Relation between Melting and Dehydrogenation Temperatures of LiAlH₄

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The effect of melting of LiAlH₄ on its dehydrogenation properties was examined using Differential Scanning Calorimetry (DSC). LiAlH₄ samples purified in advance were examined on their hydrogen desorption behaviors in the various heating conditions in which some of them were melted and the others not. Some of the as-received samples were mechanically ground in an Ar atmosphere for a short time of period using a ball milling machine and then supplied to DSC measurements. The color of the sample after milling changes from gray-beige to grey, probably due to contamination of metal elements such as iron and chromium from hardened steel vessel and balls during grinding. The rapid hydrogen desorption was observed for the samples melted by heating, whereas the insignificant hydrogen desorption was observed for the ones which were not melted by heating, in spite that heating and cooling were repeated three times. The time from melting to decomposition of LiAlH₄ accompanied by hydrogen desorption was 90 ± 30 s, independent of hydrogen desorption temperature. The samples milled in hardened steel vessel using a planetary-type ball milling machine exhibited about 2 K lower melting temperature and 15 K lower hydrogen desorption temperature than the as-purified samples. These changes can be considered to happen because contamination metal elements contributed to lowering a melting temperature and worked as a catalyst to decrease the activation energy for decomposition of liquefied LiAlH₄. These results indicate that metal elements such as iron and chromium certainly contribute to improve hydrogen desorption temperatures of alanates, as reported in many papers, but it is more important to lower their melting temperatures in order to improve their hydrogen desorption kinetics.

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1. Introduction

Storing and transporting hydrogen becomes one of the key technologies to realize hydrogen energy system in the upcoming sustainable energy era. Hydrogen storage materials are one of promising candidates because they have highest volumetric hydrogen storage density and some of them can be operated under the moderate conditions such as atmospheric pressure and room temperature. But they have disadvantage on their weight hydrogen storage density because the metal cage accommodating hydrogen atoms is usually very heavy. Some of metal hydride complexes, for instance alanates MAIH₄ and borohydrides MBH₄ (M: alkaline metal), are composed of light metal elements such as lithium and aluminum, which means they have relatively higher weight hydrogen storage capacity than conventional hydrogen storage materials using heavy metals, and therefore they are very attractive for the application to the hydrogen storage tanks in fuel cell powered electric vehicles.

In 1997, Bogdanovic and Schwickardi reported the reversible hydrogenation behavior of NaAlH₄ with an addition of some metal catalysts¹ and since then a lot of research and development²−⁹ were performed on the improvement of hydrogen desorption temperature and kinetics or the mechanism for the effect of the metal catalysts (possible dopants). On the other hand, discussion is still remained about what is most important to lower hydrogen desorption temperatures or accelerate reaction kinetics of alanates. As far as we know, catalytic effect on alanates has been studied worldwide, but is the addition of catalysts (or dopants) only the way to improve the above-mentioned properties?

In the present study, we examined about the melting and hydrogen desorption behaviors of alanates WITHOUT the addition of catalyst in order to obtain the information and new hints to improve the hydrogen desorption properties of alanates. NaAlH₄ is more attractive than LiAlH₄ on the enthalpy change in hydrogen desorption and reversibility but it is not easy to observe the hydrogen desorption phenomenon for NaAlH₄ by using thermal analysis technique, according to the results of our pre-examinations. This is probably because endothermic heat due to decomposition of NaAlH₄ accompanied by hydrogen desorption is canceled by exothermic heat due to solidification of the system accompanied by the reaction of NaAlH₄(l) → $\frac{1}{3}$Na₃AlH₆(s) + $\frac{2}{3}$Al(s) + H₂. So we tried to obtain the information about LiAlH₄, which is considered that its decomposition is exothermic, contrarily with NaAlH₄.

2. Experimental Details

Raw material was powdered LiAlH₄ (Aldrich Co. Ltd.) of 95% in purity. The color of this hydride is originally white, but that of the raw material was beige-gray, indicating it might contain some impurity, so it was solved in diethyl ether solution in which water was removed in advance and then purified by filtration followed by evaporation of solute. The color of this purified LiAlH₄ was white, indicating that impurity was effectively removed.

Some of as-received sample was ground with a ball mill equipment (Fritsch P-6). The sample was milled at 400 rpm together with hardened steel balls in a hardened steel vessel filled with Ar gas of 0.3 MPa for 1.8 ks. The melting and
dehydrogenation behaviors of the sample was examined with a differential scanning calorimeter (RIGAKU DSC8230HP), where the measurements were conducted at 10 K/min in heating and cooling rate under hydrogen atmosphere of 1 MPa. The operations described above were conducted in inert gas atmosphere dried less than 190 K of dew point, in order to avoid the reaction of the sample with oxygen and water.

3. Results

Figure 1 shows the heat flow profiles of the first heating and cooling cycle for as-purified LiAlH$_4$ samples heated up to various temperatures in DSC measurements, where heating rate is 10 K/min and atmosphere inside is 1 MPa of hydrogen. The samples were heated up to 423, 441, 455 and 473 K, respectively. The melting point of pure LiAlH$_4$ is 436–437 K, which means the sample heated up to 423 K did not undergo melting. Insignificant peaks were observed for the sample heated to 423 K, whereas the other samples showed two exothermic peaks and one endothermic peak. The exothermic peak around 430 K observed in heating was probably due to impurities which still remained even after purification treatment, because this peak was observed as very strong one for the as-received sample, without purification. The endothermic peak observed around 435–450 K was corresponding to melting of LiAlH$_4$, where the temperature was slightly higher than the known melting point due to superheating. The other exothermic peaks corresponded to the following reaction LiAlH$_4$(l) $\rightarrow \frac{1}{3}$Li$_3$AlH$_4$(s) + $\frac{2}{3}$Al(s) + H$_2$(g), which includes not only decomposition accompanied by the hydrogen desorption but also solidification of the system. Interestingly, the hydrogen desorption temperatures were respectively 430, 451 and 465 K for the samples heated up to 441, 455 and 473 K, depending on the maximum heating temperature. These three samples did not exhibit any exothermic and endothermic peaks in the second cycle of heating up to 473 K and cooling to room temperature, indicating that the decomposition described above completed within only one heating and cooling cycle.

430 K of hydrogen desorption temperature observed for the sample heated up to 441 K was lower than 436–437 K of the melting point of LiAlH$_4$, probably due to supercooling of the melt. It can be noted that the hydrogen desorption temperature is lowered by 35 K only by controlling the heating conditions such as maximum temperature.

We assumed that the difference in the hydrogen desorption temperature of LiAlH$_4$ was caused depending on the time of period after melting. The time was investigated for the three samples and the results are listed in Table 1. The time until hydrogenation after melting does not strongly depend on the hydrogen desorption temperature but can be regarded as constant, taking an experimental error into account. Experiments were conducted for the reproducibility and it was found that the time of period from melting to hydrogen desorption was approximately 90 ± 30 s, independent of temperature of the melt.

The sample heated up to 423 K was repeatedly heated to 423 K and cooled to room temperature twice more but any

![Fig. 1 Heat flow profiles of as-purified LiAlH$_4$ heated up to 423, 441, 455 and 473 K under hydrogen atmosphere of 1 MPa. Heating and cooling rate was 10 K·min$^{-1}$.](image)

| Maximum heating temperature/K | 441 | 455 | 473 |
| Hydrogen desorption temperature/K | 430 | 451 | 460 |
| Time of period from melting to decomposition/s | 80 | 95 | 105 |
peaks indicating some reactions occur were not observed. Then it was heated to 473 K and the heat flow profile is shown in Fig. 2. The sample exhibited an endothermic peak followed by an exothermic one, which are corresponding to melting and decomposition of LiAlH₄, respectively. This fact indicates that the decomposition rate of solid LiAlH₄ is very slow compared with liquid one and therefore LiAlH₄ remains to some extent even after heating and cooling of three times.

The color of the milled sample was gray, changed from that of as-received one (beige-gray). It is considered to be due to contamination from hardened steel vessel and balls during ball milling. Although it is difficult to know the quantitative amount of the impurities because the sample reacted with oxygen or water in the air before quantitative analysis, the content of impurity element such as Fe was estimated to be less than 1 mol%, judging from weight change of the sample due to milling. The heat flow profile of the milled sample is shown with that of the as-received one in Fig. 3. The melting temperature of the milled sample was slightly (about 2 K) lower than the as-received one but the dehydrogenation temperature was significantly lowered (about 15 K). Since the hydrogen desorption occurred after melting, the contamination rather than pulverization of sample powder during grinding seems to affect the change in hydrogen desorption temperature. It is well-known that some transition metal catalysts (possible dopants) significantly decrease the dehydrogenation temperature of alantes.¹⁻⁹ So it can be considered that metal contaminants such as iron and chromium are responsible for the lowering of dehydrogenation temperature.

### 4. Discussion

As described above, LiAlH₄ in liquid state shows much faster decomposition than the one in solid state and the decomposition occurs within about 90 s after melting. As found in the equation for the decomposition, the hydrogen desorption of LiAlH₄ requires not only the diffusion of hydrogen atoms but also that of the constituent metal atoms Li and Al. In liquid state, not only mutual diffusion but also convection can occur and the latter is considered to more significantly contribute to the migration of constituent atoms, so metal atoms required for the reaction can be supplied to the interface between reactant and product. Some of the product particles might be removed by convection of liquid. Therefore, the experimentally obtained facts imply that long-range diffusion of constituent metal atoms is one of the major rate-controlling factors in the decomposition reaction of LiAlH₄. Balema and Balema⁹ have pointed out that the enhancement of mass transfer in solid materials causes decomposition of LiAlH₄ with catalyst during milling, which may support our results. The report on the relation between melting and hydrogen desorption temperatures for MBH₄ (M: Li, Na, K, Rb and Cs) also indicated that the hydride with lower melting temperature possessed lower hydrogen desorption temperature,¹⁰ where the authors reported on the systematic relation between B–H atomistic vibrations in BH₄⁻ anion and melting and hydrogen desorption temperatures, and therefore further study may be necessary from the standpoint of Al–H atomistic vibration. On the other hand, the transition metals contaminating the samples during milling can be considered to contribute to the lowering of activation energy for nucleation of solid product in the present case where the decomposition occurs in liquid state, because we do not have any evidence that metal impurities can accelerate the convection of liquid LiAlH₄.

In the present study, the hydrogen desorption temperature was lowered by about 35 K by adequately adjusting the maximum heating temperature. Taking it into account that the time of period from melting to decomposition is approximately constant regardless the temperature, lowering the melting temperatures of alanates can be very effective for the improvement of their hydrogen desorption temperature and kinetics. Figure 4 shows the pseudo-binary phase diagram of NaAlCl₄–KAlCl₄ system,¹¹ which is a typical eutectic system. The melting temperatures of NaAlCl₄ and KAlCl₄ are respectively 427 and 519 K and lowered down to 402 K for the mixture with the eutectic composition of 3:7 in the molar ratio of KAlCl₄ to NaAlCl₄. In analogy of the eutectic system as shown in Fig. 4, there is some possibility to decrease the melting temperature of alanates by mixing them with other elements and compounds. We are studying about the effect of mixing of alanate with another compound on the melting and dehydrogenation temperatures and the results will be reported in other papers.
5. Conclusions

In order to obtain the information and new hints to improve the hydrogen desorption temperatures of alanates, the melting and dehydrogenation phenomena of LiAlH$_4$ were examined under the various conditions. The results can be summarized as follows:

1. The hydrogen desorption accompanied by decomposition of LiAlH$_4$ in liquid state is much faster than that in solid state. Long-range diffusion of constituent metal atoms is one of the rate-controlling factors at least for the decomposition of LiAlH$_4$.

2. The time of period from melting to hydrogen desorption is about 90 ± 30 s for the decomposition of LiAlH$_4$, independent of the temperature of melt.

3. The melting temperature of alanates can be lowered by mixing them with another elements, alloys, complexes and compounds. The hydrogen desorption properties such as temperature and kinetics would be improved by the lowering of the melting temperature.

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