Improved dehydrogenation properties of Ca(BH$_4$)$_2$-LiNH$_2$ combined system†

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Ca(BH$_4$)$_2$-LiNH$_2$ combined system is shown to release hydrogen at much lower temperature compared to the pure Ca(BH$_4$)$_2$. The improved dehydrogenation in this system can be ascribed to a combination reaction between [BH$_4$]$^-$ and [NH$_2$]$^-$ based on the reaction mechanism of positive H and negative H.

Metal borohydrides have attracted much attention as hydrogen storage materials, which exhibit higher weight capacity for hydrogen and are therefore obvious candidates to meet the capacity requirements for storing hydrogen. Among the borohydrides, LiBH$_4$, with a gravimetric capacity of 18.3%, is the most extensively studied. However, this compound is too stable to be used in hydrogen storage applications. More recently, Ca(BH$_4$)$_2$, which has more favorable thermodynamics (32 kJ mol$^{-1}$ H$_2$, estimated in theory) than LiBH$_4$, while maintaining attractive hydrogen capacity (11.4 wt.%), has been acknowledged as one of the potential candidates for hydrogen storage materials.

It was observed that α-Ca(BH$_4$)$_2$, heated under an inert or hydrogen atmosphere, was first transformed to the β-phase of Ca(BH$_4$)$_2$ at around 170 °C. Hydrogen release started at around 350 °C in two endothermic steps, and 9.4 wt.% weight loss was detected up to 530 °C. The decomposition of Ca(BH$_4$)$_2$ was assumed to be the following: Ca(BH$_4$)$_2$ → 2/3 CaH$_2$ + 1/3 CaB$_6$ + 10/3 H$_2$. However, Wang et al. found that CaB$_6$H$_2$ was in the dehydrogenated products by theoretical and experimental studies, and the presence of the dodecaborane closomolecule (B$_{12}$H$_{12}$) has been observed after decomposition of LiBH$_4$ and Mg(BH$_4$)$_2$. To further improve the dehydrogenation of Ca(BH$_4$)$_2$, Kim et al. recently investigated the effects of ball milling and additives on the dehydridding behavior of Ca(BH$_4$)$_2$ and found that the initial dehydrogenation temperature of Ca(BH$_4$)$_2$ is reduced by the addition of NbF$_5$.

Herein, we report a reactive binary mixture, Ca(BH$_4$)$_2$-LiNH$_2$, that presents a significant decrease in the dehydrogenation temperature as compared to the constituent compounds.

Ca(BH$_4$)$_2$ was synthesized by means of the metathesis of CaCl$_2$ and NaBH$_4$ in tetrahydrofuran (THF) solution according to our previous report: CaCl$_2$ + 2 NaBH$_4$ → Ca(BH$_4$)$_2$ + 2 NaCl. Fig. 1 shows the TPD-MS and volumetric release results for Ca(BH$_4$)$_2$-LiNH$_2$ samples compared with the pure Ca(BH$_4$)$_2$. For Ca(BH$_4$)$_2$, two main peaks of hydrogen evolution at 361 and 435 °C are observed in the TPD-MS curve. The above results are comparable with a previous report for Ca(BH$_4$)$_2$ decomposed under argon as a carrier gas. In the case of the Ca(BH$_4$)$_2$-2LiNH$_2$ mixture, two distinct hydrogen release events were observed with peak temperatures at 306 and 396 °C, which are much lower than those for the pure Ca(BH$_4$)$_2$. However, an apparent NH$_3$ release appeared from 50 to 300 °C. To further clarify the different decomposition properties, volumetric release measurements were conducted for these two samples, as shown in Fig. 1(b). The results for the pure Ca(BH$_4$)$_2$ show about 8.1 wt.% volumetric hydrogen release by 480 °C, which is slightly lower than the TG results (more than 9 wt.%) for Ca(BH$_4$)$_2$ prepared by drying the commercial Ca(BH$_4$)$_2$:2THF adduct. It should be noted that hydrogen released from the samples is gradually accumulated in the sample chamber. At the end of the measurement the sample reactor is filled with hydrogen of ca. 45 psi. It is likely due to the equilibrium pressure limitation that not all hydrogen can be released from the samples. For the Ca(BH$_4$)$_2$:2LiNH$_2$ sample, an apparent two step decomposition is also observed, with onset temperature for dehydrogenation at 230 °C, which is about 100 °C lower than that for the pure Ca(BH$_4$)$_2$, indicating...
significant improvement in the dehydrogenation temperature. The total dehydrogenation capacity is 7.2 wt.% up to 480 °C for the Ca(BH₄)₂-2LiNH₂ sample. Quantitative analysis of evolved gas after volumetric release measurement indicates that there is only 5900 ppm NH₃ in the exhaust gas. Thus the weight loss due to NH₃ contribution is as low as about 0.36 wt.%, which can be neglected. Furthermore, the onset decomposition temperature in TPD is slightly higher than that in volumetric release. These differences may be related to the fact that the decomposition reaction is performed under different pressures in these two cases. The TPD measurement is conducted under dynamic argon gas in open system, while the volumetric release is run under vacuum in closed reactor.

Further investigation of Ca(BH₄)₂-LiNH₂ with mole ratios of 1:1 and 1:3 were monitored by TPD and volumetric release measurements. The temperature dependences of H₂ and ammonia signals detected by MS and quantitative H₂ evolution are also measurements. The temperature dependences of H₂ and ammonia, i.e., LiNH₂, gas evidenced that the amount of ammonia, which can break at lower temperature. This suggests that Ca ions in Ca(BH₄)₂ may weaken the Li–N bonds in LiNH₂, causing them to evolve in certain temperature. This is illustrated in Fig. 1(a) and (b), respectively. TPD-MS curves show that the peak temperature for LiNH₂ content, although it was still lower than that for the pure Ca(BH₄)₂. Clearly it can release about 8.0 wt.% and 7.6 wt.% hydrogen by 480 °C for Ca(BH₄)₂-LiNH₂ and Ca(BH₄)₂-3LiNH₂, respectively. TPD-MS curves show that the peak temperature for the first-step dehydrogenation increases with increased LiNH₂ content, and some ammonia is evolved at temperature range from 50 to 300 °C for these two samples. Quantitative analysis of evolved gas evidenced that the amount of ammonia, i.e., 207 ppm and 13 100 ppm for Ca(BH₄)₂-LiNH₂ and Ca(BH₄)₂-3LiNH₂ samples, increases with increased LiNH₂ content. Analogous results were observed for Mg(BH₄)₂-LiNH₂ system.12 Compared with the pure LiNH₂, the NH₃ release temperature from the Ca(BH₄)₂-LiNH₂ mixtures decreases significantly, suggesting that, probably due to the formation of Ca–N bonds between the two compounds, the Ca(BH₄)₂ may weaken the Li–N bonds in LiNH₂, causing them to break at lower temperature. This suggests that Ca ions in Ca(BH₄)₂ may play a crucial role in determining the amount of ammonia release.

To gain further insight into the chemical reactions occurring in the ball milling process, Raman, FT-IR and XRD measurements were carried out. Fig. 2 shows Raman spectra of the samples before and after ball milling. Typical features of the [BH₄] group can be observed in the spectra of the as-prepared samples with the B–H absorption band at about 2300 cm⁻¹. However, the features for the N–H bond that can be ascribed to LiNH₂, with its characteristic bands at 3263 and 3325 cm⁻¹ have shifted to lower wave number, even though no hydrogen or ammonia was released from the mixture during preparation. Similar results are observed in FT-IR spectra (Fig. S3, ESI†). This suggests that Ca(BH₄)₂-LiNH₂ is not a simple physical mixture, but rather that new phases may be formed during the preparation. The red-shift of N–H bonds in Ca(BH₄)₂-LiNH₂ may result from its complexation with B–H bonds, to which similar results have been found in LiBH₄-LiNH₂ system,11 but it is different from Mg(BH₄)₂-LiNH₂ system, in which the characteristic bands of N–H bond almost disappeared after ball milling treatment.13 The XRD patterns (Fig. S4, ESI†) also give evidence for the formation of new phases. The as-prepared Ca(BH₄)₂-LiNH₂ samples are different from each other with no LiNH₂ and Ca(BH₄)₂ phases observed, although they do not have crystallinity as good as the starting materials. In the case of Ca(BH₄)₂-2LiNH₂ and Ca(BH₄)₂-3LiNH₂ samples, similar results from XRD, FT-IR and Raman are observed. It should be noted that B–H stretching modes of post-milled samples in FT-IR results seem to be narrower and shift relative to Ca(BH₄)₂ to the lower frequencies, especially for Ca(BH₄)₂-2LiNH₂ and Ca(BH₄)₂-3LiNH₂ (Fig. S3, ESI†).

The activation energy, E_a, during the dehydrogenation for the two steps is estimated by Kissinger’s method.14 The TPD-MS profiles at heating rates of 1.5, 2, 2.5, and 3 K min⁻¹ as a function of temperature are measured for the Ca(BH₄)₂-LiNH₂ (mole ratio 1:2) sample, as shown in Fig. 3. From the peak temperature, T_p, observed at the heating rate, β, the Kissinger plots, i.e., ln[β/T_p²] as a function of the inverse of T_p, are given in the inset of the Fig. 3. From the slope of the straight line, the activation energy E_a for the first and second step dehydrogenation is determined to be about 77.3 and 93.2 kJ mol⁻¹, respectively. To clarify the chemical reactions before and after dehydrogenation, XRD for samples collected after volumetric release measurements at different temperatures, i.e., 320 °C, 400 °C and 480 °C, are performed for Ca(BH₄)₂-2LiNH₂ shown in Fig. 4. After dehydrogenation to 320 °C, the XRD patterns correspond to CaO and LiCa₄(BN₃)₆,8 which indicates that LiCa₄(BN₃)₆ is formed in...
might be due to a combination reaction of [BH4] with [NH2], in as the reported result on Mg(NH3)nCl2/LiBH4 system. LiNH2/CaH2, LiNH2BH3, and Ca(NH2BH3)2 systems, 

the first step for hydrogen desorption. When the heat temperature is increased to 400 and 480 °C, CaH2 is observed in XRD patterns, and the peak intensity of LiCa(BN)3 decreases with increased temperature, which indicates that LiCa(BN)3 may participate in the second reaction for hydrogen desorption. In addition, we run TG-DSC measurements of post-milled samples. For example, TG-DSC results of post-milled Ca(BH4)2-2LiNH2 sample (Fig. S5, ESI†) show that there are two main peaks, i.e., an exothermic peak at 302 °C and an endothermic peak at 390 °C. This implies that there could be some reversibility in this system. However, our preliminary attempt of dehydrogenating the post-dehydrogenated powder under a H2 pressure of 50 bar in the temperature range of 20–300 °C was unsuccessful.

The improved decomposition in the Ca(BH4)2-LiNH2 system might be due to a combination reaction of [BH4] with [NH2], in which the [BH4] consists of negatively charged hydrogen, while positively charged hydrogen is bonded to N atoms in [NH2] group. This assumption is experimentally confirmed by formation of HD when we heated the post-milled Ca(BD4)2-2LiNH2 sample (Fig. S6, ESI†). In this case, the reaction of H+ + H→ H2 might be one of the driving forces making the chemical reaction take place, which has been demonstrated in the Mg(NH3)2/LiH, LiNH2/CaH2, LiNH2BH3, and Ca(NH2BH3)2 systems, as well as the reported result on Mg(NH3)2Cl2/LiBH4 system.

In summary, hydrogen desorption of Ca(BH4)2-LiNH2 binary system is released at lower temperature compared with the pure Ca(BH4)2. For example, Ca(BH4)2-3LiNH2 has a desorption capacity of 7.2 wt.% held at ~300 °C for 3 h, with the onset temperature of dehydrogenation at 200 °C. It is proposed that the improved dehydrogenation in Ca(BH4)2-LiNH2 results from a combination reaction between the [BH4] and [NH2]. Then the Ca(BH4)2-LiNH2 material is regarded as a potential candidate for hydrogen storage if the evolution of ammonia evolution during hydrogen desorption will be suppressed and the dehydrogenation temperature will be further decreased.

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Notes and references


