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Hydrogen storage properties and mechanisms of a $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3 - \text{NaAlH}_4$ combination system

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ABSTRACT

The $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3 - x\text{NaAlH}_4$ ($x = 0-4$) combination systems were prepared by ball milling, and the reversible hydrogen storage behavior and its mechanisms were investigated and discussed. Combining NaAlH_4 with $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ significantly reduces the operating dehydrogenation temperatures and effectively suppresses the emission of NH_3 by-products. The dehydrogenation onset temperature of the $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3 - 2\text{NaAlH}_4$ system is lowered to ca. 70 °C, which is much lower than the onset temperatures of either $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ or NaAlH_4 . In addition, ammonia emission from $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ is thoroughly suppressed by the addition of NaAlH_4 , leading to approximately 11.3 wt% hydrogen released upon heating to 570 °C. Further investigations revealed that at the initial heating stage, $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ first reacts with NaAlH_4 to produce NaBH_4 , Al_3Mg_2 , Mg , $\text{Al}_{0.95}\text{Mg}_{0.05}$, BN , Na and AlN along with the release of hydrogen. Further increasing the operation temperature gives rise to a chemical reaction between NaBH_4 , AlN and Mg that liberates all of the hydrogen and yields the resultant products of MgAlB_4 , BN , Na and Al_3Mg_2 . The dehydrogenated products can take up ~3.5 wt% of hydrogen at 450 °C and 100 bar of hydrogen pressure, exhibiting a partial reversibility for hydrogen storage.

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Introduction

Hydrogen is a lightweight, highly abundant and environmentally benign product; therefore, it has attracted much attention as an alternative energy source [1]. The search for safe, highly efficient and economical hydrogen-storage technologies is one of the most challenging issues in the implementation of hydrogen fuel cell technologies [2–5]. Over the

past few decades, considerable efforts have focused on storing H_2 in solid-state materials such as metal hydrides, alanates, borohydrides, imides/amides, ammonia boranes and amidoboranes due to their safe operating pressures and high hydrogen capacity [6–11].

Light-weight metal borohydrides $\text{M}(\text{BH}_4)_n$ have attracted great interest as one of the most promising hydrogen storage materials due to their high gravimetric and volumetric hydrogen capacities [12–15]. For instance, magnesium

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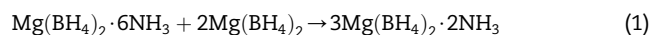
borohydride ($\text{Mg}(\text{BH}_4)_2$) possesses a theoretical gravimetric capacity of 14.9 wt% and a volumetric capacity of 112 kg/m^3 with a favorable desorption enthalpy change of $-39 \text{ kJ}/\text{mol}$ of H_2 [16], which allows for hydrogen desorption near room temperature. These characteristics make $\text{Mg}(\text{BH}_4)_2$ very competitive for mobile hydrogen storage applications. However, the material's hydrogen desorption kinetics are relatively sluggish, and the majority of hydrogen desorption from $\text{Mg}(\text{BH}_4)_2$ occurs at temperatures higher than $250 \text{ }^\circ\text{C}$, which is currently too high for practical applications in mobile power systems [15]. Numerous efforts have been devoted to addressing the problematic kinetics for hydrogen desorption from $\text{Mg}(\text{BH}_4)_2$ to make it feasible as a practical hydrogen storage material, including catalyst doping [17,18], nanoconfinement [19] and creating reactive composites [20–25]. It was reported that adding 5 mol% TiF_3 and ScCl_3 produced a five-fold increase in the dehydrogenation reaction rate of $\text{Mg}(\text{BH}_4)_2$ [26]. The dehydrogenation onset temperature for $\text{Mg}(\text{BH}_4)_2$ was reduced to $125 \text{ }^\circ\text{C}$ by co-doping with TiCl_3 and NbCl_5 [17]. The resulting TiO_2 -containing $\text{Mg}(\text{BH}_4)_2$ achieved 2.4 wt% of cycled hydrogen capacity at $271 \text{ }^\circ\text{C}$ under $\sim 140 \text{ bar}$ of H_2 pressure [27], which is superior to that of a pristine sample. The temperature for major hydrogen desorption from a $\text{Mg}(\text{BH}_4)_2$ /carbon composite was decreased to $160 \text{ }^\circ\text{C}$ [28]. A $\text{Mg}(\text{BH}_4)_2$ - 2NaAlH_4 combination system was able to release 9.1 wt% hydrogen initiated at $101 \text{ }^\circ\text{C}$ [24]. Moreover, in a composite material with $\text{Mg}(\text{BH}_4)_2$ infiltrated into a highly ordered mesoporous carbon (CMK-3) containing dispersed Ni nanoparticles, the hydrogen desorption temperature dramatically decreased, and the release rate was significantly higher [19]. A 3 $\text{Mg}(\text{BH}_4)_2$ - 3LiBH_4 - 4FGi composite began to release hydrogen at $125.7 \text{ }^\circ\text{C}$, and hydrogen desorption amounted to over 8.0 wt% [29].

Alternatively, forming NH_3 coordination compounds (i.e., ammoniates) is also an effective strategy to reduce the dehydrogenation temperature of $\text{Mg}(\text{BH}_4)_2$ due to the presence of dihydrogen bonds [30–36]. A series of ammoniates have been synthesized for $\text{Mg}(\text{BH}_4)_2$, including $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, $\text{Mg}(\text{BH}_4)_2 \cdot 3\text{NH}_3$, $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ and $\text{Mg}(\text{BH}_4)_2 \cdot \text{NH}_3$. Among these ammoniates, $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ was demonstrated to start releasing $\sim 13.1 \text{ wt}\%$ hydrogen while heating up to $400 \text{ }^\circ\text{C}$ [37]. Nevertheless, a $150 \text{ }^\circ\text{C}$ dehydrogenation temperature is still too high for practical applications. More importantly, the hydrogen that released from $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ was contaminated with ammonia. Reducing the dehydrogenation temperature of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ and depressing the evolution of ammonia as by-product have been investigated. For example, we recently reduced the dehydrogenation onset temperature of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ to $70 \text{ }^\circ\text{C}$ by partially substituting fluorine for hydrogen [38]. Additionally, hydrogen desorption from a $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ - MgH_2 combination system initiated at $70 \text{ }^\circ\text{C}$, and the total dehydrogenation amount was approximately 13.9 wt% [39]. More recently, Leng et al. reported that by combining $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ with LiAlH_4 , the hydrogen desorption temperature was reduced to $100 \text{ }^\circ\text{C}$ with superior ammonia suppression due to a combination reaction between the [Al–H] and [N–H] groups [40]. Therefore, metal hydrides or alanates may have potential to further improve the hydrogen storage properties of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$.

In this work, a reactive composite with several compositions of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ - $x\text{NaAlH}_4$ were prepared and investigated. The combination systems showed significantly improved hydrogen storage properties compared to pristine $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$. The $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ - 2NaAlH_4 combination released $\sim 11.3 \text{ wt}\%$ hydrogen initiated at $70 \text{ }^\circ\text{C}$. More importantly, the dehydrogenated $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ - 2NaAlH_4 absorbed approximately 3.5 wt% of hydrogen at 100 bar hydrogen at $450 \text{ }^\circ\text{C}$, exhibiting partial reversibility for hydrogen storage.

Experimental section

The commercial chemicals NaAlH_4 (ACROS, 93%), MgCl_2 (Alfa Aesar, 99%) and NaBH_4 (Alfa Aesar, 98%) were used as received without further purification. $\text{Mg}(\text{BH}_4)_2$ was synthesized in our laboratory through a metathesis reaction between NaBH_4 and MgCl_2 in diethyl ether as reported previously [41]. $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ was prepared by ball milling $\text{Mg}(\text{BH}_4)_2$ under 7 bar of NH_3 atmosphere. $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ was obtained by ball milling a mixture of this $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ with $\text{Mg}(\text{BH}_4)_2$ in a molar ratio of 1:2 according to the following reaction [38].



The $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ - $x\text{NaAlH}_4$ ($x = 1$ – 4) composites were prepared on a planetary ball mill (QM-3SP4) rotating at 200 rpm for 1 h. The ball-to-sample weight ratio was approximately 60:1. To compare dehydrogenation/hydrogenation properties, pure NaAlH_4 and $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ were also treated under the same conditions. The milling was set to rotate for 0.2 h in one direction, followed by a 0.1 h pause before reversing direction to inhibit powder conglutination and heat accumulation in the jar. All sample handling was conducted in a glove box (MBRAUN, Germany) filled with pure argon. H_2O and O_2 concentrations were kept below 1 ppm to prevent contamination from moisture and oxygen.

The thermal decomposition properties of the samples were analyzed by temperature-programmed desorption (TPD), differential scanning calorimetry (DSC) and volumetric release techniques. TPD measurements were conducted using a homemade apparatus equipped with an online mass spectrometer (MS). Approximately 40 mg of each sample was loaded into a homemade tube reactor. Pure Ar was used as the carrier gas. The temperature was gradually elevated from room temperature to $600 \text{ }^\circ\text{C}$ at a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$. DSC analyses were performed on a Netzsch 200 F3 unit. Approximately 2 mg of each sample was loaded and heated at a rate of $2 \text{ }^\circ\text{C}/\text{min}$ under Ar flow. In the volumetric release/soak experiment, a homemade Sieverts-type apparatus was employed, and $\sim 60 \text{ mg}$ of each sample was loaded into a stainless steel reactor inside a glove box, and the reactor was connected to the Sieverts-type system. The sample was heated from room temperature to a desired temperature at an average rate of $2 \text{ }^\circ\text{C}/\text{min}$ for dehydrogenation (initially under vacuum) and $1 \text{ }^\circ\text{C}/\text{min}$ for hydrogenation (under an initial hydrogen pressure of 100 bar). According to the automatically recorded pressures and temperatures, the amount of hydrogen desorbed/absorbed from the samples was calculated by the pressure changes in the reactor using the equation of state.

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