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Study on the hydrogen storage properties and reaction mechanism of NaAlH₄–MgH₂–LiBH₄ ternary-hydride system

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ABSTRACT

In this paper, we report the hydrogen storage properties and reaction mechanism of NaAlH₄–MgH₂–LiBH₄ (1:1:1) ternary-hydride system prepared by ball milling. It was found that during ball milling, the NaAlH₄/MgH₂/LiBH₄ combination converted readily to the mixture of LiAlH₄/MgH₂/NaBH₄ and there is a mutual destabilization among the hydrides. Three major dehydrogenation steps were observed in the system, which corresponds to the decomposition of LiAlH₄, MgH₂, and NaBH₄, respectively. The onset dehydrogenation temperature of MgH₂ in this system is observed at around 275 °C, which is over 55 °C lower from that of as-milled MgH₂. Meanwhile, NaBH₄-relevant decomposition showed significant improvement, starts to release hydrogen at 370 °C, which is reduced by about 110 °C compared to the as-milled NaBH₄. The second and third steps decomposition enthalpy of the system were determined by differential scanning calorimetry measurements and the enthalpies were changed to be 61 and 100 kJ mol⁻¹ H₂ respectively, which are smaller than that of MgH₂ and NaBH₄ alone. From the Kissinger plot, the apparent activation energy, E_A, for the decomposition of MgH₂ and NaBH₄ in the composite was reduced to 96.85 and 111.74 kJ mol⁻¹ respectively. It is believed that the enhancement of the dehydrogenation properties was attributed to the formation of intermediate compounds, including Li–Mg, Mg–Al, and Mg–Al–B alloys, upon dehydrogenation, which change the thermodynamics of the reactions through altering the de/rehydrogenation pathway.

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Introduction

Due to an ongoing environmental crisis and the increasingly limited supply of fossil fuels, hydrogen has attracted much attention as an alternative energy carrier [1]. However, hydrogen storage presents a significant challenge for the development of a hydrogen economy, especially in relation to hydrogen-powered vehicles. There are three methods used to

store hydrogen, specifically: high pressure storage, cryogenics, as well as chemical compounds that reversibly release H₂ upon heating (solid-state storage). Among these methods, solid-state storage has become an attractive option due to its high volumetric hydrogen capacity and favorable safety considerations. However, until now, there has been no single material that can satisfy all the requirements for an on-board hydrogen storage material which is suitable for mobile applications [2].

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The high decomposition temperature and slow de/absorption kinetics are two major challenges facing the development of a solid-state hydrogen storage material based on chemisorptions such as metal hydride (e.g. MgH_2) and complex hydride (e.g. LiBH_4) [1]. For example, MgH_2 requires a temperature of 300 °C at 1 bar H_2 to release hydrogen, while LiBH_4 starts to release hydrogen at a level above 380 °C. Moreover, only half of the hydrogen can be released before 600 °C. This temperature is too high for practical onboard applications [3]. In an attempt to improve the hydrogen storage properties of metal hydride and complex hydride, an abundance of studies have been performed. These include, namely: reducing the size of particles by using ball milling [4,5]; utilization of additives, which can facilitate hydrogen de/absorption kinetics [6–21]; and design of so-called reactive hydride composites (RHCs) [15,22–39]. The RHCs method could be regarded as a quite different approach. This approach is aimed at modifying the thermodynamics and kinetics of the hydrogen sorption reaction by mixing two or more hydrides [27,28,32,40–44]. Thermodynamic destabilization is achieved when the mixed hydrides react and form a new intermediate species that may facilitate thermodynamic and kinetic properties of hydrogen release and uptake [45–48].

Recently, a study by Mao et al. [49] has shown that there is a mutual destabilization between the hydrides in the ternary $\text{LiAlH}_4\text{--MgH}_2\text{--LiBH}_4$ system, which exhibits superior hydrogen storage properties compared with the unary components (LiAlH_4 , MgH_2 and LiBH_4). From the XRD analysis, they found that the intermediate compounds, Li–Mg, Mg–Al, and Mg–Al–B alloys, (formed during dehydrogenation), may improve the thermodynamics of reactions by changing the de/rehydrogenation pathway.

The basic idea in this study is to explore the utilization of other complex hydrides as the Al source in the $\text{MgH}_2\text{--LiBH}_4$ composite system. In a previous study, we have shown that a $\text{MgH}_2\text{--NaAlH}_4$ composite system improved dehydrogenation performance compared with as-milled pure NaAlH_4 and pure MgH_2 alone [22]. It is believed that the formation of the NaMgH_3 and $\text{Mg}_{17}\text{Al}_{12}$ phases during the dehydrogenation process plays a critical role in the enhancement of dehydrogenation in the $\text{MgH}_2\text{--NaAlH}_4$ composite. In addition, Shi et al. [50] and Ravnsbaek et al. [51] reported a $\text{LiBH}_4\text{--NaAlH}_4$ composite, in which this mixed system is found to have initiated a transformation to $\text{LiAlH}_4\text{--NaBH}_4$. They claimed that there is mutual destabilization existing in the $\text{LiBH}_4\text{--NaAlH}_4$ composite. Therefore, in the present study, the dehydrogenation properties of the ternary-hydride system, $\text{NaAlH}_4\text{--MgH}_2\text{--LiBH}_4$ was prepared and investigated, in order to improve the hydrogen storage properties through mutual interaction among the three hydrides. To the best of the author's knowledge, no studies have been reported on the hydrogen storage properties and reaction mechanism of the $\text{NaAlH}_4\text{--MgH}_2\text{--LiBH}_4$ ternary-hydride system.

Experimental details

LiAlH_4 (powder, reagent grade, 95%), NaAlH_4 (hydrogen storage grade), MgH_2 (hydrogen storage grade), NaBH_4 (hydrogen storage grade, $\geq 98\%$), and LiBH_4 (hydrogen storage grade,

$\geq 90\%$) were purchased from Sigma Aldrich and were used as received with no further purification. Ball milling (BM) of NaAlH_4 , MgH_2 , and LiBH_4 powders in the mole ratio of 1:1:1 was performed in a planetary ball mill (NQM-0.4) for 1 h at the rate of 400 rpm. Handling of the samples was conducted in an MBraun Unilab glove box filled with high purity Ar atmosphere. Samples were put into a sealed stainless steel vial together with hardened stainless steel balls. The ratio of the weight of balls to the weight of powder was 30:1. For comparison purposes, pristine LiAlH_4 , MgH_2 and NaBH_4 were also milled for a period of 1 h.

The thermal desorption performances and re/dehydrogenation kinetics experiments were performed in a Sievert-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. For the thermal desorption performances experiment, all the samples were heated in a vacuum chamber, and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the thermal desorption performances experiment was 5 °C min^{-1} , and samples were heated from room temperature to desired temperature. The re/de-hydrogenation kinetics measurements were performed at the desired temperature with initial hydrogen pressures of 5.0 MPa and 0.01 MPa respectively.

XRD analysis was performed using a Rigaku MiniFlex II diffractometer with Cu K_α radiation. $\theta\text{--}2\theta$ scans were carried out over diffraction angles from 25° to 80° with a speed of 2.00° min^{-1} . Before the measurement, a small amount of sample was spread uniformly on the sample holder, which was wrapped with plastic wrap to prevent oxidation.

Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. The sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the TGA/DSC apparatus. An empty alumina crucible was used for reference. The samples were heated from room temperature to 500 °C under an argon flow of 30 ml min^{-1} , and different heating rates were used.

Results and discussion

Fig. 1 presents the thermal desorption performances curves of the as-milled $\text{NaAlH}_4\text{--MgH}_2\text{--LiBH}_4$ (molar ratio 1:1:1). From the curve, the $\text{NaAlH}_4\text{--MgH}_2\text{--LiBH}_4$ sample clearly showed three major stages of dehydrogenation that occurred during the heating process. These include, namely: the first stage, which took place within the temperature range of 150–230 °C; the second dehydrogenation stage, starting at approximately 275 °C and completed at about 350 °C; and the final stage, which occurred at a temperature of about 370 °C and was completed at about 475 °C.

To clarify the dehydrogenation mechanism in every stage, XRD measurements were employed as shown in Fig. 2. After 1 h milling (Fig. 2(a)), it can be seen that the peaks of the starting materials, NaAlH_4 and LiBH_4 , were absent. Further, new peaks corresponding to the formation of LiAlH_4 and

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