MH_n additives are effective to decrease the by-product gas emissions from AB. However, the desorbed H_2 amounts and kinetics are not sufficient for practical applications. Therefore, another additive or catalyst addition to AB- MH_n mixtures should be considered. Also, other novel hydrogen storage materials containing AB should be explored. For instance, AB combined with g- C_3N_4 (graphitic carbon nitride) system attracts attention as metal-free catalysis of AB.¹¹ The biggest disadvantage of AB is its poor reversibility. Therefore, the strategy for its regeneration also should be considered. For example, nano-confinement could pave the way for rehydrogenation route of AB.¹² Also, $Na_2Mg(NH_2BH_3)_4-Mg(NH_2)_2$ ¹³ or AB- $Al(BH_4)_3$ ¹⁴ system showed the H_2 desorption reaction in endothermic reaction. These findings would give some hints for a future work.

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Appendix. Experimental methodology

1. Mechanical ball-milling method for sample preparation

Mechanical ball-milling is originally designed for producing oxide-dispersion strengthened (ODS) nickel- and iron-based superalloys.¹ Table A-1 summarizes the attributes of mechanical ball-milling. Refinement of grain sizes down to nanometer ranges or inducement of chemical reactions at low temperatures can be achieved by mechanical ball-milling method. Basically, the samples were synthesized by

Table A-1 Attributes of mechanical alloying (reprinted from ref. 1).

Production of fine dispersion of second phase (usually oxide) particles
Extension of solid solubility limits
Refinement of grain sizes down to nanometer range
Synthesis of novel crystalline and quasicrystalline phases
Development of amorphous (glassy) phases
Disordering of ordered intermetallics
Possibility of alloying of difficult to alloy elements
Inducement of chemical (displacement) reactions at low temperatures
Scaleable process

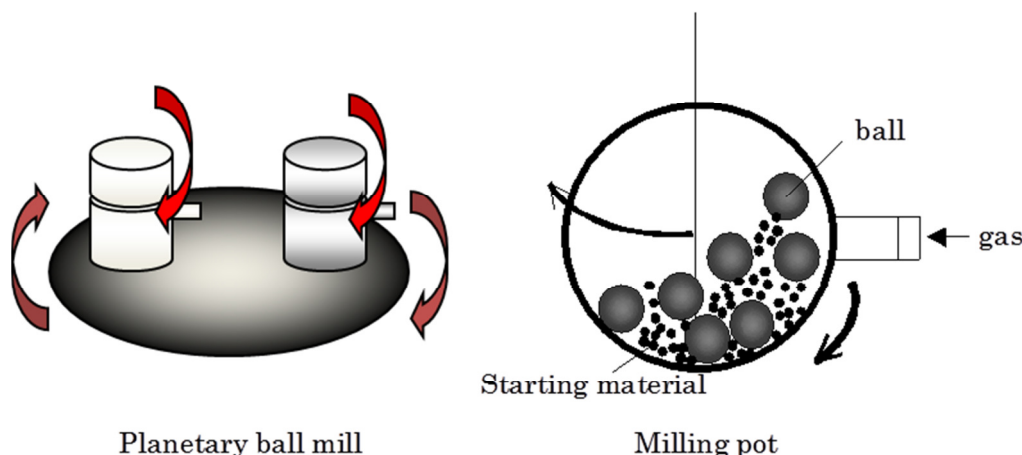
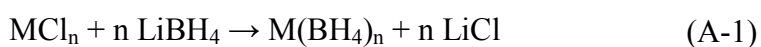


Fig. A-1 The image of planetary ball-mill apparatus and milling pot.

ball-milling in this study. A planetary ball-mill apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls and 300 mg samples (ball : powder ratio = 70 : 1, by mass) was used. Fig. A-1 shows the image of planetary ball-mill apparatus and milling pot. On the milling pot, a quick connector is equipped for introducing H_2 gas. Thus, it is possible to vacuum or introduce gases to the pot through the Sievert's-type equipment.

Mechanical ball-milling has been used for synthesizing various kinds of hydrogen storage materials, such as BCC alloys,^{2,3} binary hydrides,^{4,5} and complex hydrides.^{6,7} Fig. A-2 shows the image of ball collision effects.⁸ Mechanical milling acts as a combination of compression and shear on the powder.⁸ At the first step, elastic deformations occur. As energy increases, the second step of plastic deformation, an irreversible deformation occurs. At the final stage, chemical reaction, amorphization occurs.

The synthesis of hydrogen storage materials by mechanochemical reactions are one of the common methods. For example, metal borohydrides ($M(BH_4)_n$) can be synthesized by the reaction as follows.⁹



The reaction is a metathesis, an ion-exchange reaction during ball-milling. By this reaction, many kinds of $M(BH_4)_n$ were synthesized.⁹ Some metal amidoborane phases

also can be obtained by metathesis reactions.¹⁰

Metastable phases also can be synthesized by ball-milling. For instance, γ -MgH₂ phase, which is formed by heating α -MgH₂ in a multianvil press at 2 GPa pressure to 1070 K,¹⁰ can be obtained by mechanical milling of stable β -MgH₂ under Ar atmosphere.⁵ Thus, the internal pressure of the material at mechanical impact may reach the GPa order.⁸ In case of metal amidoborane phase, β -LiNH₂BH₃ can be obtained under mechanical milling.¹¹

In this study, mechanical ball-milling was applied to synthesize novel hydrogen-rich phases. This method can expect to synthesize novel phases by mechanochemical reactions.

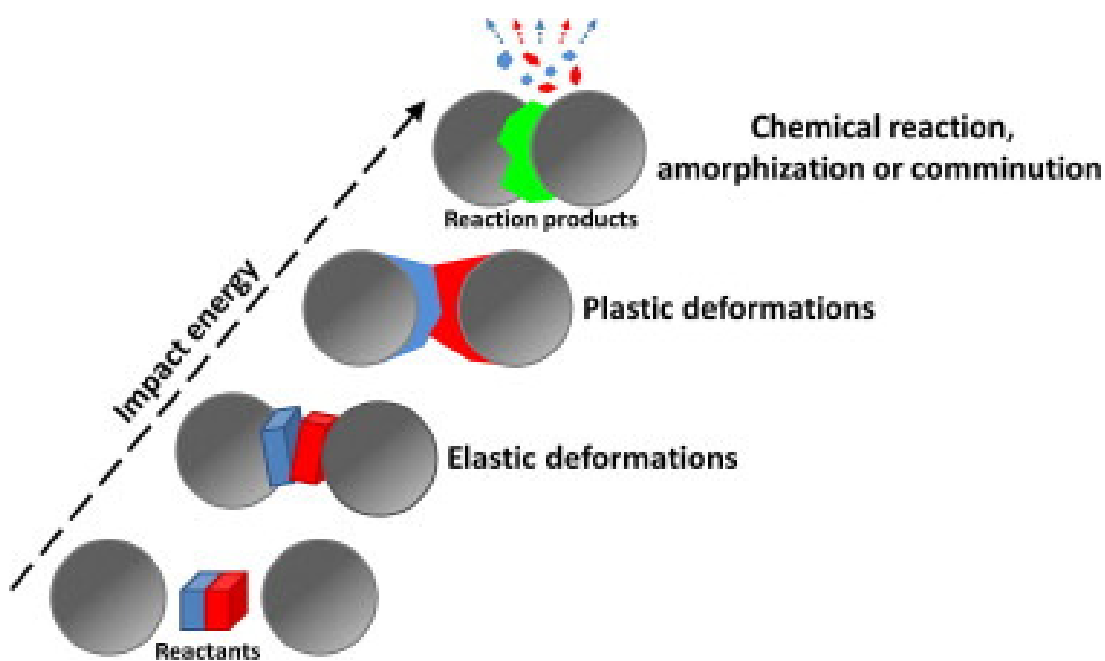


Fig. A-2 The image of ball collision effects on the mixtures as a function of ball impact energy (reprinted from ref. 8)

2. Experimental procedures

2.1 Powder X-ray diffraction (XRD)

Powder XRD (PANalytical, X'Pert Pro, Cu K α radiation) was performed to identify the crystalline phases of samples. The energy output was 40 kV, 40 mA. To avoid the sample oxidation, sample set was performed in an Ar purified glovebox (O₂ concentration < 5 ppm). The samples were placed on a glass plate and then sealed with a polyimide sheet (Kapton, The Nilaco Co. Ltd.). As shown in Fig. A-3, the broad diffraction peaks around 20° and 27° in all the profiles originate from the polyimide sheet and grease.

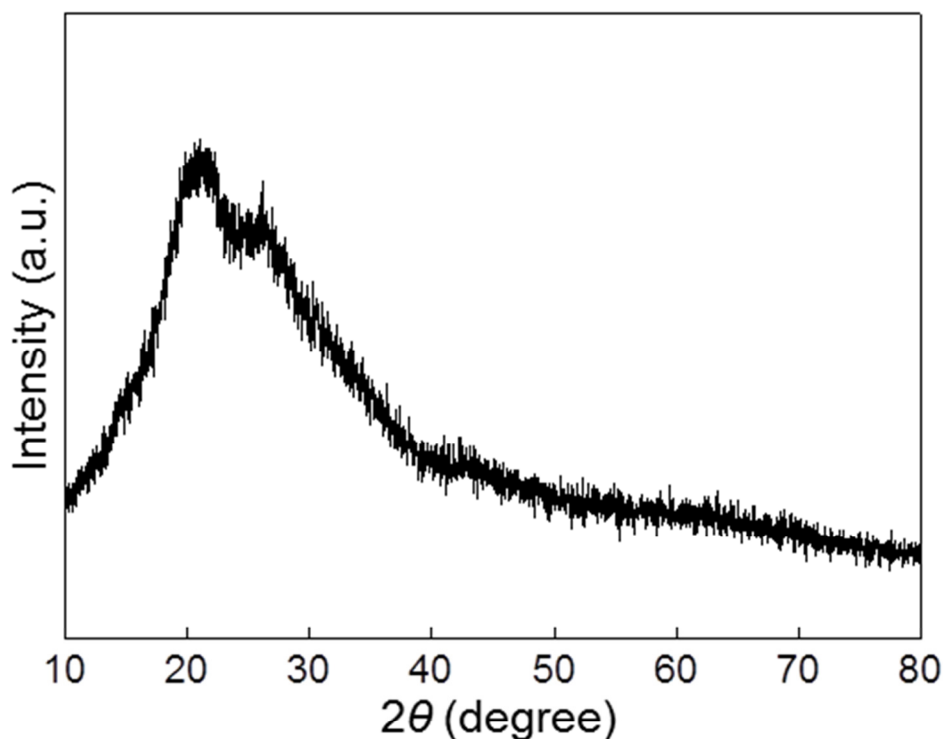


Fig. A-3 The XRD profile of glass plate with the polyimide sheet and grease.

2.2 Thermogravimetry – differential thermal analysis – mass spectrometry (TG-DTA-MS)

H₂ desorption properties of samples were analyzed by using TG-DTA (Bruker, 2000SA) combined with MS (ULVAC, BGM-102). The desorbed gases are carried from TG-DTA apparatus to MS through a capillary by flowing high purity He gas (purity > 99.9999 %) as a carrier gas. The apparatus was installed in a glovebox filled with purified Ar gas. Therefore, the TG-DTA-MS measurements were performed without exposing the samples to air. In this study, most of the samples desorbed not only H₂ but also other by-product gases. Therefore, the amount of H₂ was estimated by using the method as below. First, the value of integral for MS peak was determined for each desorbed gas. Then, the value of integral for by-product gas was normalized by that for H₂. The normalized value of integral (based on the volume ratio) was changed to the mass ratio. By using the derived mass ratio and the total mass loss obtained from TG results, the mass loss of each gas was estimated. This method is not a quantitative analysis because the rate of ionization is different from each gas. However, qualitative comparison would be possible.

2.3 Nuclear Magnetic Resonance (NMR)

The decomposition products of AB or metal amidoborane are often difficult to analyze because of their amorphous(-like) structure.^{12,13} Nuclear magnetic resonance (NMR) spectroscopy is an effective tool to analyze such kind of amorphous structure. In this study, solid-state ^{11}B and ^{27}Al magic angle spinning - nuclear magnetic resonance (MAS-NMR) spectra were recorded on a JNM-ECA600 spectrometer (JEOL) at a magnetic field of 14.1 T with the ^{11}B resonant frequency of 192.6 MHz. All the samples were spun at 15 kHz, using 4 mm ZrO_2 rotors filled in argon atmosphere. Chemical shifts were referenced to saturated H_3BO_3 aqueous solution at 19.49 ppm for ^{11}B and AlCl_3 aqueous solution at -0.10 ppm for ^{27}Al . Single-pulse excitations of 2.0-3.0 μs and relaxation delays of 2.0-11.0 s for ^{11}B and 1.5-10.0 s for ^{27}Al were employed.

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