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Hydrogen release of catalyzed lithium aluminum hydride by a mechanochemical reaction

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Abstract

The effects of various catalysts on the H₂ release characteristics of LiAlH₄ were studied. It was established that the catalytic activity defined by the H₂ desorption capacity by a mechanochemical reaction decreased in the series TiCl₃ > ZrCl₄ > VCl₃ > NiCl₂ > ZnCl₂. Transition metal trialuminides Al₃X (X = Ti, Zr, V, Ni) were prepared by the mechanochemical reaction of LiAlH₄ and the metal chlorides, while the reaction of LiAlH₄ and ZnCl₂ 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: TiCl₃, ZrCl₄; 2: VCl₃, NiCl₂, Ni, nano-Ni) from the viewpoint of the H₂ desorption mechanism. © 2007 Published by Elsevier B.V.

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1. Introduction

A high-pressure MH tank with a heat-exchanger module containing $Ti_{1.1}CrMn$ (300 kg) has been developed [1–3]. The measured H₂ capacity at 35 MPa was 7.3 kg H₂/180 L (outer volume), which was 2.5 times of the high-pressure tank (35 MPa). 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 (420 kg) because the gravimetric H₂ density of $Ti_{1.1}CrMn$ had a low value of 1.8 wt%. Storage of high H₂ densities in light weight solids is a solution to this problem.

Light weight complex hydrides, such as sodium aluminum hydride (NaAlH₄) [4–8] and lithium aluminum hydride (LiAlH₄) [9–12] are considered attractive as hydrogen storage materials due to their large hydrogen content. The reversible hydrogen storage has been formed by doping NaAlH₄ with transition metal-based catalysts [4–8]. Unfortunately, only 3–4.5 wt% H₂ can be stored and recovered in reasonable time at 373–398 K [7]. For useable H₂ storage, H₂ absorption and desorption around room temperature is necessary. It has been

0925-8388/\$ – see front matter © 2007 Published by Elsevier B.V. doi:10.1016/j.jallcom.2007.08.015 reported that LiAlH₄ can be easily transformed into lithium hexahydridoaluminate Li₃AlH₆, Al and H₂ in the presence of catalysts or prolonged ball-milling at room temperature, which corresponds to the H₂ desorption capacity of 5.3 wt% [9–12].

In this paper, the effect of various metal chlorides and elemental nickel on dehydrogenation properties of LiAlH₄ will be presented.

2. Experimental

2.1. Materials

Lithium aluminum hydride LiAlH₄ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 37.95, density: 0.92 g/cm³), titanium trichrolide TiCl₃ (Sigma–Aldrich, molecular weight: 154.26), zirconium tetrachloride ZrCl₄ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 233.03), vanadium trichloride VCl₃ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 157.30), nickel dichloride NiCl₂ (Kojundo Chemical Laboratory Co., Ltd., molecular weight: 129.62), zinc chloride ZnCl₂ (Wako Pure Chemical Industries, Ltd. Japan, molecular weight: 136.30), nickel Ni (Soekawa Chemicals Co., Ltd., diameter: 0.8 μ m) 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 LiAlH₄ 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).

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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. H₂ 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 Cu K α radiation (50 kV, 300 mA) filtered by a monochrometer using Rigaku Rint-TTR.

3. Results and discussion

LiAlH₄ doped with 5 wt% of TiCl₃ desorbed only 0.3 wt% of H₂ by the TPD measurement T < 600 K, which indicated 7.2 wt% of H₂ was desorbed during ball-milling for 24 h at room temperature. The H₂ desorption capacity of ball-milled LiAlH₄ doped with various metal chlorides (5 wt%, milling: 24 h) decreased in the series [TiCl₃ (7.2 wt%) > ZrCl₄ (6.4 wt%) > VCl₃ (4.8 wt%) > NiCl₂ (1.1 wt%) > ZnCl₂ (0)]. The ball-milled LiAlH₄ doped with ZnCl₂ did not destabilize LiAlH₄.

The X-ray diffraction (XRD) patterns of the LiAlH₄ doped with metal chlorides were measured after ball-milling. The XRD patterns of the ball-milled LiAlH₄ doped with TiCl₃ for 5 min, 1 h, and 24 h, the ball-milled LiAlH₄ for 24 h and LiAlH₄ together with the data of Li₃AlH₆ [13], LiCl [13], LiH [13] and Al [13] are shown in Fig. 1. The ball-milled LiAlH₄ for 5 min also includes Li₃AlH₆. Prolonged ball-milling for 1 h leads to an increase of Al content and the absence of LiAlH₄. The ballmilled LiAlH₄ doped with TiCl₃ 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 H₂ released from the ball-milled specimen doped with TiCl₃ is 7.2 wt% (7.6 g of H₂ per 100 g of LiAlH₄). It has been reported that LiAlH₄ releases H₂ in two decomposition steps upon heating below 600 K [14].

$$\text{LiAlH}_4 \rightarrow \frac{1}{3}\text{Li}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \tag{1}$$





Fig. 1. XRD patterns of ball-milled LiAlH₄ doped with TiCl₃ and LiAlH₄, together with the data of Li_3AlH_6 , LiCl, LiH and Al.



Fig. 2. HRTEM image and EDS spectra of ball-milled LiAlH₄ doped with TiCl₃ for 24 h.

The first and the second steps can ideally release 5.3 and 2.6 wt% H₂ relative to LiAlH₄, respectively. Therefore, the XRD results indicate that the H₂ desorption of the LiAlH₄ doped with TiCl₃ occurs by the two-step reactions (1) and (2).

Fig. 2 shows a HRTEM image of the LiAlH₄ doped with TiCl₃ 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 electron micrograph are attributed to Ti and Al as shown in Fig. 2. Since Cl is not observed in the dark portions, it is revealed that the ball-milled LiAlH₄ doped with TiCl₃ forms a nano-composite material of LiAlH₄ and Al-Ti, while Cl and Al were detected in the light colored portions.

Fig. 3 shows XRD patterns for the ball-milled LiAlH₄ doped with TiCl₃ (taken in 1:1 weight ratio, 4:1 molar ratio) and the annealed ball-milled LiAlH₄ doped with TiCl₃ (taken in 95:5 weight ratio) together with the data of Al₃Ti [13] and LiCl [13]. According to the literature [15], Al₃Ti intermetallic phase crystallizes in two polymorphic modifications: tetragonal or cubic. We notice that the diffraction peaks of the ball-milled LiAlH₄ doped with TiCl₃ (50 wt%) at 2θ of 39.1° , 45.1° , 65.6° and 79.2° come form (111), (200), (220) and (311) planes of Al₃Ti, 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 LiAlH₄ doped with TiCl₃ (50 wt%) also shows diffraction peaks at 2θ of 30.1° , 34.9° , 50.2° , 59.6° , 62.5° , 81.5° , 84.1° , corresponding to (111),



Fig. 3. XRD patterns of ball-milled LiAlH₄ doped with TiCl₃, together with the data of Al₃Ti and LiCl.



Fig. 4. XRD patterns of ball-milled LiAlH₄ doped with metal chloride (50 wt%), together with the data of Al_3V , Al_3Ni , Al_3Zr , Zn, LiCl and Al.

(200), (220), (311), (222), (331) and (420) planes of LiCl. Thus, the reaction of LiAlH₄ and TiCl₃ can be expressed by reaction (3).

$$3\text{LiAlH}_4 + \text{TiCl}_3 \rightarrow \text{Al}_3\text{Ti} + 3\text{LiCl} + 6\text{H}_2$$
 (3)

Fig. 4 shows XRD patterns for ball-milled LiAlH₄ doped with various metal chlorides (1:1 weight ratio, 3–6:1 molar ratio) together with the data of Al₃Zr [16], Al₃V [13], Al₃Ni [13]. The diffraction peaks of the ball-milled LiAlH₄ doped with ZrCl₄ observed at 2θ of 38.2°, 44.5°, 64.7° and 77.7° correspond to those of cubic Al₃Zr [16]. This means that Al₃Zr with cubic structure is formed by a mechanochemical reaction of LiAlH₄ and ZrCl₄. Bragg peaks corresponding to LiCl and Al₃V or Al₃Ni are found in those XRD patterns. Then LiAlH₄ and the transition metal chlorides take the following reaction path.

$$4\text{LiAlH}_4 + 2\text{rCl}_4 \rightarrow \text{Al}_3\text{Zr} + \text{Al} + 4\text{LiCl} + 8\text{H}_2 \tag{4}$$

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

$$3\text{LiAlH}_4 + \text{NiCl}_2 \rightarrow \text{Al}_3\text{Ni} + \text{LiH} + 2\text{LiCl} + 5.5\text{H}_2$$
 (6)

Mechanochemical reaction is an effective process for introducing metastable structure such as cubic Al₃Ti [15] and cubic Al₃Zr [16]. The transition metal trialuminides Al₃X (Ti, Zr, V, Ni) intermetallic phases prepared by the mechanochemical reaction of metal chlorides and LiAlH₄ may act as dehydrogenation catalysts. Fig. 4 also presents the XRD patterns of the ball-milled LiAlH₄ doped with ZnCl₂ 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 LiAlH₄ and ZnCl₂ 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 dcharacter of the metallic bond and the electronegativity are



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

indicators of the electronic structure of the metal. The percentage d-character and the electronegativity have been correlated in an empirical way with catalytic data [17,18]. Fig. 5 displays the correlation of the H₂ 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 H₂ desorption capacity as shown in Fig. 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 LiAlH₄ doped with 5 wt% of nano-Ni for 24 h desorbed 2.5 wt% of H₂ by the TPD measurement T < 600 K. This indicated 5 wt% of H₂ was desorbed during ball-milling at room temperature, while the H₂ desorption capacities of the ball-milled LiAlH₄ doped with Ni was only 0.7 wt% at room temperature. It is clear from the results that H₂ 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 Fig. 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), LiAlH₄ dissociates with the evolution of hydrogen to form Li₃AlH₆ and Al. Then, the weight ratio of Al to Li₃AlH₆ should be constant below H₂ desorption capacity 5.3 wt%. The diffraction peaks of the specimen in Fig. 6 at 2θ of 21.9° and 38.5° are assigned to the reflection of 1 0 0 for Li₃AlH₆ and 1 1 1 for Al, respectively. The relative peak intensity $I_{[Al(111)]}/I_{[Li_3AlH_6(100)]}$ is assumingly proportional to the weight ratio of Li₃AlH₆ and Al. Fig. 7 shows the relationship between the H₂ desorption capacity of the ball-milled LiAlH₄ doped with a catalyst and the relative peak intensity. We found



Fig. 6. XRD patterns of ball-milled LiAlH₄ doped with Ni and nano-Ni.



Fig. 7. Relative peak intensity $I_{[Al(1 1 1)]}/I_{[Li_3AlH_6(1 0 0)]}$ vs. H₂ desorption capacity.

that the catalysts are classified to two groups. The relative peak intensity of the specimen doped with VCl₃, NiCl₂, Ni or nano-Ni is 3–8 and approximately independent of the capacity. We confirmed that the mechanochemical reaction of LiAlH₄ in the presence of the catalysts induces the transformation of LiAlH₄ into Li₃AlH₆, Al and H₂ and is expressed by reaction (1). As shown in Fig. 7, one can see that the intensity of the ball-milled LiAlH₄ doped with TiCl₃ or ZrCl₄ is remarkably increased with the desorption capacity. The relative intensity of the ball-milled LiAlH₄ doped with TiCl₃ exceeds 10 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 TiCl₃ or ZrCl₄ results in a hydrogen release due to the first step and second step reactions catalyzed by the product of reaction (3) below the H₂ desorption capacity of 5 wt%.

It should be noted that reversible H_2 absorption/desorption of LiAlH₄ is one of the most important properties of the material, determining its potential for practical H_2 storage applications. Although, it is obvious that LiAlH₄ 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.

4. 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 TiCl₃ and ZrCl₄ eliminated first and second steps of reactions (1) and (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.

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