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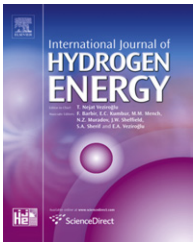

# Hydrogen storage properties and mechanisms of the $Mg(BH_4)_2$–$NaAlH_4$ system

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## ABSTRACT

Hydrogen storage properties and mechanisms of the combined $Mg(BH_4)_2$–$NaAlH_4$ system were investigated systematically. It was found that during ball milling, the $Mg(BH_4)_2$–$xNaAlH_4$ combination converted readily to the mixture of $NaBH_4$ and $Mg(AlH_4)_2$ with a metathesis reaction. The post-milled samples exhibited an apparent discrepancy in the hydrogen desorption behavior with respect to the pristine $Mg(BH_4)_2$ and $NaAlH_4$. Approximately 9.1 wt% of hydrogen was released from the $Mg(BH_4)_2$–$2NaAlH_4$ composite milled for 24 h with an onset temperature of 101 °C, which is lowered by 105 and 139 °C than that of $NaAlH_4$ and $Mg(BH_4)_2$, respectively. At initial heating stage, $Mg(AlH_4)_2$ decomposed first to produce $MgH_2$ and Al with hydrogen release. Further elevating operation temperatures gave rise to the reaction between $MgH_2$ and Al and the self-decomposition of $MgH_2$ to release more hydrogen and form the $Al_{0.9}Mg_{0.1}$ solid solution and Mg. Finally, $NaBH_4$ reacted with Mg and partial $Al_{0.9}Mg_{0.1}$ to liberate all of hydrogen and yield the resultant products of $MgAlB_4$, $Al_3Mg_2$ and Na. The dehydrogenated sample could take up ~6.5 wt% of hydrogen at 400 °C and 100 atm of hydrogen pressure through a more complicated reaction process. The hydrogenated products consisted of $NaBH_4$, $MgH_2$ and Al, indicating that the presence of $Mg(AlH_4)_2$ is significantly favorable for reversible hydrogen storage in $NaBH_4$ at moderate temperature and hydrogen pressure.

## 1. Introduction

Storing hydrogen in solid state holds great promise for on-board applications in view of safety, efficiency and economy [1–3]. Complex hydrides of light metals have attracted growing attention in the past decade as alternative hydrogen storage materials due to their high gravimetric and volumetric hydrogen densities [4–6]. A variety of complex hydrides including alanates ($AlH_4^-$), borohydrides ($BH_4^-$) and amides/imides ($NH_2^-/NH^{2-}$) have been developed for their hydrogen storage performances [7–18]. Among them, metal borohydrides $M(BH_4)_n$, with *M* a light metal cation and *n* the valence of metal *M*, are of particular interest [10]. $LiBH_4$, with a gravimetric hydrogen density of 18.3 wt%, was investigated extensively as a prototype in the family of metal borohydrides [11]. However, the majority of hydrogen evolution proceeded at 400 °C, which is too high for practical applications. A recent study by Nakamori et al. revealed that the thermodynamic stability of $M(BH_4)_2$ is closely correlated with the Pauling electronegativity ($\chi_p$) of *M* [19]. It was predicted that $Mg(BH_4)_2$

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is less stable than $LiBH_4$ because of the higher Pauling electronegativity of Mg (1.31) than that of Li (0.98), which makes $Mg(BH_4)_2$ more interesting for hydrogen storage applications than $LiBH_4$.

With a high theoretical hydrogen capacity of 14.9 wt% and suitable thermodynamic property, $Mg(BH_4)_2$ has recently been the object of intense research as a potential candidate meeting the requirements for on-board hydrogen storage [10,20–25]. Considerable work has been carried out for $Mg(BH_4)_2$, including theoretical calculations, synthesis methods, structural analyses, and de-/hydrogenation behaviors [20–31]. Chłopek et al. developed a direct synthesis of $Mg(BH_4)_2$ in pure form by a reaction of $MgH_2$ with aminoboranes [20]. Depending on the synthesis condition, $Mg(BH_4)_2$ crystallized in two different phases of the hexagonal structure ($\alpha$ phase, $P6_122$ space group) and the orthorhombic structure ($\beta$ phase, Fddd space group). Upon heating, a polymorphic phase transform first took place from the $\alpha$ phase to the $\beta$ phase in $Mg(BH_4)_2$ at around 190 °C, and more than 13 wt% of hydrogen was released by a stepwise decomposition reaction in the temperature range of 270–500 °C [21]. Attempts on rehydrogenation found that approximately 6.1 wt% of hydrogen could be recharged into the dehydrogenated $Mg(BH_4)_2$ at 270 °C and 400 bar with the formation of intermediate, $MgB_{12}H_{12}$ [22]. Encouragingly, Severa et al. demonstrated recently that $MgB_2$ could be hydrogenated to convert into $Mg(BH_4)_2$ under 950 bar and 400 °C, which shows that a complete de-/hydrogenation reversibility is possible for $Mg(BH_4)_2$ [26]. This finding further lights up the hope in establishing $Mg(BH_4)_2$ as a potential solution for on-board hydrogen storage. Unfortunately, the quite high operating temperature and pressure for de-/hydrogenation of the pristine $Mg(BH_4)_2$ limit its practical application at the moment. It is therefore of great interest to improve hydrogen storage thermodynamics and kinetics of $Mg(BH_4)_2$. Newhouse et al. reported that the hydrogen desorption kinetics of $Mg(BH_4)_2$ was significantly improved by the addition of 5 mol% of $TiF_3$ and $ScCl_3$ as hydrogen desorption of the samples with additives reach 95% completion at 300 °C, five times faster than without additives [27]. Fichtner et al. obtained more than 50 °C reduction in the ending temperature of dehydrogenation by impregnating $Mg(BH_4)_2$ into the voids of active carbon with a pore diameter of $<2$ nm [28]. More interestingly, the onset temperature for hydrogen desorption was decreased from 270 °C to 160 °C by combining $Mg(BH_4)_2$ and $LiNH_2$ with a molar ratio of 1:1 [32]. Hydrogen release from the $Mg(BH_4)_2$–$LiNH_2$ combination amounted to 7.2 wt% at 300 °C while it was less than 0.5 wt% for the pure $Mg(BH_4)_2$ under the same conditions. This result indicates that the hydrogen storage properties of $Mg(BH_4)_2$ can be effectively improved by combining with other complex hydrides to form a reactive composite.

In the present study, a reactive composite system of $Mg(BH_4)_2$–$NaAlH_4$ is designed and prepared by ball milling the corresponding chemicals. The compositional dependence of the dehydrogenation behavior of the composites is systematically investigated by TPD and volumetric release. A dramatic reduction in the onset temperature for hydrogen desorption from the samples with $NaAlH_4$ is achieved. The dehydrogenation/hydrogenation mechanisms are elucidated in detail based on XRD and FTIR analyses.

## 2. Experimental section

The commercial $NaAlH_4$ (98% purity) was purchased from J & K Chemical Ltd. and used as received without further purification. $Mg(BH_4)_2$ was synthesized in our own laboratory through a metathesis reaction between $NaBH_4$ (98% purity, Alfa Aesar) and $MgCl_2$ (99% purity, Alfa Aesar) in diethyl ether based on a modified procedure developed by Soloveichik et al. [24]. The resultant product was confirmed as $\beta$-$Mg(BH_4)_2$ by X-ray diffraction (XRD) (Fig. 1a) [24], and its purity was estimated to be 96% by volumetric release associated with mass spectrometry (MS) analyses (Fig. 1b and c). The $Mg(BH_4)_2$–$xNaAlH_4$ composites with $x = 0.5$, 1, and 2 were prepared by ball milling the corresponding chemicals on a planetary ball mill (QM-3SP4) rotating at 500 rpm for 24 h. The ball-to-sample weight ratio was about 120:1. For comparison purposes, the pristine $NaAlH_4$ and $Mg(BH_4)_2$ were also prepared under the same conditions. All the handling of samples was conducted in a glovebox (MBRAUN) equipped with a circulation purifier to keep the concentration of $O_2$ and $H_2O$ below 1 ppm.

Temperature-programmed-desorption (TPD) measurements were performed on a home-made apparatus attached with an online gas chromatography (GC) and mass spectrometer (MS). About 40 mg of sample was loaded into a specially designed tube reactor which allows pure argon to get through upon being heated. The temperature was gradually elevated from room temperature to 600 °C at a ramping rate of 2 °C/min. The quantitative dehydrogenation and rehydrogenation behaviors were further determined by volumetric method with a home-made Sieverts-type apparatus. Approximately 80 mg of sample was loaded into a stainless steel reactor which was then connected to the Sieverts-type apparatus. The system was first evacuated to $10^{-3}$ Torr, and then heated from room temperature to a desired temperature at 2 °C/min (initially in vacuum) for dehydrogenation and 1 °C/min (initially in 100 bar $H_2$) for rehydrogenation. The amount of hydrogen desorbed/absorbed in the experiments was calculated according to the pressure change in the system using the equation of state.

X-ray diffraction (XRD) examinations were conducted on a Phillips X'Pert Pro X-ray Diffractometer with Cu K$\alpha$ radiation at 40 kV and 40 mA. XRD data were collected from 10° to 90° ($2\theta$) with step increments of 0.05° at room temperature. A specially designed sample container was used to protect samples from oxygen and moisture contaminations during transfer and testing. Vibrational characteristics of Al–H and B–H bonds were identified by a Bruker Tensor 27 Fourier Transform Infrared Spectrometer (FTIR). Transmittance mode was adopted, and the pellet sample was prepared by pressing the mixture of the powder sample and potassium bromide (KBr) at a weight ratio of about 100:1. The spectrum was created from 26 scans accumulated with a resolution of 4 $cm^{-1}$.

## 3. Results and discussion

After 24 h of ball milling, no pressure increase was detected within the milling jar for the $Mg(BH_4)_2$–$xNaAlH_4$ composites,