Hydrogen release of catalyzed lithium aluminum hydride by a mechanochemical reaction

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Abstract

The effects of various catalysts on the H_2 release characteristics of $LiAlH_4$ were studied. It was established that the catalytic activity defined by the H_2 desorption capacity by a mechanochemical reaction decreased in the series $TiCl_3 > ZrCl_4 > VCl_3 > NiCl_2 > ZnCl_2$. Transition metal trialuminides Al_3X (X=Ti, Zr, V, Ni) were prepared by the mechanochemical reaction of $LiAlH_4$ and the metal chlorides, while the reaction of $LiAlH_4$ and $ZnCl_2$ yields Zn. The high catalytic activity was attributed to the lower percentage d-character and the electronegativity of those transition metals. The catalytic activity of Ni was also improved with decreasing the Ni particle size. Those catalysts were classified to two groups (1. $TiCl_3$, $ZrCl_4$, 2. VCl_3, $NiCl_2$, Ni, nano-Ni) from the viewpoint of the H_2 desorption mechanism.

1. Introduction

A high-pressure MH tank with a heat-exchanger module containing $Ti_{1.1}CrMn$ (300kg) has been developed [1-3]. The measured H_2 capacity at 35 MPa was $7.3kgH_2/180L$ (outer volume), which was 2.5 times of the high pressure tank (35MPa). This indicated that FCV with the high-pressure MH tank has a driving range of about 700 km. But, the high-pressure MH tank was heavy (420kg) because the gravimetric H_2 density of $Ti_{1.1}CrMn$ had a low value of 1.8 wt%. Storage of high H_2 densities in light weight solids is a solution to this problem.

Light weight complex hydrides, such as sodium aluminum hydride ($NaAlH_4$) [4-8] and lithium aluminum hydride ($LiAlH_4$) [9-12] are considered attractive as hydrogen storage materials due to their large hydrogen content. The reversible hydrogen storage has been formed by doping $NaAlH_4$ with transition metal-based catalysts [4-8]. Unfortunately, only 3-4.5 wt % H_2 can be stored and recovered in reasonable time at 373-398 K [7]. For useable H_2 storage, H_2 absorption and desorption around room temperature is necessary. It has been reported that $LiAlH_4$ can be easily transformed into lithium hexahydridoaluminate Li_3AlH_6, Al and H_2 in the presence of catalysts or prolonged ball-milling at room temperature, which corresponds to the H_2 desorption capacity of 5.3 wt% [9-12].

In this paper, the effect of various metal chlorides and elemental nickel on dehydrogenation properties of $LiAlH_4$ will be presented.

2. Experimental

2.1 Materials

Lithium aluminum hydride $LiAlH_4$ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 37.95, density: 0.92 g/cm^3), titanium trichrolide $TiCl_3$ (Sigma-Aldrich, molecular weight:154.26), zirconium tetrachloride $ZrCl_4$ (Wako Pure Chemical Industries,

Ltd. Japan, molecular weight: 233.03), vanadium trichloride VCl_3 (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 157.30), nickel dichloride $NiCl_2$ (Kojundo Chemical Laboratory Co., Ltd., molecular weight:129.62), zinc chloride $ZnCl_2$ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 136.30), nickel Ni (Soekawa Chemicals Co., Ltd., diameter: 0.8 μm) and nano-Ni (Shinku Yakin Kogyo KK, Japan, diameter: approximately 20 nm) were used in this study. The mill container (Cr-Mo steel pot, internal volume: 300 mL) was loaded with 5 g of $LiAlH_4$ and a catalyst with 95:5 or 1:1 weight ratio and 40 pieces of steel ball with a diameter of 9.5 mm. The mixtures were milled at 400 rpm for 5 min-24 h in an Ar gas pressure of 0.1 MPa at room temperature (296 K) using a planetary ball mill (Fritsch P-5).

2.2 Characterization

With a specially designed apparatus, temperature programmed desorption (TPD) scans were carried out at a heating rate of 2 K/min in an Ar flow of 85 mL/min. H_2 desorption capacities were estimated from the peak area of the TPD spectra. Transmission electron micrographs were obtained with a high-resolution transmission electron microscope (JEOL JEM-2010FEF) using an acceleration voltage of 200 kV. The composition of specimens was measured by an energy dispersive X-ray spectroscopy (EDS). X-ray diffraction intensity curves in an inert atmosphere (Ar) were recorded with CuKα radiation (50 kV, 300 mA) filtered by a monochrometer using Rigaku Rint-TTR.

3. Results and discussion

$LiAlH_4$ doped with 5 wt% of $TiCl_3$ desorbed only 0.3 wt% of H_2 by the TPD measurement T<600K, which indicated 7.2 wt% of H_2 was desorbed during ball-milling for 24 h at room temperature. The H_2 desorption capacity of ball-milled $LiAlH_4$ doped with various metal chlorides (5 wt%, milling: 24 h) decreased in the series [$TiCl_3$ (7.2 wt%) >

$ZrCl_4$ (6.4 wt%)>VCl_3 (4.8 wt%)>$NiCl_2$ (1.1 wt%)>$ZnCl_2$ (0)].   The ball-milled $LiAlH_4$ doped with $ZnCl_2$ did not destabilize $LiAlH_4$.

   The X-ray diffraction (XRD) patterns of the $LiAlH_4$ doped with metal chlorides were measured after ball milling.   The XRD patterns of the ball-milled $LiAlH_4$ doped with $TiCl_3$ for 5 min, 1 h, and 24 h, the ball-milled $LiAlH_4$ for 24 h and $LiAlH_4$ together with the data of Li_3AlH_6 [13], LiCl [13], LiH [13] and Al [13] are shown in Figure 1.   The ball-milled $LiAlH_4$ for 5 min also includes Li_3AlH_6.   Prolonged ball-milling for 1 h leads to an increase of Al content and the absence of $LiAlH_4$.   The ball-milled $LiAlH_4$ doped with $TiCl_3$ for 24 h is found to include LiCl and Al.   As LiH and Al peaks overlap on the XRD curves, LiH could also be included in those specimens.   The H_2 released from the ball-milled specimen doped with $TiCl_3$ is 7.2 wt% (7.6 g of H_2 per 100 g of $LiAlH_4$).   It has been reported that $LiAlH_4$ releases H_2 in two decomposition steps upon heating below 600 K [14].

   $LiAlH_4 \rightarrow 1/3 Li_3AlH_6 + 2/3 Al + H_2$ (1)

   $1/3 Li_3AlH_6 + 2/3 Al + H_2 \rightarrow LiH + Al + 3/2 H_2$ (2)

The first and the second steps can ideally release 5.3 wt% and 2.6 wt% H_2 relative to $LiAlH_4$, respectively.   Therefore, the XRD results indicate that the H_2 desorption of the $LiAlH_4$ doped with $TiCl_3$ occurs by the two-step reactions (1) and (2).

   Figure 2 shows a HRTEM image of the $LiAlH_4$ doped with $TiCl_3$ ball-milled for 24 h. The ball-milled specimen that appears in the HRTEM image exhibits many dark portions. The size of the dark portions is several 10 nm.   EDS analysis is specific to the region marked by square.   The EDS results show that the dark portions of the transmission

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electron micrograph are attributed to Ti and Al as shown in Figure 2. Since Cl is not observed in the dark portions, it is revealed that the ball-milled $LiAlH_4$ doped with $TiCl_3$ forms a nano-composite material of $LiAlH_4$ and Al-Ti, while Cl and Al were detected in the light colored portions.

Figure 3 shows XRD patterns for the ball-milled $LiAlH_4$ doped with $TiCl_3$ (taken in 1:1 weight ratio, 4:1 molar ratio) and the annealed ball-milled $LiAlH_4$ doped with $TiCl_3$ (taken in 95:5 weight ratio) together with the data of Al_3Ti [13] and LiCl [13]. According to the literature [15] , Al_3Ti intermetallic phase crystallizes in two polymorphic modifications: tetragonal or cubic. We notice that the diffraction peaks of the ball-milled $LiAlH_4$ doped with $TiCl_3$ (50 wt%) at 2θ of 39.1°, 45.1° , 65.6° and 79.2° come form (111), (200), (220) and (311) planes of Al_3Ti, in which the unit cell is cubic [11, 15]. We observe a shoulder around 2θ of 39° in the XRD pattern of the annealed specimen (423 K, 6 h). The XRD pattern of the ball-milled $LiAlH_4$ doped with $TiCl_3$ (50wt%) also shows diffraction peaks at 2θ of 30.1°, 34.9°, 50.2° , 59.6°, 62.5°, 81.5°, 84.1°, corresponding to (111), (200), (220), (311), (222), (331) and (420) planes of LiCl. Thus the reaction of $LiAlH_4$ and $TiCl_3$ can be expressed by reaction (3)

$$3LiAlH_4+TiCl_3 \rightarrow Al_3Ti+3LiCl+6H_2$$
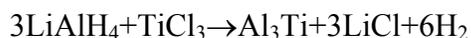
(3)

Figure 4 shows XRD patterns for ball-milled $LiAlH_4$ doped with various metal chlorides (1:1 weight ratio, 3-6:1 molar ratio) together with the data of Al_3Zr [16], Al_3V [13], Al_3Ni [13]. The diffraction peaks of the ball-milled $LiAlH_4$ doped with $ZrCl_4$ observed at 2θ of 38.2°, 44.5°, 64.7° and 77.7° correspond to those of cubic Al_3Zr [16]. This means that Al_3Zr with cubic structure is formed by a mechanochemical reaction of $LiAlH_4$ and $ZrCl_4$.

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Bragg peaks corresponding to LiCl and Al$_3$V or Al$_3$Ni are found in those XRD patterns. Then LiAlH$_4$ and the transition metal chlorides take the following reaction path.

$$4\text{LiAlH}_4+\text{ZrCl}_4\rightarrow\text{Al}_3\text{Zr}+\text{Al}+4\text{LiCl}+8\text{H}_2 \tag{4}$$

$$3\text{LiAlH}_4+\text{VCl}_3\rightarrow\text{Al}_3\text{V}+3\text{LiCl}+6\text{H}_2$$
(5)

$$3\text{LiAlH}_4+\text{NiCl}_2\rightarrow\text{Al}_3\text{Ni}+\text{LiH}+2\text{LiCl}+5.5\text{H}_2 \tag{6}$$
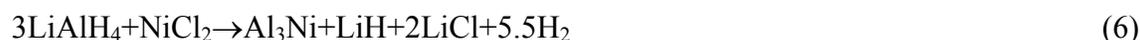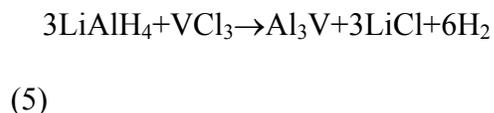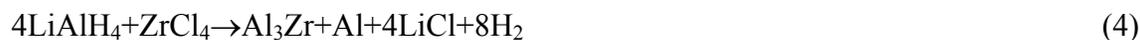
Mechanochemical reaction is an effective process for introducing metastable structure such as cubic Al$_3$Ti [15] and cubic Al$_3$Zr [16]. The transition metal trialuminides Al$_3$X (Ti, Zr, V, Ni) intermetallic phases prepared by the mechanochemical reaction of metal chlorides and LiAlH$_4$ may act as dehydrogenation catalysts. Figure 4 also presents the XRD patterns of the ball-milled LiAlH$_4$ doped with ZnCl$_2$ together with the data of Zn, LiCl and Al. The diffraction peaks at 2θ of 43.3°, 34.9° and 38.6° are raised from (101), (200) and (111) planes of Zn, LiCl and Al, respectively. The reaction of LiAlH$_4$ and ZnCl$_2$ is represented as follows.

$$2\text{LiAlH}_4+\text{ZnCl}_2\rightarrow\text{Zn}+2\text{Al}+2\text{LiCl}+4\text{H}_2 \tag{7}$$

In the first transition series, the 3d-orbitals of Zn are fully occupied by electron. The occupied d-orbitals lose the catalytic activity [17]. Thus, vacant d-orbital correlates with the interaction between H$_2$ molecule and transition metals.

For the transition metals having d-hole, the percentage d-character of the metallic bond and the electronegativity are indicators of the electronic structure of the metal. The percentage d-character and the electronegativuty have been correlated in an empirical way with catalytic data [17, 18]. Figure 5 displays the correlation of the H_2 desorption capacity during ball-milling with the percentage d-character and the electronegativity of the transition metals [17-19]. The capacity decreases with the percentage d-character. The behavior indicates that d-electron facilitates the interaction between transition metal and hydrogen by decreasing the percentage d-character. A smaller electronegativity gives a larger H_2 desorption capacity as shown in Figure 5. This means that the binding is ionic. The ionic binding between metal and hydrogen plays an important role for the catalytic activity. For transition metals, the heat of adsorption of hydrogen increases with decreasing of the percentage d-character. Therefore, the high catalytic activity of Ti and Zr might be achieved by strong chemisorption of hydrogen.

The ball-milled $LiAlH_4$ doped with 5 wt% of nano-Ni for 24 h desorbed 2.5 wt% of H_2 by the TPD measurement T<600 K. This indicated 5 wt% of H_2 was desorbed during ball-milling at room temperature, while the H_2 desorption capacities of the ball-milled $LiAlH_4$ doped with Ni was only 0.7 wt% at room temperature. It is clear from the results that H_2 desorption is remarkably improved by using the nano catalyst at room temperature. The structure of the ball-milled specimens doped with Ni and nano-Ni was characterized by the X-ray diffraction method. The XRD patterns of the ball-milled specimens are shown in Figure 6. We notice that the diffraction peak of the specimen at 51.8° is raised from (200) planes of Ni, in which the unit cell of Ni is cubic in shape. Thus it is suggested that the catalytic activity is improved with decreasing Ni particle size.

In the first step reaction (1), $LiAlH_4$ dissociates with the evolution of hydrogen to form Li_3AlH_6 and Al. Then, the weight ratio of Al to Li_3AlH_6 should be constant below H_2

desorption capacity 5.3 wt%. The diffraction peaks of the specimen in Figure 6 at 2θ of 21.9° and 38.5° are assigned to the reflection of 100 for Li_3AlH_6 and 111 for Al, respectively. The relative peak intensity $I_{[Al(111)]}/I_{[Li_3AlH_6(100)]}$ is assumingly proportional to the weight ratio of Li_3AlH_6 and Al. Figure 7 shows the relationship between the H_2 desorption capacity of the ball-milled $LiAlH_4$ doped with a catalyst and the relative peak intensity. We found that the catalysts are classified to two groups. The relative peak intensity of the specimen doped with VCl_3, $NiCl_2$, Ni or nano-Ni is 3-8 and approximately independent of the capacity. We confirmed that the mechanochemical reaction of $LiAlH_4$ in the presence of the catalysts induces the transformation of $LiAlH_4$ into Li_3AlH_6, Al and H_2 and is expressed by reaction (1). As shown in Figure 7, one can see that the intensity of the ball-milled $LiAlH_4$ doped with $TiCl_3$ or $ZrCl_4$ is remarkably increased with the desorption capacity. The relative intensity of the ball-milled $LiAlH_4$ doped with $TiCl_3$ exceeds ten times of the specimen doped with another group of catalysts around the desorption capacity of 4 wt%. This can be understood by considering that doping with $TiCl_3$ or $ZrCl_4$ results in a hydrogen release due to the first step and second step reactions catalyzed by the product of reaction (3) below the H_2 desorption capacity of 5 wt%.

It should be noted that reversible H_2 absorption/desorption of $LiAlH_4$ is one of the most important properties of the material, determing its potential for practical H_2 storage applications. Although, it is obvious that $LiAlH_4$ is not reversible because of its high dissociation pressure based on the low heat of formation [14]. Further studies are necessary to improve the reversibility. Partial atom substitutions and the mixture composed of other complex hydride may provide reversible hydrogen storage materials.

Conclusions

We found that the H_2 desorption capacity, which is an indicator of the catalytic activity, increased with decreasing of the percentage d-character, the electronegativity and the catalytic size of the transition metal. Doping with $TiCl_3$ and $ZrCl_4$ eliminated first and second steps of reactions (1), (2), while doping with other catalysts only eliminated first step reaction. It is presumed that the strong chemisorption ability of Ti and Zr towards hydrogen, which concludes in the formation of a metal-hydride phase, is responsible for the catalytic activity.

Acknowledgements

FIGURE CAPTIONS

Figure 1. XRD patterns of ball-milled $LiAlH_4$ doped with $TiCl_3$ and $LiAlH_4$, together with the data of Li_3AlH_6, LiCl, LiH and Al.

Figure 2. HRTEM image and EDS spectra of ball-milled $LiAlH_4$ doped with $TiCl_3$ for 24 h.

Figure 3. XRD patterns of ball-milled $LiAlH_4$ doped with $TiCl_3$, together with the data of Al_3Ti and LiCl.

Figure 4. XRD patterns of ball-milled $LiAlH_4$ doped with metal chloride (50 wt%), together with the data of Al_3V, Al_3Ni, Al_3Zr, Zn, LiCl and Al.

Figure 5. Correlation of H_2 desorption capacity at room temperature with percentage d-character and electronegativity.

Figure 6. XRD patterns of ball-milled $LiAlH_4$ doped with Ni and nano-Ni.

Figure 7. Relative peak intensity $I_{[Al(111)]}/I_{[Li_3AlH_6(100)]}$ vs. H_2 desorption capacity.

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Figure 1. XRD patterns of ball-milled LiAlH$_4$ doped with TiCl$_3$ and LiAlH$_4$, together with the data of Li$_3$AlH$_6$, LiCl, LiH and Al.

Figure 2. HRTEM image and EDS spectra of ball-milled LiAlH$_4$ doped with TiCl$_3$ for 24 h.

Figure 3. XRD patterns of ball-milled LiAlH$_4$ doped with TiCl$_3$, together with the data of Al$_3$Ti and LiCl.

Figure 4. XRD patterns of ball-milled LiAlH$_4$ doped with metal chloride (50 wt%), together with the data of Al$_3$V, Al$_3$Ni, Al$_3$Zr, Zn, LiCl and Al.

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