Thermodynamical stabilities of metal-borohydrides

Y. Nakamori [a,*], H.-W. Li [a], K. Kikuchi [a], M. Aoki [b], K. Miwa [b],
S. Towata [b], S. Orimo [a]

[a] *Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan*
[b] *Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*

Abstract

Metal-borohydrides $M(BH_4)_n$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn (fourth period in periodic table) and Al; n = 2–4) were synthesized by a mechanical milling process according to the following reaction: $MCl_n + nLiBH_4 \rightarrow M(BH_4)_n + nLiCl$. The thermal desorption properties of $M(BH_4)_n$ were investigated by gas-chromatography and mass-spectroscopy combined with thermogravimetry. The results indicate that the hydrogen desorption temperature T_d of $M(BH_4)_n$ correlates with the Pauling electronegativity χ_P of M; that is, T_d decreases with increasing values of χ_P. The components of desorbed gas for M = Ca, Sc, Ti, V and Cr ($\chi_P \leq 1.5$) are hydrogen only, while those for M = Mn, Zn and Al ($\chi_P \geq 1.5$) contain borane and hydrogen. Therefore, the appropriate χ_P in $M(BH_4)_n$ for hydrogen storage is expected to be smaller than 1.5, and the resulting predicted relationship between the heat of formation of $M(BH_4)_n$ and χ_P is a useful indicator for estimating the enthalpy change for the desorption reaction for $M(BH_4)_n$.
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1. Introduction

Complex hydrides have attracted growing interest as hydrogen storage materials because of their high gravimetric hydrogen densities [1–2]. Bogdanović and Schwickardi have reported that catalyzed sodium alanate ($NaAlH_4$) undergoes reversible hydrogen desorption and re-absorption reactions at moderate conditions [3]. Motivated by this report, many attempts have been made to enhance the hydrogen desorption and absorption reactions for alkali complex hydrides [4–10].

Among the alkali complex hydrides, lithium borohydride ($LiBH_4$) is one of the candidates for use as a hydrogen storage material because of its extremely high gravimetric hydrogen density. $LiBH_4$ desorbs approximately 14 mass% of hydrogen through the decomposition reaction as follows [11]:

$$LiBH_4 \rightarrow LiH + B + \tfrac{3}{2}H_2 \qquad (1)$$

However, the hydrogen desorption temperature is higher than the required temperature for solid state hydrogen storage materials. Züttel et al. have reported that $LiBH_4$ mixed with SiO_2 des-

orbs hydrogen below 673 K, a lower temperature than for $LiBH_4$ [12]. Vajo et al. have reported that mechanically milled mixtures of $LiBH_4 + (1/2)MgH_2$ were destabilized than pure $LiBH_4$ and underwent reversible absorption and desorption reactions [13]. In order to decrease the hydrogen desorption temperature T_d and to improve the reversible reaction properties, systematic understandings of the thermodynamic stabilities of $M(BH_4)_n$ are of great importance.

Recently, we have theoretically investigated a series of $M(BH_4)_n$ including (M = Li, Na, K, Cu, Mg, Zn, Sc, Zr, Hf and Ti) [14,15] theoretically and experimentally. The results revealed that the charge compensation by M^{n+} is a key feature for the stability of $M(BH_4)$, and that the hydrogen desorption temperature T_d of $M(BH_4)_n$ decreases with increasing electronegativity χ_P of M. Moreover, M with a larger χ_P becomes a di-, tri- or tetra-valent cation of M^{n+}, and M^{n+} combines with n moles of $[BH_4]^-$ to form $M(BH_4)_n$. This means that $M(BH_4)_n$ maintain high gravimetric hydrogen density as shown in Table 1.

In this study, metal-borohydrides $M(BH_4)_n$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn (fourth period in periodic table) and Al; n = 2–4) are synthesized, and the purposes are (i) to clarify whether our proposed correlation between the stability of borohydrides and the electronegativity of M can be extended also to these $M(BH_4)_n$

Table 1
Summary of the hydrogen desorption properties of $M(BH_4)_n + n$LiCl (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al)

$M(BH_4)_n$	$Ca(BH_4)_2$	$Sc(BH_4)_3$	$Ti(BH_4)_3$	$V(BH_4)_3$	$Cr(BH_4)_2$	$Mn(BH_4)_2$	$Zn(BH_4)_2$	$Al(BH_4)_3$
Electronegativity χ_P of M	1.0	1.3	1.5	1.6	1.6	1.5	1.6	1.5
Gravimetric hydrogen density (mass%)	11.6	13.5	13.1	12.7	9.9	9.5	8.5	16.9
Gravimetric hydrogen density with nLiCl (mass%)	5.2	5.6	5.5	5.4	4.8	4.8	4.5	6.1
Observed weight loss (mass%)	4.2	4.2	0.1	0.1	0.1	9.1	13.0	23.4
Desorbed temperature T_d (first peak temperature in Fig. 4)	747	529	395	~400	~400	442	433	334[a]
Desorbed gases	H_2	H_2	H_2[b]	H_2[b]	H_2[b]	H_2, B_2H_6	H_2, B_2H_6	H_2, B_2H_6

[a] The thermal desorption temperature for $Al(BH_4)_3$ was defined as the first peak temperature of Fig. 6 (detected by mass-spectroscopy).

[b] The components of desorbed gas are confirmed to be only hydrogen according to the accuracy of our apparatus. However, the desorbed borane is undeniable, because the amount of desorbed gas is very small.

and (ii) to select the appropriate M for the borohydrides as hydrogen storage materials.

2. Experimental

The starting materials were purchased from Aldrich Co., Ltd.; anhydrous MCl_n (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al) with 99.9–99.999% purities, $LiBH_4$ and $NaBH_4$ with 95–99.9% purities. Then, the mixture of MCl_n and nLiBH$_4$/nNaBH$_4$ was mechanically milled under 0.1 MPa argon gas atmosphere for 5 h in order to synthesize $M(BH_4)_n$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al). Mechanochemical syntheses have been reported for the preparation of $Zn(BH_4)_2$ [16] and $Zr(BH_4)_4$ [17]. The expected reaction during milling is expressed as follows:

$$MCl_n + n\text{LiBH}_4 \rightarrow M(BH_4)_n + n\text{LiCl} \tag{2}$$

$$MCl_n + n\text{NaBH}_4 \rightarrow M(BH_4)_n + n\text{NaCl} \tag{2'}$$

The samples thus prepared were examined by powder X-ray diffraction measurement (PANalytical X'PERT with Cu Kα radiation), Raman spectroscopy (Nicolet, Almega-HD, 532 nm laser with back scattering geometry) and thermal desorption spectroscopy detected by gas chromatography (GL Science GC323, Ar flow rate of 40 ml/min and a heating rate of 5 K/min), and by mass-spectroscopy (Anelva M-QA200TS, He flow rate of 100 ml/min and heating rate of 5 K/min) combined with thermogravimetry (Rigaku, TG8120, He flow rate of 100 ml/min and a heating rate of 5 K/min). The samples were always handled in a glove box filled with purified Ar/He (dew point below 183 K) without exposing the samples to air. The experimental details were described elsewhere [18].

3. Results and discussion

3.1. Syntheses of M(BH4)n

Fig. 1(a and b) shows the powder X-ray diffraction profiles of the samples after mechanical milling of $MCl_n + n$LiBH$_4$ and $MCl_n + n$NaBH$_4$, respectively. There are broad diffraction peaks around 20° in all profiles of Fig. 1(a), originating from the diffraction of tape covering the samples to avoid (hydro-)oxidation by exposure to air. In Fig. 1(a), the diffraction peaks measured after mechanical milling of $MCl_n + n$LiBH$_4$ are identified as LiCl, although peak shifts were observed, probably due to the partial substitution of M for Li in LiCl. There are no diffraction peaks of the starting materials of MCl_n and $LiBH_4$, indicating that the reaction in Eq. (2) has progressed to completion. On the other hand, the starting materials of MCl_n and $NaBH_4$ were obviously present confirmed in the diffraction profiles for M = Ca, Sc and Al, as shown in Fig. 1(b). Moreover, the peak positions of NaCl in the profiles prepared by mechanical milling of $MCl_n + n$NaBH$_4$ shift to lower angles for M = Ti,

V, Cr, Mn and Zn. These results indicate that the reaction of Eq. (2') did not proceed to completion under the milling conditions in this experiment. In other words, the reaction of Eq. (2) (starting materials of $MCl_n + n$LiBH$_4$) proceeds easier than the reaction of Eq. (2') (starting materials of $MCl_n + n$NaBH$_4$) in the mechanical milling process.

The enthalpy changes of the synthesis reactions for Eqs. (2) and (2'), ΔH_{syn}, are deduced using our calculated heat of formation for $M(BH_4)_n$, ΔH_{boro} [14] and those reported for MCl_n, e.g., −408 and −411 kJ/mol for LiCl and NaCl, respectively [19]. The results are shown in Fig. 2. The calculated values of the enthalpy changes for Eq. (2') have more negative values than
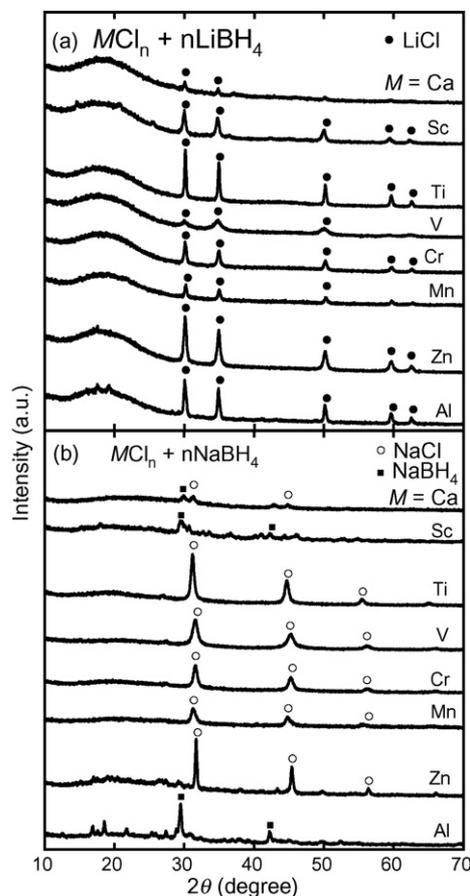

Fig. 1. Powder X-ray diffraction profiles of the samples after mechanical milling of (a) $MCl_n + n$LiBH$_4$ and (b) $MCl_n + n$NaBH$_4$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al).
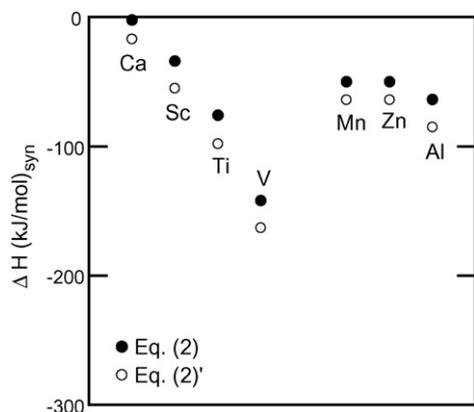
Fig. 2. Deduced enthalpy changes of the synthesis reactions for Eqs. (2) and (2′), ΔH_{syn}. The heats of formation of $M(BH_4)_n$, ΔH_{boro}, for M = Li, Na, Ca, Sc, Zn and Al from our previous work were used (−161, −156, −151, −71.7, 15.4 and −9.5 kJ/mol BH_4, respectively), while the remaining heats of formation were deduced using the linear relationship $\Delta H = 248.7\chi_P − 390.8$ in the units of kJ/mol BH_4 [14]. The reported values for LiCl (−408 kJ/mol) and NaCl (−411 kJ/mol) [19] were also used for these calculations.

those of Eq. (2). Therefore, the reaction in Eq. (2′) is expected to proceed easier, while the reaction of Eq. (2) proceeds readily in this experiment. One of the reasons for the progression of the reaction of Eq. (2) seems to be faster kinetics due to the similar ionic radii of Li^+ and M^{n+} in the solid–solid cation exchange reaction; the ionic radius of Li^+ (0.076 nm) is closer to those of Sc^{3+} (0.075 nm), Ti^{3+} (0.067 nm), V^{3+} (0.079 nm), Cr^{2+} (0.073 nm), Mn^{2+} (0.067 nm) Zn^{2+} (0.074 nm) and Al^{3+} (0.054 nm) than that of Na^+ (0.102 nm) [20].

There are no X-ray diffraction peaks of $M(BH_4)_n$ in the profiles of the samples prepared by mechanical milling, probably due to the absence of any long range order in the structure. Therefore, the atomic vibrations were investigated by Raman spectroscopy in order to confirm the existence of $M(BH_4)_n$. The Raman spectra of the samples measured after mechanical milling of $MCl_n + nLiBH_4$ are shown in Fig. 3. The spectrum of $LiBH_4$ is also shown as reference [18]. The Raman peaks were observed at around 2200–2500 and 1100–1400 cm^{-1} for M = Li, Ca, Sc, Ti, Cr, Mn, Zn and Al. These results agree fairly well with theoretical predictions for free $[BH_4]^-$ anion; the normal mode frequencies are 2225 cm^{-1} and 2236 cm^{-1} for B−H stretching modes and 1029 cm^{-1} and 1154 cm^{-1} for B−H bending modes [21]. Raman spectroscopy measurements for M = V were not successful because the sample was charred by laser irradiation. The products of Eq. (2), LiCl and $M(BH_4)_n$, were confirmed in the samples by powder X-ray diffraction measurements and Raman spectroscopy, respectively, except for M = V.

3.2. Thermal desorption properties of $M(BH_4)_n$

Fig. 4 shows the thermal desorption profiles of the mixture of $MCl_n + nLiBH_4$ (M = Ca, Sc, Ti, V, Cr, Mn, and Zn) after mechanical milling as detected by gas-chromatography. The previous results for M = Li, Na and K are shown for reference [14]. Although the samples contain not only $M(BH_4)_n$ but also LiCl, the thermal desorption profiles originate only from
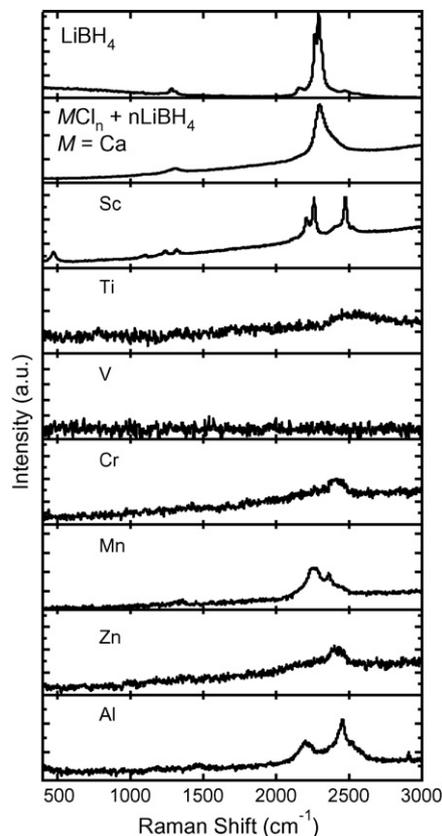

Fig. 3. Raman spectra of the samples measured after mechanical milling of $MCl_n + nLiBH_4$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al). The Raman spectrum of $LiBH_4$ is also shown for reference.

$M(BH_4)_n$, because LiCl decomposes at temperatures higher than 878 K. The hydrogen desorption peaks of $M(BH_4)_n$ decrease with increasing values of χ_P of M. Here, the desorption temperature T_d was defined as the temperature of the first peak, and T_d as a function of χ_P was plotted in Fig. 5. A linear relationship was observed between T_d and χ_P, indicating that χ_P
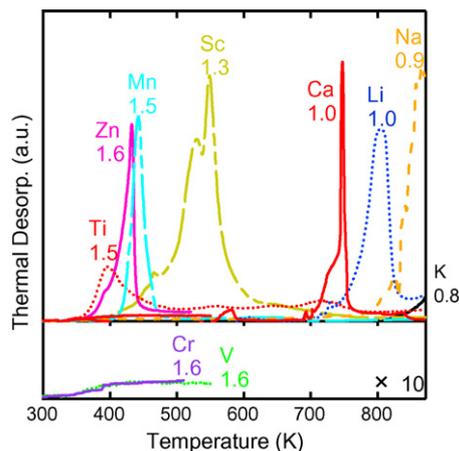

Fig. 4. Thermal desorption profiles of the samples of $MCl_n + nLiBH_4$ (M = Ca, Sc, Ti, V, Cr, Mn, and Zn) after mechanical milling detected by gas-chromatography. The results of MBH_4 (M = Li, Na and K) are also shown as references. Pauling electronegativity χ_P is shown below each M. The decomposition reaction for M = Al cannot be studied because its boiling temperature is 317 K.
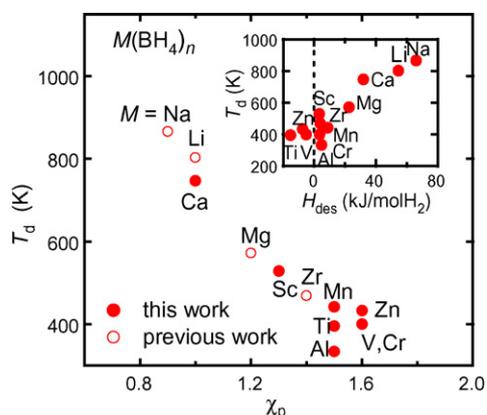
Fig. 5. The desorption temperature T_d as a function of the Pauling electronegativity χ_p. The previous results for $M(BH_4)_n$ ($M = Li$, Na, Mg and Zr) are also shown as references [14]. (The thermal desorption temperature for $Al(BH_4)_3$ was the first peak temperature of Fig. 6). The inset shows the correlation between T_d and estimated ΔH_{des} for the desorption reaction.

is a good indicator for approximate estimations of the T_d of $M(BH_4)_n$ (M = elements of fourth period in periodic table and Al), approximately.

Since $M(BH_4)_n$ desorbs hydrogen accompanying the formation of hydrides and/or borides, the stabilities of the decomposed products should be taken into account. We assume that $M(BH_4)_n$ (M = Sc, Ti and V) decompose into hydrides in the first desorption reaction as follows:

$$M(BH_4)_n \rightarrow MH_m + nB + \tfrac{1}{2}(4n - m)H_2 \qquad (3)$$
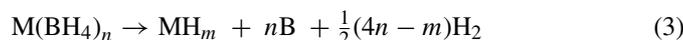
For M = Cr, Mn, Zn and Al, decomposition into elements was assumed due to the instability of MH_m. The decomposition reaction for $Ca(BH_4)_2$ is described in literature [22]; $Ca(BH_4)_2$ decomposes to $2/3CaH_2$, $1/3CaB_6$ and $10/3H_2$. The enthalpy change for the desorption reaction, ΔH_{des}, was estimated using the predicted ΔH_{boro} for $M(BH_4)_n$ [14] and the reported experimental data for product e.g., ΔH_{hyd} [1,2,23]. The estimated ΔH_{des} as a function of observed T_d is depicted in the inset of Fig. 5. A good correlation between ΔH_{des} and T_d was observed, indicating that ΔH_{des} can be approximately estimated using the reported ΔH_{boro} [14]. However, there is a deviation from linear in the relationship between ΔH_{des} and T_d for M = Mn, Cr and Al ($\chi_P \geq 1.5$). This difference might be due to the weak ionic bonding between M^{n+} and $[BH_4]^-$ because of their unclosed and delocalized 3d electron shell. Another possibility for the cause of the deviation is that the assumption of desorption reaction is incorrect, or that kinetics influence the observed T_d. In order to discuss ΔH_{des} in detail for the desorption reaction, we are currently investigating the actual hydrogen desorption equation using well crystallized $M(BH_4)_n$ synthesized in solution.

Finally, mass-spectroscopy and thermogravimetry have been carried out in order to investigate the components of the desorbed gas. From the results of mass-spectroscopy (Fig. 6(a)), the components of desorbed gas for M = Ca, Sc, Ti, V and Cr ($\chi_P \leq 1.6$) are confirmed to be only hydrogen within the accuracy of our apparatus. However, those for M = Mn, Zn and Al ($\chi_P \geq 1.5$) contain borane in addition to hydrogen. Weight loss for M = Mn, Zn and Al as observed by thermogravimetry are larger than the

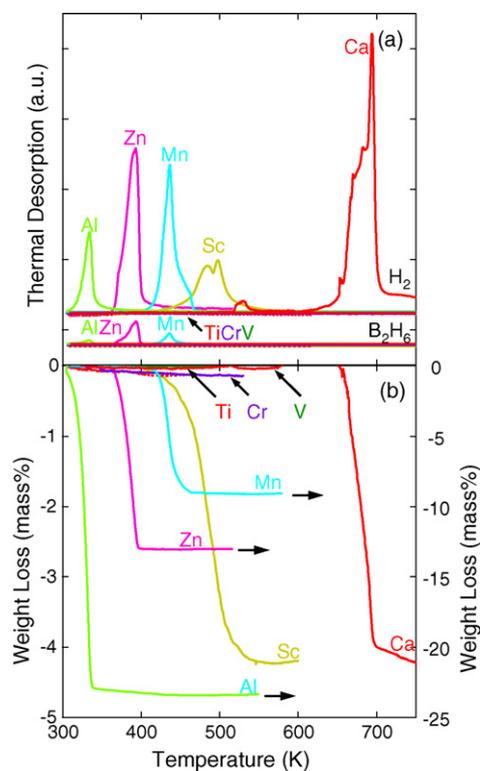Fig. 6. Thermal desorption profiles of the samples of $MCl_n + nLiBH_4$ (M = Ca, Sc, Ti, V, Cr, Mn, Zn and Al) after mechanical milling detected by (a) mass-spectroscopy and (b) thermogravimetry. In (b), the right vertical axis is for M = Mn, Zn Al. The differences in the peak features and peak temperatures between the thermal desorption profiles detected by gas-chromatography (Fig. 4) and those detected by mass-spectroscopy (a) seems to be due to different conditions, such as heating atmospheres, gas-flow rates, temperatures and the length of gas flow routes.

theoretical values, as shown in Table 1. On the other hand, the measured weight losses for M = Ti, V and Cr ($\chi_P = 1.5$ and 1.6) are significantly smaller than the theoretical values, while those for M = Ca and Sc correspond to the theoretical values as summarized in Table 1. Therefore, $M(BH_4)_n$ ($\chi_P < 1.5$) is expected to be a candidate hydrogen storage material with appropriate stability and without desorbing borane. The adjustment of the desorption temperature using two kind of mixed cations is also under investigation [24].

4. Summary

In order to clarify the correlation between the stability of borohydrides and the cation electronegativity χ_P of M, $M(BH_4)_n$ (M = Ca, Sc, Ti, V, Cr, Mn, Zr (elements at fourth period in periodic table) and Al; n = 2–4) were synthesized by mechanical milling and the thermal desorption properties were investigated. The mixture of MCl_n and $nLiBH_4$ changes into $M(BH_4)_n$ with $nLiCl$ by mechanical milling, which was confirmed by Raman spectroscopy and powder X-ray diffraction measurement, respectively. The results of thermal desorption reactions indicated that T_d decreases with increasing values of χ_P of $M(BH_4)_n$ (M = element in the fourth period in the periodic table or Al). The estimated ΔH_{des} for the desorption reaction corre-

lates well with T_d, whereas a deviation from a linear relationship appears in $M(BH_4)_n$ with $\chi_P \geq 1.5$. Moreover, the components of desorbed gas from M = Mn, Zn and Al ($\chi_P \geq 1.5$) contain borane, and a small amount of hydrogen is confirmed for M = Ti, V, Cr ($\chi_P \geq 1.5$). Therefore, the appropriate χ_P of $M(BH_4)_n$ for hydrogen storage is expected to be smaller than 1.5, and the predicted relationship between ΔH_{boro} and χ_P is a useful indicator for estimating ΔH_{des} for $M(BH_4)_n$.

Acknowledgements

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