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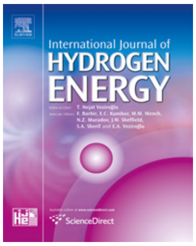

The dehydrogenation performance and reaction mechanisms of Li_3AlH_6 with TiF_3 additive

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ABSTRACT

For Li_3AlH_6 prepared by mechanical milling method, the dissociation reaction enthalpy and activation energy are calculated to be 22.1 kJ mol^{-1} H_2 and 133.7 ± 2.7 kJ mol^{-1}, respectively. The dehydrogenation performance of Li_3AlH_6 is greatly enhanced by TiF_3 additive, especially in the kinetic behaviors. For the Li_3AlH_6 + 10 mol% TiF_3 sample, the starting temperature of dehydrogenation is obviously decreased by 60 °C from that of pure Li_3AlH_6 (190 °C), and 3.0 wt.% H_2 may be released within 1000 s at 120 °C under an initial vacuum. With the amount of TiF_3 increasing, the starting temperature decreases and the kinetics improves due to the decrease in the activation energy. The X-ray diffraction (XRD) together with thermogravimetric analysis (TGA) results show that there are three mechanochemical reactions involved during milling: i) $Li_3AlH_6 + TiF_3 \rightarrow 3\,LiF + Al + Ti + 3H_2$, ii) $Ti + H_2 \rightarrow TiH_2$, iii) $3\,Al + Ti \rightarrow Al_3Ti$. The in-situ formed Ti species (TiH_2 and Al_3Ti) co-catalyze the thermal dehydrogenation of Li_3AlH_6.

1. Introduction

Hydrogen storage is a key technical challenge for onboard application of hydrogen. High-pressure and cryogenic hydrogen storage systems are impractical for vehicular applications due to safety concerns and volumetric constraints. Attention has been focused on solid-state hydrogen storage materials due to the significant advantages related to safety, energy efficiency and operational convenience [1,2]. Metal hydrides [3], complex hydrides [4], carbon materials [5], and MOFs [6] are all investigated as hydrogen carriers. Among these materials, light metal complex hydrides have attracted intensive research interest because of their high hydrogen storage capacities and moderate working temperatures. Lithium alanate ($LiAlH_4$) is one of the promising hydrogen storage materials and has been widely investigated in recent years. It can decompose in three steps (R_1, R_2 and R_3) with a hydrogen liberation amounting to 10.6 wt.%. [7,8]

$$3\,LiAlH_4 \xrightarrow{150\sim175\,^{\circ}C} Li_3AlH_6 + 2Al + 3H_2, \quad (5.3\,wt.\%H_2) \qquad R1$$

$$Li_3AlH_6 \xrightarrow{180\sim220\,^{\circ}C} 3\,LiH + Al + 3/2\,H_2, \quad (2.6\,wt.\%\,H_2) \qquad R2$$

$$3\,LiH + 3\,Al \xrightarrow{>400\,^{\circ}C} 3\,LiAl + 3/2\,H_2(2.6\,wt.\%H_2) \qquad R3$$

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The first two reactions, R_1 and R_2, attract much attention at present, since their reaction temperatures are close to the working temperature of fuel cell system. Various catalysts have been added to $LiAlH_4$ to improve its hydrogen storage properties, including such effective metal halides as $TiCl_3 \cdot 1/3AlCl_3$ [9,10], VCl_3 [10], $NiCl_2$ [11] and TiF_3 [12,13]. Under the catalysis of these metal halides, $LiAlH_4$ decomposes partly below 100 °C mainly corresponding to R_1 stage. However, the equilibrium pressure for R_1 is estimated to be above 100 MPa at 25 °C [14]. On the other hand, the equilibrium pressure for R_2 is much lower. By *ab initio* calculations, Ke et al. [15] predicted the equilibrium pressure for R_2 to be around 10 MPa at 0 °C. It means that Li_3AlH_6 is a thermodynamically attractive complex for hydrogen storage with a capacity of 5.6 wt.% H_2.

The method for the preparation of Li_3AlH_6 via the mechanochemical reaction between $LiAlH_4$ and LiH (R_4) has been widely used in the past decade [8,16–18]. The dehydrogenation temperature of Li_3AlH_6 has been reduced by about 30 °C and the kinetics has been significantly improved by Ti_5Si_3 [19] or Al_3Ti [20] additives. $TiCl_3$ [18–20] shows more pronounced catalytic effect on R_2, since it reacts with Li_3AlH_6 to form Al_3Ti, which may act as a dehydrogenation catalyst. $Ti(OPr)_4$ is also a remarkable catalyst [17], which was co-milled with $LiAlH_4$ and LiH to produce nanocrystalline Ti-doped Li_3AlH_6 with a starting dehydrogenation temperature of 100 °C induced by the $Ti^0/Ti^{3+}/Ti^{4+}$ defect sites.

$$LiAlH_4 + 2LiH \xrightarrow{\text{ball milling}} Li_3AlH_6 \qquad R4$$

In the past few years, TiF_3 has attracted broad scientific interest due to its excellent catalytic effect on many metal hydrides, such as MgH_2 [21], Mg_2NiH_4 [21], Na_2LiAlH_6 [22]. Wang et al. reported that TiF_3 is superior to $TiCl_3$ as a dopant precursor in preparation of catalytically enhanced $NaAlH_4$ [23] and Na_3AlH_6 [24] systems. They believed that the F^- anion is substantially incorporated into the doped structure, and in some way contributes to the catalytic enhancement. Our previous studies have demonstrated the significant catalytic effect of TiF_3 on both $LiBH_4$ [25] and $LiAlH_4$ [13]. In the case of $LiAlH_4$, adding 4 mol% TiF_3 makes $LiAlH_4$ start to decompose at 80 °C with 6.3 wt.% H_2 release up to 200 °C. TiF_3 probably reacts with $LiAlH_4$ to form the catalyst, Al_3Ti, which catalyzes the mechanochemical reactions during ball milling and the thermochemical reactions under increased temperature. However, the catalytic effect of TiF_3 on Li_3AlH_6 is still unclear. We are curious if the same pathway occurs in the reactions. In order to find the answer to this question we further explore the dehydrogenation performance and reaction mechanisms of Li_3AlH_6 with TiF_3 additive.

On the other hand, the enthalpy change of reaction (ΔH) and apparent activation energy (E_a) are two important thermal parameters to evaluate the thermodynamic and kinetic properties of a material or reaction [26]. Although numerous results related to these two parameters of Li_3AlH_6 (R_2) have been reported, they are all based on the products of $LiAlH_4$ decomposition (R_1). The data related to pure Li_3AlH_6 prepared by ball milling have not been previously reported to the best of our knowledge.

In this work, we prepared pristine Li_3AlH_6 and Li_3AlH_6 with TiF_3 additive through mechanochemical milling. Both the thermal properties and the dehydrogenation performance of as-prepared Li_3AlH_6 with TiF_3 additive were investigated. The reaction mechanisms of Li_3AlH_6 with TiF_3 additive were also discussed.

2. Experimental

2.1. *Sample preparation*

The starting materials, LiH (98%), $LiAlH_4$ (97%) and TiF_3 (99%) were all purchased from Alfa Aesar and used without further purification. All material handlings were performed in an MBraun Unilab glove box filled with high purity Ar (99.999%), with oxygen and water vapor contents both less than 0.1 ppm.

Li_3AlH_6 was synthesized through the mechanochemical reaction between LiH and $LiAlH_4$ similar to the method reported in the literature [17–20]. LiH and $LiAlH_4$ with a mole ratio of 2:1 were loaded into a 100 mL stainless milling pot with 24 steel balls (10 mm in diameter). Ball milling was performed using a QM-1SP2 planetary ball mill under 0.1 MPa argon atmosphere at a rotation speed of 541 rpm. We obtained pure Li_3AlH_6 after 8 h milling.

Different amounts (2, 10, 20, 25 and 50 mol%) of TiF_3 were added to Li_3AlH_6, respectively. All the mixtures were milled for 0.5 h under the same conditions as those used above.

2.2. *Sample characterization*

XRD analysis was carried out using a PANalytical X-ray Diffractometer (X'Pert MPD PRO, Cu K_α, 40 kV, 40 mA). The samples were shielded by Mylar films (diffraction peak $\sim 26^\circ$ 2θ) from the atmospheric oxygen and moisture.

Thermogravimetric analysis (TGA) was carried out in Cahn Thermax 500 with a heating rate of 10 °C min^{-1} in a flow of high purity Ar.

Differential scanning calorimetry (DSC) was conducted using a TA Q1000 at different heating rates (2.5, 5, 10 and 20 °C min^{-1}) under a flow (50 ml min^{-1}) of high purity Ar.

The isothermal dehydrogenation was performed using a Sieverts-type apparatus (PCT, Advanced Materials Corporation, USA) under an initial pressure of 10^{-5} MPa H_2.

The surface morphology of the composites was observed using scanning electron microscopy (SEM, JSM6360LV).

3. Results and discussion

3.1. *XRD characterization and thermal properties of as-prepared Li_3AlH_6*

The XRD pattern of as-prepared Li_3AlH_6 is shown in Fig. 1. All the reflections belong to Li_3AlH_6, and are in good agreement with the literature [16–20]. This means that Li_3AlH_6 could be prepared by the reaction between $LiAlH_4$ and LiH (R_4) within 8 h. By means of the Scherrer equation [$\beta = \lambda/(B \cos \theta)$, where β is the crystallite size, λ is the X-ray wavelength and B is the full width at half maximum (FWHM)], the average crystallite size of Li_3AlH_6 could be determined as 22 nm.

Fig. 2 shows the DSC curves of Li_3AlH_6 at different heating rates: 2.5, 5, 10 and 20 °C min^{-1}. Only one endothermic peak,