



Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Decomposition behavior of unmilled and ball milled lithium alanate (LiAlH_4) including long-term storage and moisture effects

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ARTICLE INFO

Article history:

Received 25 April 2010
 Received in revised form 5 May 2010
 Accepted 7 May 2010
 Available online 20 May 2010

Keywords:

Solid state hydrogen storage
 Hydrogen storage materials
 Desorption temperature and kinetics
 Lithium alanate (LiAlH_4)
 Ball milling
 X-ray diffraction (XRD)
 Differential scanning calorimetry (DSC)

ABSTRACT

A comprehensive study of the decomposition behavior of as received and mechanically (ball) milled LiAlH_4 has been carried out using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and volumetric hydrogen desorption in a Sieverts-type apparatus. Alfa Aesar LiAlH_4 powder investigated in this work has the average particle size of $9.9 \pm 5.2 \mu\text{m}$ as compared to $50\text{--}150 \mu\text{m}$ for Sigma–Aldrich LiAlH_4 investigated by Ares et al. [9]. High energy ball milling reduced the particle size of the present LiAlH_4 to $2.8 \pm 2.3 \mu\text{m}$. In general, comparing the results of our microstructural studies with those reported by Ares et al. [9] it is clear that the morphology, microstructure and chemistry of LiAlH_4 can be very dissimilar depending on the supplier from which LiAlH_4 powder was purchased. We do not observe a partial decomposition of LiAlH_4 during milling up to 5 h under high energy impact mode. The observed melting of LiAlH_4 in a DSC test is a very volatile event where the liquid LiAlH_4 starts foaming and flowing out of the alumina crucible. After completion of solidification and desorption at temperatures above melting the powder resembles a lava rock. A thermal sectioning in DSC tests at pre-determined temperatures and subsequent XRD studies show that LiAlH_4 starts decomposing into Li_3AlH_6 immediately after melting. Li_3AlH_6 seems to be already solidified before it starts decomposing in the next stage. All volumetric desorption curves at the $120\text{--}300^\circ\text{C}$ range clearly exhibit a two-stage desorption process, Stage I and II. As received LiAlH_4 is able, in a fully solid state, to desorb at 120°C under pressure of 0.1 MPa H_2 (atmospheric) as much as 7.1 wt.\% H_2 within $\sim 259,000 \text{ s}$ ($\sim 72 \text{ h}$), i.e. $\sim 93\%$ of the purity-corrected H_2 content from the reactions in Stage I ($\text{LiAlH}_4(\text{s}) \rightarrow (1/3)\text{Li}_3\text{AlH}_6(\text{s}) + (2/3)\text{Al}(\text{s}) + \text{H}_2$) and Stage II ($(1/3)\text{Li}_3\text{AlH}_6(\text{s}) \rightarrow \text{LiH} + (1/3)\text{Al} + 0.5\text{H}_2$). The apparent activation energy for Stage I and II for unmilled LiAlH_4 is equal to ~ 111 and $\sim 100 \text{ kJ/mol}$, respectively. For the ball milled LiAlH_4 the apparent activation energy for Stage I and II is slightly lower ~ 92.5 and $\sim 92 \text{ kJ/mol}$, respectively. The water absorption up to 11.7% due to exposure to air for 1 h does not change in any drastic way the hydrogen desorption rate of ball milled LiAlH_4 in Stage I. Flammability tests show that the ball milled LiAlH_4 powder does not self-ignite on contact with air but can only be ignited by scraping the cylinder walls with a metal tool and then the powder burns with an open flame.

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