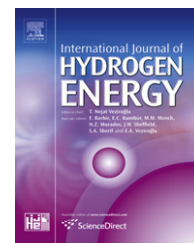


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Reversible hydrogenation/dehydrogenation performances of the $\text{Na}_2\text{LiAlH}_6\text{-Mg}(\text{NH}_2)_2$ system

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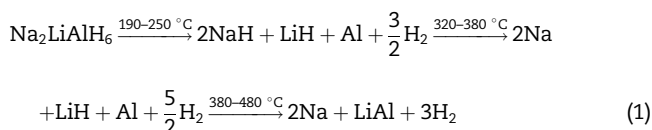
ABSTRACT

Complex hydrides and Metal–N–H-based materials have attracted considerable attention due to their high hydrogen content. In this paper, a novel amide–hydride combined system was prepared by ball milling a mixture of $\text{Na}_2\text{LiAlH}_6\text{-Mg}(\text{NH}_2)_2$ in a molar ratio of 1:1.5. The hydrogen storage performances of the $\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$ system were systematically investigated by a series of dehydrogenation/hydrogenation evaluation and structural analyses. It was found that a total of ~5.08 wt% of hydrogen, equivalent to 8.65 moles of H atoms, was desorbed from the $\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$ combined system. In-depth investigations revealed that the variable milling treatments resulted in the different dehydrogenation reaction pathways due to the combination of Al and N caused by the energetic milling. Hydrogen uptake experiment indicated that only ~4 moles of H atoms could be reversibly stored in the $\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$ system perhaps due to the formation of AlN and Mg_3N_2 after dehydrogenation.

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1. Introduction

Hydrogen is regarded as a promising candidate to solve future sustainable energy supply problems for its abundant availability, environmental friendliness and high energy content [1]. However, the storage of hydrogen in a safe and economical way is a major challenge for practical on-board applications. In last decades, complex hydrides based on Al–H group, such as NaAlH_4 , LiAlH_4 , Na_3AlH_6 , Li_3AlH_6 and $\text{Na}_2\text{LiAlH}_6$ have received considerable attention as some of the most potential hydrogen storage materials due to their light weight and high hydrogen content [2–10]. Among them, $\text{Na}_2\text{LiAlH}_6$ was demonstrated to be totally reversible with 6.7 wt% of hydrogen storage capacity by the following sequential reactions [10].



However, the complete hydrogen desorption of $\text{Na}_2\text{LiAlH}_6$ requires a rather high operating temperature since the decomposition of NaH and LiH occurs at a temperature range from 320 to 480 °C, which is too high for practical applications.

Recently, it was found that the dehydrogenation temperature of the complex hydride could be significantly reduced by combined with metal amides [11–15]. Xiong et al. reported that ~6 wt% of hydrogen was evolved from the 1:1 molar mixture of LiNH_2 and LiAlH_4 during ball milling [11]. Investigations on the mixture of $1\text{LiNH}_2\text{-}2\text{LiAlH}_4$ addressed that ~8.1 wt% of hydrogen was released in the temperature range of 85–320 °C by means of thermogravimetric analysis [12]. More interestingly, about 5 wt% of hydrogen could be reversibly stored in the $\text{LiNH}_2\text{-LiAlH}_4$ system with a molar ratio of 2:1 [13]. As LiAlH_4 was combined with NaNH_2 in a molar ratio of 1:1, more than 5 wt% of hydrogen could be quickly released at 120 °C exothermically [14]. Further investigations on the LiAlH_4 and $\text{Mg}(\text{NH}_2)_2$ (1:1) system showed that totally 8.4 wt% of hydrogen

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was liberated under moderate conditions [15]. Moreover, Pinkerton et al. also revealed that 1 mole of LiBH_4 reacted with 2 moles of LiNH_2 to desorb more than 10 wt% of hydrogen below 350°C [16], which is distinctly lower than the dehydrogenation temperature for the self-decomposition of LiBH_4 ($\sim 600^\circ\text{C}$) [17]. Apparently, the combinations of complex hydrides and amides will result in some novel interesting hydrogen storage systems with lower dehydrogenation temperature and high hydrogen content. It can be therefore expected that the hydrogen storage performances of $\text{Na}_2\text{LiAlH}_6$ will be improved by introducing proportionally metal amides.

In this work, for reducing the dehydrogenation temperature and improving the overall hydrogen storage properties of mixed alanate $\text{Na}_2\text{LiAlH}_6$, $\text{Mg}(\text{NH}_2)_2$ was introduced and a novel $\text{Na}_2\text{LiAlH}_6\text{-Mg}(\text{NH}_2)_2$ system with an optimal molar ratio of 1:1.5 was formed on the basis of the previous reports [18,19]. It was found that ~ 5.08 wt% of hydrogen was desorbed from the newly developed system below 350°C , and 4 equiv of H atoms could be recharged at 250°C and 115 bar of hydrogen pressure. Moreover, the detailed mechanisms for hydrogen desorption were also discussed and elucidated.

2. Experimental

Commercial NaH and LiAlH_4 were purchased from Sigma-Aldrich and Alfa Aesar with claimed purities of 95% and 97%, respectively. $\text{Na}_2\text{LiAlH}_6$ was obtained by ball milling a 2:1 molar mixture of NaH and LiAlH_4 under 1 bar pure argon atmosphere for 24 h on a planetary ball mill (QM-3SP4, Nanjing) at 500 rpm. $\text{Mg}(\text{NH}_2)_2$ was synthesized in our laboratory by reacting pre-milled Mg powder (purity 99%, Sinopharm) under 7 bar ammonia atmosphere at about 300°C . The $\text{Na}_2\text{LiAlH}_6\text{-Mg}(\text{NH}_2)_2$ samples were prepared by ball milling corresponding chemicals in a molar ratio of 1:1.5 for different periods. Two rotary speeds, 500 rpm and 100 rpm were adopted for mechanochemical reaction and uniform mixing, respectively. The milling jar is equipped with a gas valve which can be connected to a pressure gauge to measure the pressure change within the milling jar after ball milling. The milling was set to revolve for 0.2 h in one direction, pause 0.1 h, and then revolve in the reverse direction. All handling of the sample was performed in an MBRAUN glovebox filled with argon gas to prevent moisture and oxygen contaminations (O_2 : <1 ppm, H_2O : <1 ppm).

Temperature-programmed desorption (TPD) experiment was performed on a homemade system with an online gas chromatograph (GC) attached. A continuous flow of pure argon at a speed of 20 mL/min was used as carrier gas. Approximately 25 mg of sample was loaded and gradually heated from 20 to 420°C at a rate of $2^\circ\text{C}/\text{min}$.

Quantitative measurements on hydrogen release/uptake were determined by volumetric method with a homemade Sieverts-type apparatus. Typically, 150 mg of sample was loaded in a stainless-steel tube reactor each time in a glovebox, and then the tube reactor was connected to the Sieverts-type apparatus. The sample was heated from room temperature at an average ramp of $2^\circ\text{C}/\text{min}$ (initially in vacuum) for desorption and $1^\circ\text{C}/\text{min}$ (initially in 115 bar H_2)

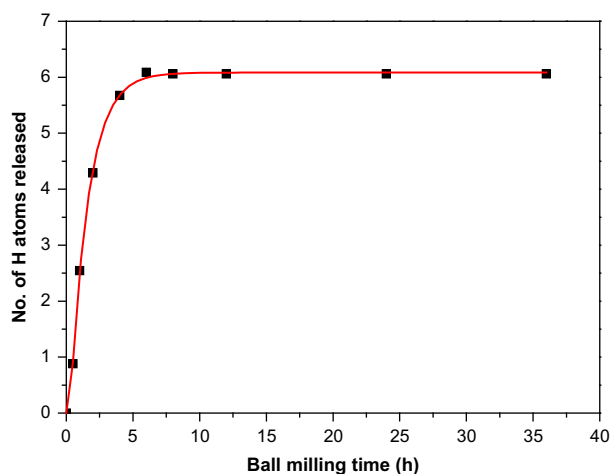


Fig. 1 – Time dependence of hydrogen released from $\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$ system during ball milling.

for absorption, respectively. Temperatures and pressures of the sample were automatically monitored and recorded. The amounts of hydrogen absorbed/desorbed of the samples were obtained by calculating pressure changes in the calibrated volume and the reactor using the equation of state. The desorption heat effect of the sample was examined by differential scanning calorimetry (DSC) on a Netzsch STA 449 F3 with an online mass spectrometer (QMS 403C, Netzsch). Approximately 2.5 mg of sample was loaded into the crucible each time and heated up to 400°C at a rate of $4^\circ\text{C}/\text{min}$. High purity argon was used as purge gas.

The phase structures of the samples were identified by an X'Pert PRO (PANalytical) X-ray diffractometer with Cu K_α radiation at 40 kV and 40 mA. XRD data were collected from 10° to 90° (2θ) with step increments of 0.05° at room temperature. Samples were protected from contacting air and moisture with argon atmosphere using a homemade container during sample transfer and testing. FTIR spectra were conducted on a Bruker Vector 22 FTIR spectrometer. The sample was prepared by pressing a mixture of the powder sample and potassium bromide (KBr) at a weight ratio of 1:20 to form a pellet. Transmission mode was applied and each spectrum was created from 25 scans accumulated with a resolution of 4 cm^{-1} .

3. Results and discussion

The pressure in the milling jar increased gradually with time as the mixture of $1\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$ was mechanically milled at 500 rpm, indicating that a gaseous product was generated. Mass spectrometer analysis showed that the gaseous product was pure hydrogen. By applying the equation of state, the corresponding amount of hydrogen desorbed in milling process was obtained as shown in Fig. 1. It can be seen that the hydrogen desorption rate is fast in the initial milling period, and then slows down after 4 h of milling. When the milling time was extended to 6 h, about 6.05 moles of H atoms were detached from 1 mole of $\text{Na}_2\text{LiAlH}_6\text{-1.5Mg}(\text{NH}_2)_2$, which corresponds to 3.55 wt % of the starting mixture. It is well

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