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A study on the hydrogen storage properties and reaction mechanism of $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ composite system

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ABSTRACT

In this work, the hydrogen storage properties of different molar ratio (in mole of 1:3 and 1:4) $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ system is investigated for the first time. X-ray diffraction and Fourier transform infrared results show that the $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ with molar ratio of 1:3 and 1:4 composite was transformed to Li_3AlH_6 and NaBH_4 phases via a metathesis reaction during a ball-milling process for 6 h. Temperature-programmed-desorption (TPD) results show three stages of decomposition for the $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ (in mole ratio of 1:3 and 1:4) composite resulting from Li_3AlH_6 and NaBH_4 phases. From the TPD graph, the $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ composite with molar ratio of 1:4 had showed better performance of hydrogenation properties compared to with molar ratio of 1:3. The composite began to release hydrogen at 180 °C in relation to decomposition of the Li_3AlH_6 stage into LiH and Al. The NaBH_4 stage then began to decompose at approximately 380 °C, after reacting with Al to form an intermetallic phase, AlB_2 , which occurred at 100 °C lower than as-milled NaBH_4 . At 430 °C, the un-reacted NaBH_4 was decomposed after catalysing with AlB_2 . Kissinger analysis shows the apparent activation energy of NaBH_4 decomposition in the hydrides composite was reduced by about 75 kJ/mol compared to the as-milled NaBH_4 . The rehydrogenation process evidenced the reversibility of NaBH_4 . Based on these results, the intermetallic phase, AlB_2 , is considered to have played an important role by lowering the operating temperature and providing access to the full hydrogen content in the $\text{Na}_3\text{AlH}_6\text{--LiBH}_4$ composite system.

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Introduction

Water is the only associated combustion produce of hydrogen, and it is therefore considered to be environmentally friendly.

As such, it has potential to be a future carrier of renewable and clean energy sources [1]. However, problems associated with hydrogen storage currently restrict its use. Hydrogen storage at a high gaseous pressure [2] and in cryogenic liquefaction [3]

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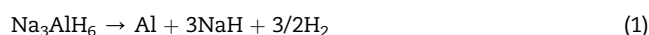
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has been reported in literature, but both these methods require additional costs due to high pressure containment or maintaining cryogenic temperatures [4]. Therefore, determining a solid state hydrogen storage method is of considerable interest and has been the subject of several studies [5,6], but no single solid state material has yet been identified to fulfil hydrogen energy application criteria.

In an attempt to determine the ideal material for use in hydrogen technology, tremendous efforts have been devoted towards enhancing the hydrogen storage properties of metal hydride and complex hydride, for example by reducing the particle size by ball-milling [7], adding a catalyst [8–14], ball milling assisted by dielectric barrier discharge plasma [15,16], a combination of hydride materials known as reactive hydride composites (RHCs) [17–21], and hydrogen generation enhancements by hydrolysis approach [22–24]. In relation to the need to meet targets to provide potential hydrogen storage material, a considerable amount of research has focused on RHCs. A RHC is the reaction between two or more hydrides, which forms a new intermediate phase that could improve the thermodynamic and kinetic properties of hydrogen uptake and release [25,26]. To date, several studies have reported RHC systems such as $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ [27], $\text{Na}_3\text{AlH}_6\text{-MgH}_2$ [28], $\text{LiAlH}_4\text{-LiNH}_2$ [29], $\text{LiNH}_2\text{-2LiH}$ [30], $2\text{LiBH}_4\text{-MgH}_2$ [31], $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ [32], $\text{Ca}(\text{BH}_4)_2\text{-MgH}_2$ [33], $2\text{NaBH}_4\text{-MgH}_2$ [34] and $\text{NaAlH}_4\text{-Mg}(\text{BH}_4)_2$ [35]. However, there are currently issues with sluggish sorption kinetics, and therefore this novel class of materials does not yet fulfil the requirements for use with hydrogen technology.

Work done by Ravnsbaek and Jensen [36] on the $\text{NaAlH}_4\text{-LiBH}_4$ composite system had revealed that the combination of NaAlH_4 with LiBH_4 had formed new products which were LiAlH_4 and NaBH_4 through a metathesis reaction. Based on their work, it is interesting to explore the combination of LiBH_4 with the product of the first step decomposition of NaAlH_4 , which is Na_3AlH_6 . Even though Na_3AlH_6 is the product after the first decomposition of NaAlH_4 , different results could be achieved as compared to the NaAlH_4 . It is because Na_3AlH_6 can be operated at a lower pressure (up to 2.5 MPa) as compared to NaAlH_4 (up to 10 MPa) [37]. Therefore, a combination of two interesting solid-state hydrogen storage materials, sodium aluminium hexahydride (Na_3AlH_6) and lithium borohydride (LiBH_4) are introduced as components in a RHC system. Na_3AlH_6 is a very interesting material as it has an equilibrium pressure of 0.1 MPa at 373 K, with reaction enthalpies of 47 kJ/mol [38]. The decomposition of Na_3AlH_6 , is as follows,



The high theoretical hydrogen storage amount of metal borohydride is also of considerable interest in hydrogen research. LiBH_4 has a high theoretical gravimetric capacity (18.5 wt% of H_2) [39], but its slow reaction kinetics and high thermodynamic stability forbid its practical usage [40]. The dehydrogenation reaction proceeds as follows in the case of pure LiBH_4 [41],



To the best of the authors' knowledge, no studies have reported the hydrogen storage properties and reaction mechanism of $\text{Na}_3\text{AlH}_6\text{-LiBH}_4$ composite. Work conducted by Thaweelap and Utke [42] on the $\text{LiAlH}_4\text{-LiBH}_4$ system showed the formations of $\text{Li}_x\text{Al}_{(1-x)}\text{B}_2$ and LiH-Al containing phase during dehydrogenation favor decomposition of LiH , leading to enhancement of hydrogen capacity, and stabilization of boron in solid state, resulting in improvement of hydrogen storage properties. In addition, Lu and Fang [29] discovered that LiNH_2 effectively destabilized LiAlH_4 by reacting with LiH during the heating process, thereby releasing a high hydrogen capacity (8.1 wt%) at lower temperatures. Furthermore, Pinkerton et al. [43] showed formation of the new quaternary hydride, $\text{Li}_3\text{BN}_2\text{H}_8$, after milling LiBH_4 with LiNH_2 , which can release exceed 10 wt% of hydrogen above 250 °C. These results demonstrate that using combinations of different hydrides is an effective way to achieve a high hydrogen storage material with a lower operating temperature.

Therefore, in this study, the hydrogen sorption properties of the RHC system, $\text{Na}_3\text{AlH}_6\text{-LiBH}_4$, are investigated and compared with bare NaBH_4 to determine its hydrogen storage properties as a potential solid-state material. In particular, the hydrogen storage properties of the $\text{Na}_3\text{AlH}_6\text{-LiBH}_4$ composite are investigated using a Sieverts-type pressure-composition-temperature (PCT) apparatus and differential scanning calorimetry (DSC). Fourier transform infrared (FTIR) and X-ray diffraction (XRD) are then applied to determine the reaction mechanism before and after decomposition, as well as after conducting a rehydrogenation process with the dehydrogenated sample. The possible reaction mechanism of $\text{Na}_3\text{AlH}_6\text{-LiBH}_4$ is then discussed.

Experimental details

The starting materials, NaAlH_4 (hydrogen storage grade, 93% purity), NaH (hydrogen storage grade, 93% purity) and LiBH_4 (hydrogen storage grade, 90% purity) were purchased from Sigma Aldrich. Na_3AlH_6 was synthesized through the mechanochemical reaction between NaH and NaAlH_4 with a mole ratio of 2:1 [44]. NaH and NaAlH_4 were milled together for 20 h at a rotation speed of 400 rpm using hardened stainless steel balls (ball-to-powder mass ratio of 40:1) in a planetary ball mill (NQM-0.4). A mixture of Na_3AlH_6 and LiBH_4 with a molar ratio of 1:3 and 1:4 was prepared by milling for 6 h under the same conditions. Pure Li_3AlH_6 and NaBH_4 were also prepared under the same conditions for comparison purposes. All experimental handling was conducted in an argon atmosphere MBraun Unilab glove box to avoid oxidation.

For the temperature-programmed-desorption (TPD) measurement, sample amounts of 60 mg were loaded into a sample vessel and heated from room temperature to 550 °C under a vacuum condition in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). Re/dehydrogenation kinetic measurements were also conducted using the same instrument. Characterization of differential scanning calorimetry was conducted using a Mettler Toledo thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)1. For this, approximately 5 mg of a sample was loaded into an alumina

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