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Thermal decomposition performance of $Ca(BH_4)_2/LiNH_2$ mixtures

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ABSTRACT

The thermal decomposition properties of $Ca(BH_4)_2/LiNH_2$ system were investigated. It was found that the mixtures started to release hydrogen at around 250 °C, but accompanied emission of ammonia at lower temperature was also occurred. XRD results revealed that, after a shot time of ball mining, the $Ca(BH_4)_2/LiNH_2$ mixtures transferred to unidentified new phases and the decomposed product mainly consists of $LiCa_4(BN_2)_3$. Further improvement on restraining the ammonia release can be achieved by heating treatment of this composite or addition of LiH to the binary system.

1. Introduction

Development of highly efficient solid-state hydrogen storage materials is a key factor in enabling technology for the coming hydrogen economy, especially for automobile applications. During the last decades, much research effort has been devoted to developing new hydrogen storage materials, such as $LiNH_2$ [1–3], $NaAlH_4$ [4–6] and MgH_2 [7–10]. Although vast improvements in the hydrogen storage properties of these materials have been achieved by catalytic or chemical modification, it has also been recognized that to solve the challenge of hydrogen storage is likely to involve more efficient complex systems.

Recently, metal borohydrides, such as $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$, have attracted wide attention due to their high gravimetric and volumetric hydrogen densities [11–20]. Among them, $LiBH_4$ with the highest theoretical hydrogen capacity of 18.3 wt.% is relatively well explored. It was shown that $LiBH_4$ can be reversibly destabilized by MgH_2 [16,17], carbon [18] and Pt [19]. Compared with $LiBH_4$, the hydrogen storage capacity of $Ca(BH_4)_2$ is low (11.6 wt.%). However, based on density functional theory (DFT) calculations, the decomposition enthalpy for $Ca(BH_4)_2$ has been estimated to be 32 kJ mol^{-1}, if the decomposition products are CaH_2, CaB_6 and H_2 [20]. This enthalpy corresponds to an equilibrium pressure of 1 bar at temperatures below 100 °C, indicating that $Ca(BH_4)_2$ has more favorable thermodynamics than $LiBH_4$ and could be considered as a potential low/medium-temperature hydride. Recently, its phase structure [21] and dehydrogenation/rehydrogenation behaviour have been reported [11,22,23]. It revealed that $Ca(BH_4)_2$ eventually decomposes in two steps between 347 and 497 °C with a total weight loss of about 9.0 wt.% and can be partly reversible under 90 bar of hydrogen at 350 °C after doping with $TiCl_3$. Clearly, the decomposition temperature of $Ca(BH_4)_2$ is still too high for a practical application and further improvement is required. Our previous results have demonstrated that $LiNH_2$ is effective in improving the dehydrogenation of $Mg(BH_4)_2$ [24]. In this paper, we reported a new combined binary system, $Ca(BH_4)_2/LiNH_2$, which exhibits improved thermodynamic properties compared to their constituent compounds.

2. Experimental

The commercial materials of $LiNH_2$ (95%, Aldrich) and $Ca(BH_4)_2$ (Aldrich) were used without further purification. About 0.5 g mixtures of $Ca(BH_4)_2/LiNH_2$ with various mole ratios were ball milled using a QM-3SP2 planetary ball mill at 470 rpm for 18 min under an inert gas (Ar). In this paper, the $Ca(BH_4)_2/LiNH_2$ with mole ratios of 1:1, 1:2, 1:3 and 1:4 were defined as S1, S2, S3 and S4, respectively. The mass ratio of the sample to the steel balls is 1:30. All sample handling was done in an argon-filled glove box.

Hydrogen release measurements were performed by thermogravimetric analysis (TG, STA 409C) connected to a mass-spectrometer (MS, QMS 403), using various heating rates under 1 atm argon and a carrier flow rate of 200 cm^3 min^{-1}. Typical sample quantities were 5–10 mg. Volumetric release for quantitative measurements of hydrogen desorption from samples were carried out on a homemade Sievert type apparatus under 1 atm Ar. Powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the crystalline phase. Samples were mounted in a glove box, and a polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement. $Ca(BH_4)_2$, $LiNH_2$ and $Ca(BH_4)_2/LiNH_2$ mixtures before and after dehydrogenation to various temperatures were characterized by Fourier transform infrared absorption spectroscopy (FTIR, Nicolet Nexus 470) using KBr pellets. Due to the high reactivity of these compounds with moisture and oxygen, all of the samples were loaded into one tube with CaF_2 windows.

The contents of H_2 and NH_3 in the emission gas were determined using gravimetric and volumetric results. Firstly, the mass percent (W_p) and mole per gram (M_p) of gas released from the sample were calculated from the weight of the sam-

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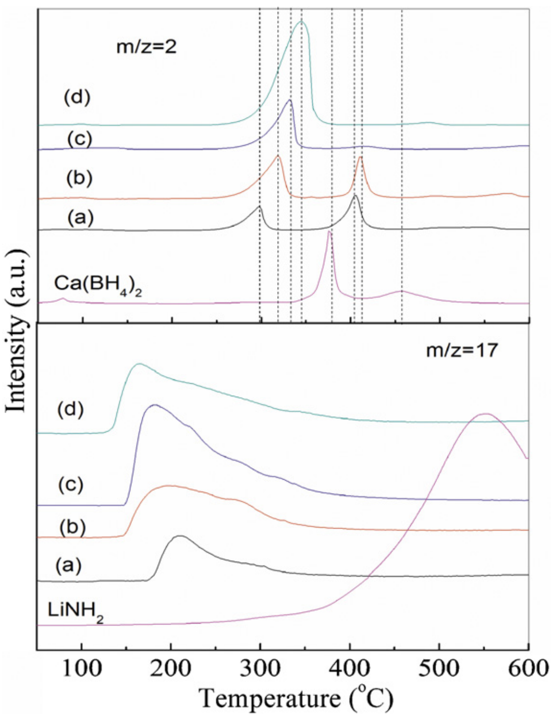

Fig. 1. MS results for $Ca(BH_4)_2/LiNH_2$ with mole ratios of (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4. The evolution of H_2 in $Ca(BH_4)_2$ and NH_3 in $LiNH_2$ was also shown for comparison. The heating rate is 10 °C/min.

ples and volumetric results, then the mole proportion of H_2 (C_{H_2}) and NH_3 (C_{NH_3}) can be calculated from the below two equations,

$$C_{H_2} + C_{NH_3} = 1 \tag{1}$$

$$(C_{H_2} \times 2.02 + C_{NH_3} \times 17.03) \times M_p = W_p. \tag{2}$$

3. Results and discussion

Fig. 1 shows the MS results for the $Ca(BH_4)_2/LiNH_2$ mixtures with various mole ratios. $Ca(BH_4)_2$ released hydrogen at above 350 °C with two peaks appeared at 378 °C and 455 °C, respectively. In the case of S1, the dehydrogenation temperature of two peaks was shifted to 297 °C and 405 °C, which are significantly decreased compared to the pure $Ca(BH_4)_2$, indicating the improved kinetics and/or thermodynamics. With the increase of $LiNH_2$ content, both of the peaks shifted to high temperature, while the intensity of the second peak weakened gradually and disappeared in S3 and S4 samples. The fact that only one peak appeared at 330 °C in S3 implies that the ratio of $Ca(BH_4)_2$ to $LiNH_2$ with 1:3 is favorable for dehydrogenation in the mixtures. Furthermore, apparent ammonia release was observed in S1–S4 samples with peak temperatures at 150–200 °C that decreased from S1 to S4 gradually, exhibiting contrary performance to the hydrogen evolution. The fact that all the $Ca(BH_4)_2/LiNH_2$ mixtures liberated ammonia at similar temperature range indicates that the emission of ammonia is not dependent with the $LiNH_2$ content in the mixtures but sensitive to the temperature. Furthermore, the release temperature of NH_3 in S1–S4 are much lower (>350 °C) than that of the pure $LiNH_2$, indicating that $Ca(BH_4)_2$ played a crucial role in breaking the Li → N bond from $LiNH_2$ to release NH_3. Due to the release of ammonia, The TG results presented large weight losses of 16.5–18.5 wt.% for S1–S4 samples. In order to obtain a precise desorption capacities of H_2 and NH_3, the volumetric measurement for the S3 sample was conducted, which gives a volumetric increase of 0.037 mol/g. Based on the TG and volumetric results, the weight loss of NH_3 and H_2 for S3 sample is ascribed to 11.85 wt.% and 6.1 wt.%, respectively, which corresponds to 0.97 equiv. NH_3 and 4.2 equiv. H_2 released from this sample.

Fig. 2a shows the XRD results for the S3 before and after dehydrogenation to 250 °C and 400 °C. The as-prepared sample did not present a physical mixture of $LiNH_2$ and $Ca(BH_4)_2$, and some unidentified new peaks were observed. It suggests that a chemical reaction between $Ca(BH_4)_2$ and $LiNH_2$ occurred even after a short-time ball milling. After heating to 250 °C, in which the NH_3 emission is almost completed, the sample was changed to a body centered cubic (BCC) structure. It suggests that during the release of NH_3, a new compound based on Ca–Li–B–N–H was formed. Further heating to 400 °C, the XRD patterns were confirmed to be a main phase of $LiCa_4(BN_2)_3$ (PDF#52-0199) with some other unidentified peaks. The infrared absorption spectra of $LiNH_2$, $Ca(BH_4)_2$ and S3 sample for heating to various temperatures were presented in Fig. 2b. The N–H symmetric and asymmetric stretching vibrations of $LiNH_2$ occurred at 3260 cm^{-1} and 3315 cm^{-1}, respectively, which are in agreement with those reported by Kojima and Kawai [25]. In the case of the as-prepared S3 sample, the N–H bands became very weak. After heating to 250 °C, no bands correspond to $LiNH_2$ or Li_2NH (two characteristic bands at 3180 cm^{-1} and 3250 cm^{-1}) were observed. It indicates that the release of NH_3 form the $Ca(BH_4)_2/LiNH_2$ mixtures is different to the decompose route of pure $LiNH_2$: $2LiNH_2 \rightarrow Li_2NH + NH_3$, suggesting the formation of new compounds as confirmed by the XRD results. The characteristic bands of $Ca(BH_4)_2$ are not changed in S3 before and after heating at 250 °C. However, after heating at 400 °C, the bands of $Ca(BH_4)_2$ disappeared and BN bonds (with characteristic bands at 815 cm^{-1} and 1360 cm^{-1}) formed [26]. From the above information, although it is difficult to understand the detailed reaction mechanism, the

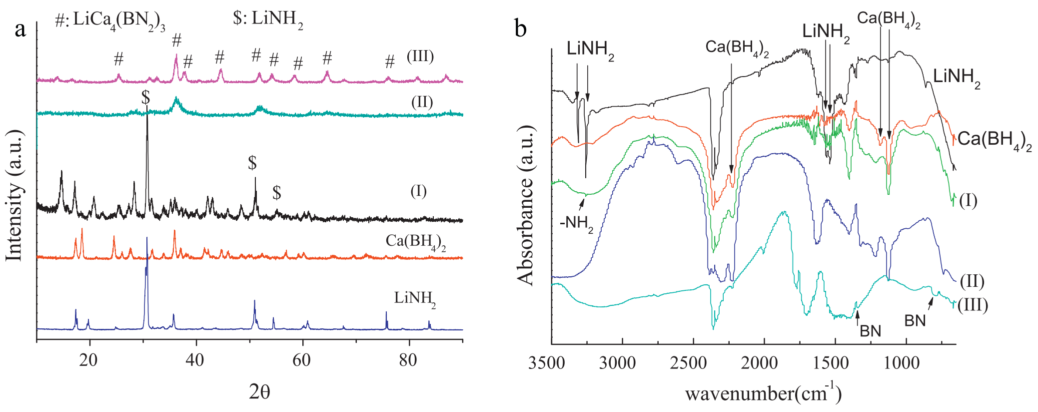

Fig. 2. (a) XRD patterns and (b) FTIR spectra for $LiNH_2$, $Ca(BH_4)_2$ and $Ca(BH_4)_2/LiNH_2$ (1:3) before dehydrogenation (I). (II) and (III) show the XRD patterns and FTIR spectra of the sample in (I) after heating to 250 °C and 400 °C, respectively.

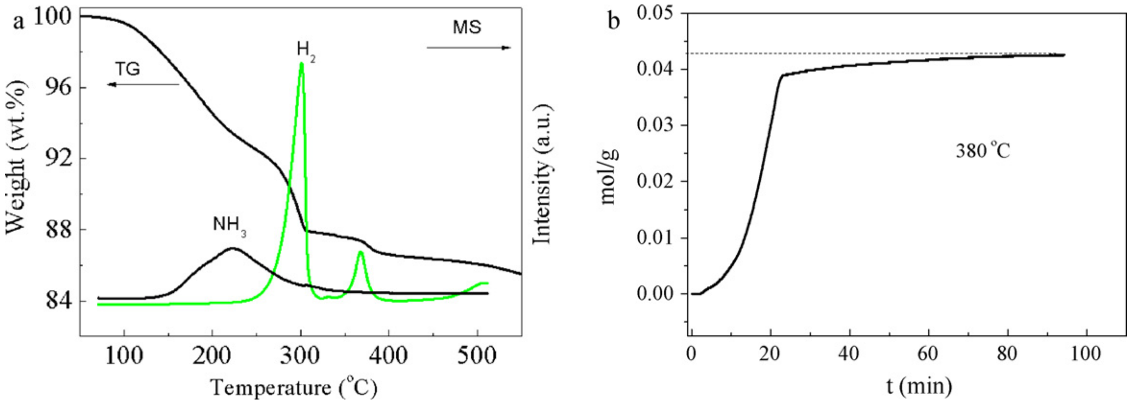

Fig. 3. (a) MS–TG curve for $Ca(BH_4)_2/LiNH_2$ (1:3) heat-treated at 300 °C for 1 h and (b) TPD curve of $Ca(BH_4)_2/LiNH_2$ (1:3) at 380 °C.

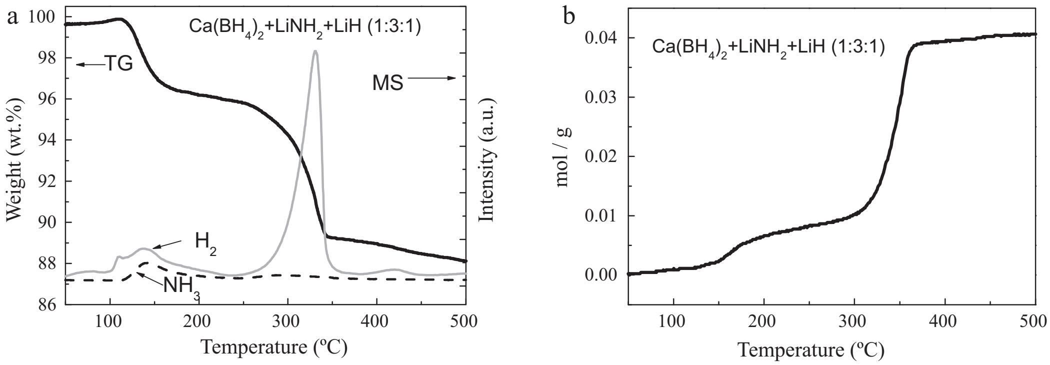

Fig. 4. (a) MS–TG and (b) TPD results for $Ca(BH_4)_2/LiNH_2/LiH$ with a mole ratio of 1:3:1. The heating rate is 10 °C/min.

improvement of the dehydrogenation in the $Ca(BH_4)_2/LiNH_2$ mixtures is most likely due to the reaction between BH_4^{-1} and NH_2^{-1}, resulting in a formation of BN compound, which has been demonstrated by many previous literatures [27–29].

Clearly, the emission of NH_3 is disadvantage for $Ca(BH_4)_2/LiNH_2$ mixtures as hydrogen sources in a practical application. In order to depress the emission of NH_3, the S3 sample was first heat-treated at 300 °C for 1 h to release ammonia and then cooled down to room temperature. Although the MS–TG results for the heat-treated S3 sample still showed apparent NH_3 released from 150 to 200 °C (Fig. 3a), the TG result revealed that the weight loss of the sample was decreased to 12.5 wt.% by 500 °C, lower than all the as-prepared $Ca(BH_4)_2/LiNH_2$ mixtures, indicating the increased H_2 release content. More interestingly, the peak temperature of dehydrogenation of the heat-treated S3 sample was further decreased to 295 °C, which is 35 °C lower than that of the as-prepared S3 sample. Additionally, as the emission of ammonia occurred in the temperature range of 100–300 °C, while hydrogen released after 250 °C, an alternative is to heat the mixture at high temperature to obtain an increased dehydrogenation content. Fig. 3b shows the decomposition curve of S3 at 380 °C. It presented a volumetric increase of 0.043 mol/g, significantly increased compared with the S3 sample heated from room temperature to 400 °C, demonstrating the increased dehydrogenation capacity. Furthermore, addition of LiH was demonstrated to be effective to depress the ammonia release. Fig. 4a shows the MS–TG results for the $Ca(BH_4)_2/LiNH_2/LiH$ (mole ratio: 1:3:1) ternary system. The emission of NH_3 was depressed significantly. The hydrogen release from 100 to 200 °C resulted in a reaction of $LiH + NH_3 \rightarrow LiNH_2 + H_2$. As the formed $LiNH_2$ will further react with $Ca(BH_4)_2$ resulting in NH_3 release, it is difficult to depress the NH_3 thoroughly. Based on the volumetric result, however, the weight loss of NH_3 and H_2 in the ternary system is 3.8 wt.% and 7.7 wt.%, respectively, which corresponds to 0.33 equiv. NH_3 and 5.66 equiv. H_2. Clearly, the emission of NH_3 content is significantly restrained compared with the $Ca(BH_4)_2/LiNH_2$ system, in which 0.97 equiv. NH_3 was released from S3.

4. Conclusion

In summary, we have demonstrated a new binary system of $Ca(BH_4)_2/LiNH_2$, which showed thermal properties that differ significantly from solid $Ca(BH_4)_2$ or $LiNH_2$ alone. During heating, the mixtures released ammonia in the temperature rage of 150–250 °C and started to release hydrogen at 250 °C, which is 100 °C lower than that of the pure $Ca(BH_4)_2$. Further improvement on dehydrogenation can be achieved through heating treatment or addition of LiH to the binary system which restrains the release of ammonia. These results suggest that dehydrogenation based on a combination of BH and NH sources is an effective route to develop new hydrogen storage system with favorable dehydrogenation properties.

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