

Thermal decomposition of Li_3AlH_6 with TiAl_3 catalyst

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Abstract

It has been found that the reaction products between TiCl_3 and Li_3AlH_6 by mechanical milling consist of LiCl and TiAl_3 together with TiH_2 . Thermodynamic calculation also predicts that TiAl_3 becomes dominant over TiH_2 with increasing temperature. Based on this, ultra-fine TiAl_3 powder having the primary particle size of about 100 nm has been mechanochemically synthesized from a mixture of TiCl_3 , AlCl_3 and Mg. The addition of this TiAl_3 powder into Li_3AlH_6 clearly shows a good catalytic effect on the thermal decomposition of Li_3AlH_6 as expected. The use of fine TiAl_3 catalyst is certainly more favorable than TiCl_3 in terms of hydrogen storage capacity as it does not produce irreversible chloride byproduct in alanates.

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1. Introduction

The development of solid-state hydrogen storage at low and medium temperatures has been recognized as one of the key technologies for hydrogen fuel cell applications. Especially for vehicular applications, it is important to find new light-weight hydrogen storage materials that exhibit high reversible hydrogen capacity [1].

Alkali and alkali-earth metal alanates (aluminum hydrides) have received great attention as promising hydrogen storage materials owing to their inherent high theoretical hydrogen capacity, since Bogdanović and Schwickardi [2] first demonstrated in 1997 that reversible hydrogen storage could be achieved under moderate conditions (temperature and pressure) with accelerated kinetics in NaAlH_4 and Na_3AlH_6 by adding a small amount of Ti-containing catalysts such as TiCl_3 and $\text{Ti}(\text{O}i\text{Bu})_4$ through wet chemistry. Following this finding, Jensen and his coworkers [3,4] reported improved kinetics by dispersing Ti-containing catalysts using a dry milling process. Currently, mechanical ball milling is being widely adopted to disperse a small amount of catalysts effectively into sodium

alanates in solid state [5,6]. In addition to sodium alanates, it has been shown that other alanates such as lithium alanates could also be catalyzed with Ti-containing materials [7]. In spite of the outstanding performance of Ti-containing catalysts, there is still no clear understanding on how they play a catalytic role in alanates. The first step toward the understanding of this catalytic mechanism would be to confirm what form of Ti exists in alanates. However, it is quite difficult to confirm unambiguously the state of Ti (e.g. metallic Ti, Ti compounds or Ti substitution in alanates) in alanates using most analytical techniques, because a very small amount of Ti-containing catalysts are usually added. On the whole, there exist two hypotheses on the Ti state in alanates. While the results of recent investigations [8–12] seem to support the hypothesis that Ti in situ forms TiAl_3 when introduced into alanates, there is another hypothesis that Ti substitutes for metal sites in alanates [13–15].

Assuming that Ti does transform into TiAl_3 in alanates, it is worthwhile to confirm its efficacy by adding TiAl_3 , instead of TiCl_3 , into alanates because TiCl_3 permanently reduces hydrogen storage capacity of alanates by reacting with part of alanates to form very stable salts such as NaCl and LiCl . In fact, Balema et al. [8] and Resan et al. [16] have recently attempted to confirm the catalytic activity of TiAl_3 by dispersing TiAl_3 powder prepared by milling the arc melted

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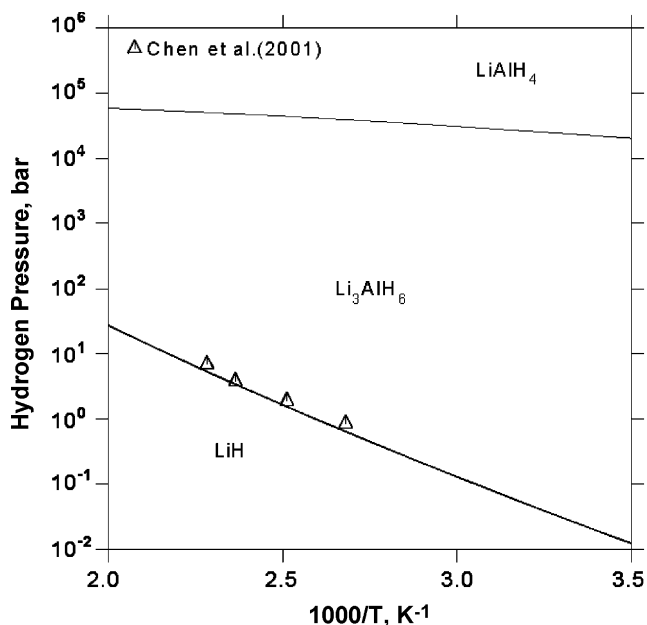


Fig. 1. Calculated stability diagram of LiH, Li_3AlH_6 and LiAlH_4 [18].

sample and commercial powder ($<150\ \mu\text{m}$), respectively, into LiAlH_4 . They showed that the addition of TiAl_3 indeed decreased the dehydrogenation starting temperature of LiAlH_4 by about $10\ ^\circ\text{C}$, although the catalytic effect may not be significant. It is, therefore, desirable to produce as fine TiAl_3 powder as possible as the catalytic efficacy will be naturally enhanced with decreasing particle size of catalyst. Mechanical milling is one of the simple and cost-effective methods for producing TiAl_3 powders. However, it might be difficult to obtain fine TiAl_3 particles using conventional milling techniques because TiAl_3 is relatively ductile and thus they easily agglomerate during milling [17].

The purpose of this study is to elucidate if TiCl_3 indeed forms TiAl_3 in Li_3AlH_6 using both experimental work and theoretical calculations and to investigate the catalytic effect of TiAl_3 on thermal decomposition (dehydrogenation) of Li_3AlH_6 using ultrafine TiAl_3 powder prepared by mechanochemical reaction between TiCl_3 , AlCl_3 and Mg powders. The main reason to adopt Li_3AlH_6 (5.6 wt.% H_2) instead of LiAlH_4 (7.9 wt.% H_2) is that the hydrogen pressure required to re-hydrogenate LiAlH_4 is estimated to be an order of 10^4 bar, according to our recent thermodynamic calculation shown in Fig. 1 [18].

2. Experimental procedure

LiAlH_4 (95%), LiH (95%), TiCl_3 (99%) and AlCl_3 (99.9%) powders were purchased from Sigma–Aldrich, and Mg (99.8%) powder from Alfa–Aesar. In order to synthesize Li_3AlH_6 mechanochemically, a 5 g mixture of LiAlH_4 and LiH with a molar ratio of 1:2 was charged together with ten 15 mm and thirty 10 mm diameter zirconia balls into a 250 ml silicon nitride bowl under an argon atmosphere in a glove box. The ball-to-powder weight ratio was approximately 37:1. The mixture was milled in a Fritsch P4 planetary mill at 350 rpm for 4 h 30 min.

A 1 g mixture of mechanochemically prepared Li_3AlH_6 and TiCl_3 was charged together with seventeen 7.9 mm diameter Cr-steel balls into a tool steel vial under an argon atmosphere. The ball-to-powder weight ratio was approximately 35:1. The mixture was milled in a SPEX-8000 mill for 2 h. Some of the milled powders were rinsed in distilled water and filtered to remove chloride formed during milling. The mole ratio between Li_3AlH_6 and TiCl_3 was changed from 1:1 to 6:1.

In order to synthesize fine TiAl_3 mechanochemically, a mixture of TiCl_3 , AlCl_3 and Mg powders with a molar ratio of 1:3:6 was milled for 4 h using the SPEX-8000 mill at the same milling condition as described before. The milled powder was rinsed in distilled water and filtered to remove MgCl_2 byproduct formed during milling.

The product powders were characterized by X-ray diffraction (XRD) using Bruker D8 Advance with $\text{Cu K}\alpha$ radiation and scanning electron microscopy (SEM) using FEI XL-30 FEG.

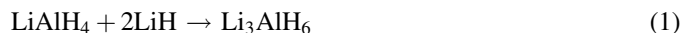
In order to confirm the catalytic effect of fine TiAl_3 on the thermal decomposition of Li_3AlH_6 , 5 mol% TiAl_3 was dispersed into Li_3AlH_6 by milling the mixture in the SPEX-8000 mill for 30 min. The same amount of TiCl_3 was also dispersed into Li_3AlH_6 for comparison. The thermal decomposition behavior of Li_3AlH_6 with and without catalyst was analyzed by differential scanning calorimetry (DSC) using NETSCH DSC204 and thermogravimetry (TG) using NETSCH TG209. The heating rate was $2\ ^\circ\text{C}/\text{min}$ and the flow rate of 99.9999% argon gas was 50 ml/min for both DSC and TG measurements. The kinetics of the thermal decomposition reaction was volumetrically measured by a Sievert type apparatus.

3. Thermodynamic calculation

Thermodynamic calculation of the Li–Al–H–Ti–Cl system was performed based on the Gibbs-energy minimization criterion [19] to understand what the equilibrium phases are in the Li_3AlH_6 and TiCl_3 mixtures. The phases included in this calculation were Li_3AlH_6 , LiAlH_4 , LiH, TiCl_3 , LiCl, Ti, Al, TiAl, TiAl_3 , Ti_3Al , TiAl_2 , $\text{Ti}_5\text{Al}_{11}$, TiH_2 and H_2 . The Gibbs energy data for Li_3AlH_6 and LiAlH_4 were taken from Ref. [18]. The data for the Ti–Al intermetallic phases and all the other phases were from the SGTE solution and substance databases, respectively, which are incorporated into Thermo-Calc [20].

4. Results and discussion

The XRD pattern of the mixture of LiAlH_4 and LiH milled for 4 h 30 min is presented in Fig. 2. The peak positions are in good agreement with those of Li_3AlH_6 obtained by Zaluski et al. [21] and Balema et al. [22]. It is, therefore, confirmed that Li_3AlH_6 forms during milling according to the following reaction:



The XRD patterns of reaction products between LiAlH_6 and TiCl_3 milled for 2 h are shown in Fig. 3. For the 6:1 mixture,

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