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Effect of ball milling time on the hydrogen storage properties of TiF₃-doped LiAlH₄

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ABSTRACT

In the present work, the catalytic effect of TiF₃ on the dehydrogenation properties of LiAlH₄ has been investigated. Decomposition of LiAlH₄ occurs during ball milling in the presence of 4 mol% TiF₃. Different ball milling times have been used, from 0.5 h to 18 h. With ball milling time increasing, the crystallite sizes of LiAlH₄ get smaller (from 69 nm to 43 nm) and the dehydrogenation temperature becomes lower (from 80 °C to 60 °C). Half an hour ball milling makes the initial dehydrogenation temperature of doped LiAlH₄ reduce to 80 °C, which is 70 °C lower than as-received LiAlH₄. About 5.0 wt.% H₂ can be released from TiF₃-doped LiAlH₄ after 18 h ball milling in the range of 60 °C–145 °C (heating rate 2 °C min⁻¹). TiF₃ probably reacts with LiAlH₄ to form the catalyst, TiAl₃. The mechanochemical and thermochemical reactions have been clarified. However, the rehydrogenation of LiAlH₄/Li₃AlH₆ can not be realized under 95 bar H₂ in the presence of TiF₃ because of their thermodynamic properties.

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1. Introduction

Hydrogen storage is the most critical issue for the application of hydrogen energy. In recent years, attention has been focused on solid hydrogen storage materials [1–3]. Among them, aluminum-based complex metal hydrides, such as lithium alanate (LiAlH₄) and sodium alanate (NaAlH₄), possess quite high hydrogen storage capacities (10.5 wt.% and 7.3 wt.% H₂, respectively), so they are viewed as some of the most promising hydrogen storage materials.

In 1997, Bogdanovic and Schwichardi [4] reported that NaAlH₄ could be reversibly dehydrogenated and rehydrogenated with dopants containing Ti. Since then, many attempts have been made to modify its hydrogen storage properties. However, NaAlH₄ can only reversibly store 5.6 wt.% H₂ at best under moderate conditions, which does not fully meet the DOE target (6.5 wt.% H₂). As a comparison, LiAlH₄ can release as much as 7.9 wt.% H₂ in two steps (R₁ and R₂) below 220 °C [5,6]. LiAlH₄ decomposes between 150–175 °C for R₁ with 5.3 wt.% H₂ and 180–220 °C for R₂ with 2.6 wt.% H₂.

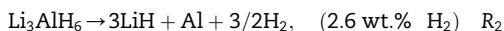
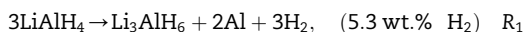
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In the last few years, a lot of studies have been done mainly focusing on how to lower the operation temperature and improve the reversibility of LiAlH_4 . Mechanical ball milling and doping are the main methods. Various dopants have been investigated and could be classified into six categories: pure metals, such as Ti [7–10], Fe [7,10], Ni [10,11], V [10] and Al [9]; alloys, like TiAl_3 [7,9], Al_3Fe [7], Ti_3Al [9] and $\text{Al}_{22}\text{Fe}_3\text{Ti}_8$ [7]; metal halides, such as TiF_3 [12], TiCl_4 [7,10,13], TiCl_3 [14], VCl_3 [15,16], AlCl_3 [10], FeCl_3 [10], LaCl_3 [11,17], ZrCl_4 [18], HfCl_4 [18], $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ [8,19] and VBr_3 [16]; metal hydrides, like TiH_2 [10]; carbon materials, such as CNFs and Vulcan XC72R [10,20]; composites, like VCl_3 @CNFs [20]. Most of these dopants do reduce the decomposition temperature of LiAlH_4 and metal halides perform best. Adding 2 mol% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ [8] or 4 mol% HfCl_4 [18] makes LiAlH_4 decompose around 100 °C. Moreover, under the catalytic effect of 5 mol% VCl_3 [15], LiAlH_4 starts to decompose at 50 °C. However, the catalytic effect of TiF_3 on LiAlH_4 is still an unsolved question [12]. TiF_3 is much lighter and possesses a better catalytic effect on the reversible de-/hydrogenation of NaAlH_4 than TiCl_3 [21,22]. Besides, quite recently Brinks et al. [23] reported that hydrogenating the ball-milled mixture of NaH , Al and TiF_3 can form an anion-substituted product, $\text{Na}_3\text{AlH}_{6-x}\text{F}_x$, which is less stable than Na_3AlH_6 .

In our previous works, we studied the obvious catalytic effects of TiF_3 on LiBH_4 [24] and $\text{MgH}_2/\text{Mg}_2\text{NiH}_4$ [25]. The purpose of this work is to investigate the catalytic characteristics of TiF_3 on the de-/hydrogenation of LiAlH_4 . The effect of different ball milling time (BMT) has been clarified. The phase changes before and after ball milling have been studied by X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR). We have used thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements to investigate the thermal behaviors. The rehydrogenation performance has been examined by a Sieverts-type apparatus.

2. Experimental

The starting materials, LiAlH_4 (97%) and TiF_3 (99%) were both purchased from Alfa Aesar, and used without further purification. Pure LiCl was obtained by dehydrating from commercial $\text{LiCl} \cdot \text{H}_2\text{O}$ (Kermel, Tianjin). All material operations were performed in an argon (99.999%) filled glove box, with oxygen and water vapour contents both less than 0.1 ppm. Ball milling was performed using a QM-1SP2 planetary ball mill under 0.1 MPa argon atmosphere at a rotation speed of 300 rpm. Typically, 1.5 g of sample with 4 mol% TiF_3 was loaded into a stainless milling pot with 24 steel balls (10 mm in diameter). Different ball milling times were used: 0.5 h, 2 h, 6 h and 18 h, respectively.

XRD analysis was carried out using a PANalytical X-ray Diffractometer (X'Pert MPD PRO, $\text{Cu K}\alpha$, 40 kV, 40 mA) over the range of 10–90° 2θ . The sample holder was filled inside the glove box, covered with Mylar film and put into a plastic box to protect the sample from atmospheric oxygen and moisture during transportation.

FTIR spectroscopy was performed using a Nicolet 380 Fourier transformed infrared spectrometer equipped in attenuated total reflection. The spectral resolution was 4 cm^{-1} . Scans between 2000 cm^{-1} and 800 cm^{-1} were done under an argon atmosphere.

Thermogravimetric analysis (TGA) was carried out in Cahn Thermax 500. Typically ca. 200 mg of sample was loaded into an Al_2O_3 crucible in the glove box. The crucible was placed in a sealed glass bottle in order to protect it against air exposure during transportation from the glove box to the instrument. Before the experiment was initiated, the system was evacuated to 10⁻¹ mbar and refilled with argon (99.999%) to 1 bar. This was repeated three times. Then, the system was flushed with argon for 20 min before heating from room temperature to 250 °C (2 °C min^{-1}) in order to keep impurities (moisture and oxygen) at a tolerable level during the experiment. The weight and temperature changes were recorded by a computer.

Differential scanning calorimetry (DSC) was conducted using a Setaram DSC 141 with a heating rate 2 °C min^{-1} in a flow (50 ml min^{-1}) of high purity helium. About 2 mg sample was used each time.

The isothermal rehydrogenation was measured using a Sieverts-type apparatus (Advanced Materials Corporation, USA) under 95 bar of H_2 at the target temperature.

3. Results and discussion

3.1. Effect of ball milling time on the LiAlH_4 phase

Through comparison of the XRD patterns of Mylar film covered samples and uncovered ones, most of the obtained hydride powders were not affected by a short-time exposure (<10 min) to ambient atmosphere [26]. Hereby we show the patterns of uncovered ones.

Fig. 1 shows the XRD patterns of as-received LiAlH_4 and ball-milled TiF_3 -doped LiAlH_4 . The peak at $2\theta = 34.8^\circ$ belongs to LiCl [19] and it appears in all the samples before and after ball milling. Fig. 1a shows the pattern of as-received LiAlH_4 . All the observed peaks, except the LiCl peaks, can be indexed to a monoclinic unit cell (P21/c) with unit cell parameters $a = 4.845 \text{ \AA}$, $b = 7.826 \text{ \AA}$, $c = 7.917 \text{ \AA}$ and $\beta = 112.5^\circ$ in agreement with the crystal structure of LiAlH_4 reported in the literature [19]. No other impurities are found.

The TiF_3 -doped LiAlH_4 samples were ball-milled for 0.5 h, 2 h, 6 h and 18 h, respectively. Their corresponding XRD patterns are b, c, d and e in Fig. 1. As shown in Fig. 1b, the diffraction peaks of LiAlH_4 become weaker and broader than those of as-received LiAlH_4 . The peak at $2\theta = 38.4^\circ$ is the Al (1 1 1) plane reflection. It indicates that LiAlH_4 has already partly decomposed into Li_3AlH_6 and Al after 0.5 h ball milling in the presence of 4 mol% TiF_3 . As compared with the reflections of LiAlH_4 , the reflections of Li_3AlH_6 ($2\theta = 21.9^\circ, 31.6^\circ$ [27]) are too weak to be observed obviously on XRD patterns for all the ball-milled samples. Generally, the diffraction peaks of LiAlH_4 become weaker and broader while peaks of Al become stronger as ball milling time increases. It is assumed that the longer the ball milling is performed, the more LiAlH_4 decomposes into Li_3AlH_6 and Al . It can be also seen in the following FTIR and TGA analyses. Ti-containing and F-containing

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