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The effects of nanometric nickel (n-Ni) catalyst on the dehydrogenation and rehydrogenation behavior of ball milled lithium alanate (LiAlH_4)

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ABSTRACT

A comprehensive study of the effects of nanometric Ni (n-Ni) additive having a specific surface area (SSA) of 9.5 and 14.5 m^2/g on the dehydrogenation and rehydrogenation behavior of 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 under 0.1 MPa H_2 pressure. The $\text{LiAlH}_4 + 1$, 5 and 10 wt.% n-Ni mixtures were processed by a simple mixing as well as low energy and high energy mechanical (ball) milling in a unique magneto-mill. No decomposition during milling up to 1 h has been observed for $\text{LiAlH}_4 + 5$ and 10 wt.% n-Ni. A mixing of $\text{LiAlH}_4 + \text{n-Ni}$ still results in the melting of LiAlH_4 . In contrast, doping with 5 and 10 wt.% n-Ni combined with high energy ball milling completely eliminates melting of LiAlH_4 . Volumetric dehydrogenation studies show that throughout the entire temperature range from 100 °C to 250 °C a $\text{LiAlH}_4 + \text{n-Ni}$ nanocomposite system ball milled under high energy mode always desorbs hydrogen in a solid state without any melting in two stages I and II. Stage I is related to the transformation of LiAlH_4 into $(\text{Li}_3\text{AlH}_6 + \text{Al} + \text{H}_2)$ and Stage II is related to the transformation of Li_3AlH_6 into $(\text{LiH} + \text{Al} + \text{H}_2)$. The apparent activation energy of Stage I and II equals ~ 70 and ~ 100 kJ/mol, respectively. This can be compared with the apparent activation energy of ball milled undoped LiAlH_4 equal to about 90 kJ/mol for both Stage I and II as reported in Ref. [9]. It is also shown that n-Ni is a very potent catalyst destabilizing a ball milled mixture of $\text{LiAlH}_4 + 5$ wt.% to the extent that it is capable to desorb slowly quite substantial quantities of hydrogen at RT, 40 and 80 °C. The rate of H_2 release during storage at this temperature range can be easily regulated by increasing or decreasing temperature. These virtues make the $\text{LiAlH}_4 + 5$ wt.% n-Ni mixture a potential hydrogen storage material for applications where a continuous supply of hydrogen is required for a prolonged service time as, for example, in some chemical processes where the presence of a reducing atmosphere is required. Rehydrogenation attempts of ball milled dehydrogenated $\text{LiAlH}_4 + 5$ wt.% n-Ni have been made. The dehydrogenation temperatures were selected in such a manner as to rehydrogenate either starting from the $(\text{Li}_3\text{AlH}_6 + \text{Al})$ (dehydrogenation at 120 °C) or from the $(\text{LiH} + \text{Al})$ (dehydrogenation at 170 and 250 °C) phase composition. Rehydrogenation temperatures and pressures of H_2 were in the range of 55–250 °C and 0.2–10 MPa, respectively. Unfortunately, no successful rehydrogenation has been observed under these conditions.

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