Direct Dry Syntheses and Thermal Analyses of a Series of Aluminum Complex Hydrides

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Synthesis of a series of aluminum complex hydrides, namely, LiAlH₄, Li₃AlH₆, NaAlH₄, Na₃AlH₆, Mg(AlH₄)₂, MgAlH₆, Ca(AlH₄)₂, and CaAlH₄, was attempted by the mechanochemical milling of AlH₃ and the other elemental hydrides. Aluminum complex hydrides, except MgAlH₆, were synthesized, and their dehydriding (decomposition) properties were systematically investigated by thermogravimetry. The dehydriding temperatures possibly showed a correlation with the geometrical distances in space between M⁺ (M₀) and H in the crystal structures of the aluminum complex hydrides. [doi:10.2320/matertrans.MER2008251]

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1. Introduction

Aluminum complex hydrides M(AlH₄)ₙ (M: typically alkali or alkaline-earth metals; n: valence of M) have been intensively studied as candidates for hydrogen storage materials because of their high gravimetric hydrogen densities, reversible reactions under moderate conditions (temperatures and hydrogen pressures), and also their release of hydrogen without impurity gases.¹⁻¹¹ It has been reported that M'AlH₄ (M': alkali metals) decomposes into M'₃AlH₆ upon heating and that one molar of hydrogen is released.¹¹

\[ M'AlH₄ → 1/3M'₃AlH₆ + 2/3Al + H₂ \]  \( (1) \)

For example, LiAlH₄ decomposes into Li₃AlH₆, which has isolated AlH₄-units in the crystal structure.¹¹⁻¹³ On the other hand, M'(AlH₄)₂ (M': alkali-earth metals) has been reported to decompose into the intermediate phase, M'₂AlH₃, as follows:¹⁰,¹¹,¹⁴⁻¹⁶

\[ M'(AlH₄)₂ → M'₂AlH₃ + Al + 3/2H₂ \]  \( (2) \)

Ca(AlH₄)₂ decomposes into CaAlH₆, which has corner-shared AlH₄-units in the crystal structure.¹⁴⁻¹⁵ Corner-shared AlH₄-units are probably a characteristic of aluminum complex hydrides containing alkaline-earth metals (Ex. BaAl-H₃¹⁷), although the structure of MgAlH₆ is still unclear.¹⁸⁻²⁰

Systematic studies on aluminum complex hydrides are quite important to obtain further insights on various complex hydrides as candidates for hydrogen storage materials. For example, on the basis of theoretical studies, Løvvik et al. predicted that an interaction between M⁺ and H can affect the thermal stability of M'AlH₄ and M'₃AlH₆.²¹ These interactions were explained given the existence of a geometrical space between M⁺ and H along with the results of crystal orbital overlap population (COOP) calculation. Experimental data on crystal structures and thermal analyses of aluminum complex hydrides are indispensable for confirming the results of theoretical studies.

For performing systematic experimental studies, the synthesis of solvent-free high-quality samples of aluminum complex hydrides are required. There are two methods for the synthesis of hydrides: wet synthesis (metathesis and precipitation reactions in solutions)²² and dry synthesis (solid-solid and/or solid-gas reactions).¹¹ In the latter case, for example, LiAlH₄ has been synthesized from LiH, Al and TiCl₃,²³ Na₃AlH₆ has been synthesized from NaH, Al and TiF₃,²⁴,²⁵ and Ca(AlH₄)₂ has been synthesized from CaCl₂ and NaAlH₄.²⁶

In the present study, for synthesizing aluminum complex hydrides, we focused on the “direct” dry synthesis method, namely, the mechanochemical milling of elemental hydrides AlH₃ and M'H or M'H₂ (M': Li, Na; M⁺': Mg, Ca).²⁷,²⁸ The possible advantages of this simple but reliable synthesis method are as follows: (1) elemental hydrides including AlH₃ are inductile materials (in contrast to Al) that promote mechanochemical milling and (2) AlH₃ exhibits an unstable property, the observed formation enthalpy of which is 9–12 kJ/mol AlH₃²⁹⁻³¹ and also promotes the formation of more stable complex hydrides.¹¹,³²

In the present study, firstly, a series of aluminum complex hydrides was synthesized by the direct dry synthesis method from elemental hydrides. Secondly, the samples were studied to elucidate the thermal properties of the complex hydrides. Finally, the obtained data were used to show a possible correlation between the dehydriding (decomposition) temperatures, and the geometrical distances in space between M⁺ (M₀) and H in the crystal structures for a series of aluminum complex hydrides.

2. Experimental Procedures

The starting elemental hydride α-AlH₃ was prepared in ether according to the chemical reactions of LiAlH₄ and AlCl₃ (as described in Ref. 33), and X-ray diffraction peak positions were identified as α-AlH₃ (Fig. 1).³⁴ Powders of elemental hydrides, namely, LiH (CERAC 99.99%), NaH (Aldrich 95%), MgH₂ (Alfa Aesar 98%), CaH₂ (Aldrich 99.99%), and AlH₃, were mixed with chemical compositions of LiAlH₄, Li₃AlH₆, NaAlH₄, Na₃AlH₆, Mg(AlH₄)₂, MgAlH₆, Ca(AlH₄)₂, and CaAlH₄. A mixture of AlH₃ and the other elemental hydrides (weighing a total of 200 mg) was...
mechanochemically milled by using Fritsch P7 at 400 rpm at a hydrogen gas pressure of 0.3 MPa for up to 20 h, milling times of 5 min being alternated with 5 min of rest. All the samples were investigated by using an X-ray diffractometer (PANalytical X’PERT, with Cu-Kα radiation). Simulated X-ray diffraction patterns were generated by PowderCell 1.0. To investigate the dehydriding (decomposition) temperatures and the amounts of released hydrogen, the samples were then studied by thermogravimetry (TG, Rigaku TG-8210, with an Al sample holder) and heated up to 673 K at 5 K/min in a He gas flow of 150 ml/min. All the samples were handled in an Ar- or He-gas-filled glove box with a dew point below 183 K and with less than 1 ppm of O₂ in order to avoid (hydro-)oxidation.

3. Results and Discussion

Mechanochemical milling of only α-AlH₃ accelerates the dehydriding (decomposition) reaction and forms elemental Al in less than 1 h, especially at the beginning stage of the milling. Interestingly, the successful milling of α-AlH₃ together with the other elemental hydrides, however, results in the synthesis of aluminum complex hydrides, as explained below. It is assumed that the other elemental hydrides that are attached to the surface of α-AlH₃ prevent the dehydriding (decomposition) reaction of α-AlH₃, although the detailed mechanism is still under investigation.

LiAlH₄ and Li₃AlH₆ were synthesized by the mechanochemical milling of LiH and α-AlH₃ for 5 h. The X-ray diffraction patterns in Fig. 2 are in good agreement with the simulated patterns. By the same synthesis procedures (the milling time was optimized for each hydride), NaAlH₄ (milling time: 5 h), Na₃AlH₆ (10 h), Mg(AlH₄)₂ (10 h), Ca(AlH₄)₂ (10 h), and CaAlH₅ (5.5 h) were also identified from X-ray diffraction patterns (Fig. 2). Although MgAlH₅ has been reported to be formed from Mg(AlH₄)₂ as an intermediate phase, no evidence of its formation was obtained under the present synthesis conditions. The X-ray diffraction patterns of the samples (5 and 20 h) corresponded to Mg(AlH₄)₂, MgH₂, α-AlH₃, and Al peaks (Fig. 2).

![Fig. 1 X-ray diffraction patterns of observed (top) and simulated (bottom) α-AlH₃.](image1)

![Fig. 2 Observed X-ray diffraction patterns of LiAlH₄, Li₃AlH₆, NaAlH₄, Na₃AlH₆, Mg(AlH₄)₂, Ca(AlH₄)₂, and CaAlH₅ (MgAlH₅ was not actually formed under the present synthesis conditions). Simulated X-ray diffraction patterns of LiAlH₄, Li₃AlH₆, NaAlH₄, Na₃AlH₆, Mg(AlH₄)₂, MgH₂, (MgAlH₅), NaAlH₄, Mg(AlH₄)₂, MgH₂, Mg(AlH₄)₂, Ca(AlH₄)₂, and CaAlH₅ locate under each observed pattern.](image2)
The unit cell parameters of all the aluminum complex hydrides, except MgAlH₄, were calculated by TREOR⁴² and PIRUM⁴³ and are summarized in Table 1.

Dehydriding properties of thus synthesized M’AlH₄, M₃AlH₆, M”(AlH₄)₂ and M”AlH₃ were systematically investigated by thermogravimetry (TG), as shown in Fig. 3. Upon heating, LiAlH₄ has been reported to decompose and release hydrogen according to the following reactions:¹¹,¹²)

LiAlH₄

→ 1/3Li₃AlH₆ + 2/3Al + H₂ ↑ (−5.3 mass%) (3a)

→ LiH + Al + 1/2H₂ ↑ (−2.7 mass%) (3b)

→ LiAl + 1/2H₂ ↑ (−2.7 mass%) (3c)

As shown in Fig. 3(a), LiAlH₄ exhibited two-step mass changes from hydrogen release with amounts of 4.7 mass% (onset temperature of 426 K) and 2.3 mass% (459 K) that correspond to eqs. (3a) and (3b), respectively. Furthermore, Li₃AlH₆ is also assumed to obey the following reactions:

Li₃AlH₆ → 3LiH + Al + 3/2H₂ ↑ (−5.6 mass%) (3d)

→ Li-Al alloy + 3/2H₂ ↑ (−5.6 mass%) (3e)

In fact, we can confirm that 4.9 mass% of hydrogen was released from Li₃AlH₆ (476 K), corresponding to eq. (3d) (also shown in Fig. 3(a)).

Next, NaAlH₄ has been reported to decompose and release hydrogen according to the following reactions:¹³–³⁵,⁷,¹¹,³²)

NaAlH₄

→ 1/3Na₃AlH₆ + 2/3Al + H₂ ↑ (−3.7 mass%) (4a)

→ NaH + Al + 1/2H₂ ↑ (−1.9 mass%) (4b)

→ Na + Al + 1/2H₂ ↑ (−1.9 mass%) (4c)

As shown in Fig. 3(c), NaAlH₄ exhibited two-step hydrogen release with amounts of 2.7 mass% (507 K) and 2.9 mass% (610 K) that correspond to eqs. (4d) and (4e), respectively (Fig. 3(b)).

Furthermore, Mg(AlH₄)₂ has been reported to decompose and release hydrogen according to the following reactions:¹⁰,¹¹,¹⁶)

Mg(AlH₄)₂

→ MgH₂ + 2Al + 3H₂ ↑ (−7.0 mass%) (5a)

→ Mg + 2Al + H₂ ↑ (−2.3 mass%) (5b)

As shown in Fig. 3(c), Mg(AlH₄)₂ exhibited two-step hydrogen releases with amounts of 5.5 mass% (410 K) and 1.9 mass% (534 K) that correspond to eqs. (5a) and (5b), respectively.

Finally, the reactions for Ca(AlH₄)₂ are suggested to be as follows:¹⁴,¹⁵)

Ca(AlH₄)₂

→ CaH₂ + 3Al + 3/2H₂ ↑ (−3.0 mass%) (6a)

→ CaH₂ + 2Al + 3/2H₂ ↑ (−3.0 mass%) (6b)

→ Ca-Al alloy + H₂ ↑ (−2.0 mass%) (6c)

According to Fig. 3(d), Ca(AlH₄)₂ released 2.2 mass% (415 K) and 2.2 mass% (499 K) of hydrogen by a two-step
reaction, which correspond to eqs. (6a) and (6b). On the other hand, compared to the reported one-step reaction of (6c), hydrogen was released by a two-step reaction, i.e., 0.4 mass% (561 K) and 0.2 mass% (618 K). A similar phenomenon also appears in the dehydriding reaction of the synthesized CaAlH$_5$, although it is predicted to release hydrogen according to the following reactions:

$$\text{CaAlH}_5 \rightarrow \text{CaH}_2 + \text{Al} + 3/2\text{H}_2 \uparrow (-4.2 \text{ mass}) \quad (6d)$$

$$\rightarrow \text{Ca-Al alloy} + \text{H}_2 \uparrow (-2.8 \text{ mass}) \quad (6e)$$

The dehydriding temperatures and the amounts of hydrogen release for all the samples are basically comparable to the previously reported dehydriding reactions. The results indicate that the direct solid reaction of $M\text{H}_n$ and $\text{AlH}_3$ by using mechanochemical milling is a new and reliable synthesis process of the aluminum complex hydrides. The optimization of the synthesis condition is under investigation to obtain higher quality aluminum complex hydrides with different thermodynamic stabilities.

It is generally known that in the aluminum complex hydrides, hydrogen covalently bonds to Al in complex anions, $[\text{AlH}_4^-]$ or $[\text{AlH}_6]^{3-}$, which form an ionic bonding with $M^{n+}$. On the other hand, a recent theoretical study proposed that there is a possible weak $M$-$H$ bonding, the strength of which depends on the distance in space between $M$ and $H$. In other words, a shorter $M$-$H$ distance weakens the Al-$H$ bonding and leads to a lower dehydriding temperature. Therefore, the onset temperatures of the dehydriding reaction of aluminum complex hydrides are plotted as a function of the distances in space between $M'$ ($M''$) and $H$. In this study, in order to estimate the distances, averaged $M'$ ($M''$)-$H$ distances were subtracted from total distances of the ionic radius of $H$ (0.110 nm) and that of $M'$. The result, shown in Fig. 4, roughly indicates that the shorter the distance in space between $M'$ ($M''$) and $H$, the stronger the interaction between them. This induces breakage of the Al-$H$ bonds and lowers the dehydriding (decomposition) temperatures of the aluminum complex hydrides.

Detailed studies on the dehydriding reactions of the aluminum complex hydrides including Ca(AlH$_4)_2$ and CaAlH$_5$, and on the correlation between dehydriding (decomposition) temperature and distance are required to obtain further insights on various complex hydrides for potential use as hydrogen storage materials.

4. Conclusions

The direct dry synthesis method was employed to obtain the aluminum complex hydrides from elemental hydrides. The hydrides, except MgAlH$_4$, were successfully synthesized and characterized by using a powder X-ray diffractometer.
Moreover, the dehydriding (decomposition) temperatures and the amounts of released hydrogen upon heating were investigated by TG. By the comparison study, the possible and the amounts of released hydrogen upon heating were

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complex hydrides was indicated.

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Fig. 4 Correlation between dehydrying temperature compared with the distances in space between M(\textsuperscript{M'}) and H. A six-coordinated ionic radius of Li was used for LiAlH\textsubscript{4} because five-coordinated ionic radius has not been reported. The dehydriding temperature of NaAlH\textsubscript{4} (483 K) was obtained from Ref. 44). Na\textsubscript{2}AlH\textsubscript{4} has two atomic positions for Na where one Na atom has eight-coordinations (0.219 nm on distance in space between Na and H) and the other has six-coordinations (0.133 nm). Li\textsubscript{2}AlH\textsubscript{4} and CaAlH\textsubscript{4} each have two plots that are Li\textsubscript{2}AlH\textsubscript{4} (495 K)/CaAlH\textsubscript{4} (499 K) decomposed from Li\textsubscript{2}AlH\textsubscript{4}/Ca(AlH\textsubscript{2})\textsubscript{2}, and directly synthesized Li\textsubscript{2}AlH\textsubscript{4} (476 K)/CaAlH\textsubscript{4} (530 K). BaAlH\textsubscript{4} was plotted on the basis of information provided in Ref. 45.

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