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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.[1] Among the borohydrides, LiBH$_4$, with a gravimetric capacity of 18.3%, is the most extensively studied.[2] 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)[3] than LiBH$_4$, while maintaining attractive hydrogen capacity (11.4 wt.%), has been acknowledged as one of the potential candidates for hydrogen storage materials.[4]

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$_4$)$_2 \rightarrow$ 2/3 CaH$_2$ + 1/3 CaB$_6$ + 10/3 H$_2$. However, Wang *et al.* found that CaB$_{12}$H$_{12}$ was in the dehydrogenated products by theoretical and experimental studies,[5] and the presence of the dodecaborane closomolecule (B$_{12}$H$_{12}$) has been observed after decomposition of LiBH$_4$ and Mg(BH$_4$)$_2$.[6] To further improve the dehydrogenation of Ca(BH$_4$)$_2$, Kim *et al.* recently investigated the effects of ball milling and additives on the dehydriding 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$_5$.[7] 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$_4 \rightarrow$ Ca(BH$_4$)$_2$ + 2 NaCl.[8] 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.[9] In the case of the Ca(BH$_4$)$_2$-2LiNH$_2$ mixture,

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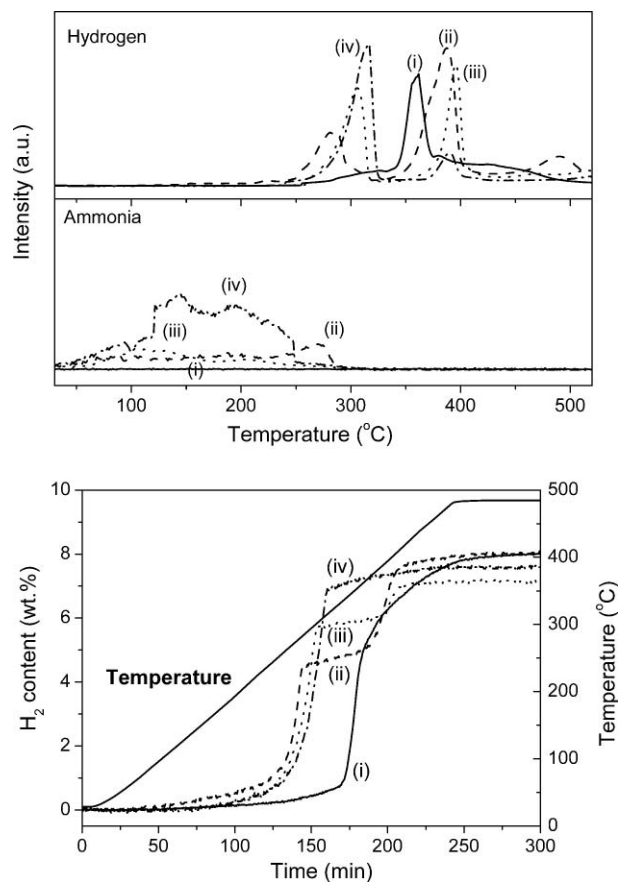
Fig. 1 TPD-MS (top) and volumetric release (bottom) results for (i) Ca(BH$_4$)$_2$, (ii) Ca(BH$_4$)$_2$-LiNH$_2$, (iii) Ca(BH$_4$)$_2$-2LiNH$_2$ and (iv) Ca(BH$_4$)$_2$-3LiNH$_2$.

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.[10] 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 $Ca(BH_4)_2$-2$LiNH_2$ sample. Quantitative analysis of evolved gas after volumetric release measurement indicates that there is only 5900 ppm NH_3 in the exhaust gas. Thus the weight loss due to NH_3 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 $Ca(BH_4)_2$-$LiNH_2$ with mole ratios of 1:1 and 1:3 were monitored by TPD and volumetric release measurements. The temperature dependences of H_2 and ammonia signals detected by MS and quantitative H_2 evolution are also illustrated in Fig. 1(a) and (b), respectively. It revealed that, from volumetric release measurements, the onset temperature for hydrogen desorption shifted to higher temperature with increased $LiNH_2$ content, although it was still lower than that for the pure $Ca(BH_4)_2$. Clearly it can release about 8.0 wt.% and 7.6 wt.% hydrogen by 480 °C for $Ca(BH_4)_2$-$LiNH_2$ and $Ca(BH_4)_2$-3$LiNH_2$, respectively. TPD-MS curves show that the peak temperature for the first-step dehydrogenation increases with increased $LiNH_2$ 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 $Ca(BH_4)_2$-$LiNH_2$ and $Ca(BH_4)_2$-3$LiNH_2$ samples, increases with increased $LiNH_2$ content. Analogous results were observed for $Mg(BH_4)_2$-$LiNH_2$ system.[11] Compared with the pure $LiNH_2$,[12] the NH_3 release temperature from the $Ca(BH_4)_2$-$LiNH_2$ mixtures decreases significantly, suggesting that, probably due to the formation of Ca–N bonds between the two compounds, the $Ca(BH_4)_2$ may weaken the Li–N bonds in $LiNH_2$, causing them to break at lower temperature. This suggests that Ca ions in $Ca(BH_4)_2$ 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 [BH_4] group can be observed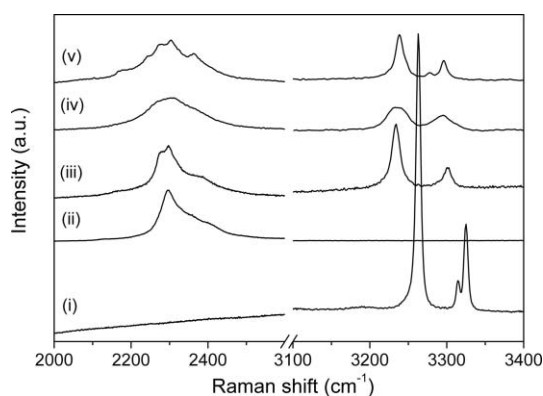 in the spectra of the as-prepared samples with the B–H absorption band at about 2300 cm^{-1}. However, the features for the N–H bond that can be ascribed to $LiNH_2$, with its characteristic bands at 3263 and 3325 cm^{-1} have shifted to lower wave number, even though no hydrogen or ammonia was released from the mixture during preparation. Similar results are observed in FT-IR spectra (Fig. S3, ESI†). This suggests that $Ca(BH_4)_2$-$LiNH_2$ 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 $Ca(BH_4)_2$-$LiNH_2$ may result from its complexation with B–H bonds, to which similar results have been found in $LiBH_4$-$LiNH_2$ system,[13] but it is different from $Mg(BH_4)_2$-$LiNH_2$ system, in which the characteristic bands of N–H bond almost disappeared after ball milling treatment.[11] The XRD patterns (Fig. S4, ESI†) also give evidence for the formation of new phases. The as-prepared $Ca(BH_4)_2$-$LiNH_2$ samples are different from each other with no $LiNH_2$ and $Ca(BH_4)_2$ phases observed, although they do not have crystallinity as good as the starting materials. In the case of $Ca(BH_4)_2$-2$LiNH_2$ and $Ca(BH_4)_2$-3$LiNH_2$ 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 $Ca(BH_4)_2$ to the lower frequencies, especially for $Ca(BH_4)_2$-2$LiNH_2$ and $Ca(BH_4)_2$-3$LiNH_2$ (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 $Ca(BH_4)_2$-$LiNH_2$ (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_P^2] 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 $Ca(BH_4)_2$-2$LiNH_2$ shown in Fig. 4. After dehydrogenation to 320 °C, the XRD patterns correspond to CaO and $LiCa_4(BN_2)_3$,[8] which indicates that $LiCa_4(BN_2)_3$ is formed in

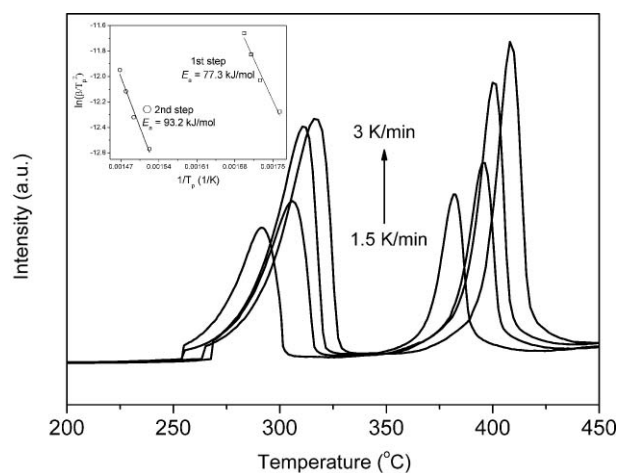**Fig. 2** Raman spectra of (i) $LiNH_2$, (ii) $Ca(BH_4)_2$, (iii) $Ca(BH_4)_2$-$LiNH_2$, (iv) $Ca(BH_4)_2$-2$LiNH_2$ and (v) $Ca(BH_4)_2$-3$LiNH_2$.

Fig. 3 TPD-MS results for $Ca(BH_4)_2$-2$LiNH_2$ at various heating rates. The inset shows the Kissinger plots.

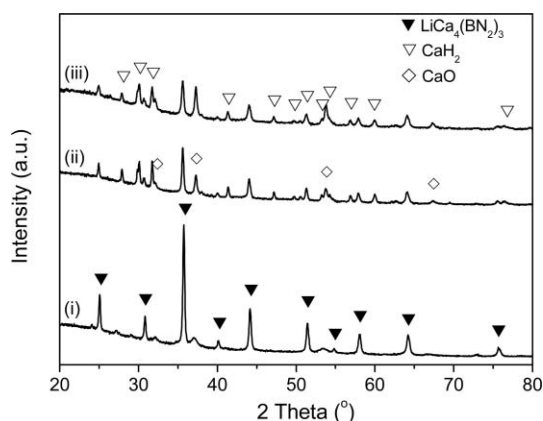**Fig. 4** XRD results for $Ca(BH_4)_2$-$2LiNH_2$ samples after volumetric release at (i) 320 °C, (ii) 400 °C, and (iii) 480 °C.

the first step for hydrogen desorption. When the heat temperature is increased to 400 and 480 °C, CaH_2 is observed in XRD patterns, and the peak intensity of $LiCa_4(BN_2)_3$ decreases with increased temperature, which indicates that $LiCa_4(BN_2)_3$ 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 $Ca(BH_4)_2$-$2LiNH_2$ 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 rehydrogenating the post-dehydrogenated powder under a H_2 pressure of 50 bar in the temperature range of 20–300 °C was unsuccessful.

The improved decomposition in the $Ca(BH_4)_2$-$LiNH_2$ system might be due to a combination reaction of $[BH_4]$ with $[NH_2]$, in which the $[BH_4]$ consists of negatively charged hydrogen, while positively charged hydrogen is bonded to N atoms in $[NH_2]$ group. This assumption is experimentally confirmed by formation of HD when we heated the post-milled $Ca(BD_4)_2$-$2LiNH_2$ sample (Fig. S6, ESI†). In this case, the reaction of $H^{\delta+} + H^{\delta-} \rightarrow H_2$ might be one of the driving forces making the chemical reaction take place, which has been demonstrated in the $Mg(NH_2)_2$/LiH, $LiNH_2$/CaH_2, $LiNH_2BH_3$, and $Ca(NH_2BH_3)_2$ systems,[15] as well as the reported result on $Mg(NH_3)_nCl_2$/$LiBH_4$ system.[16]

In summary, hydrogen desorption of $Ca(BH_4)_2$-$LiNH_2$ binary system is released at lower temperature compared with the pure $Ca(BH_4)_2$. For example, $Ca(BH_4)_2$-$3LiNH_2$ 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 $Ca(BH_4)_2$-$LiNH_2$ results from a combination reaction between the $[BH_4]$ and $[NH_2]$. Then the

$Ca(BH_4)_2$-$LiNH_2$ 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.

Notes and references

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