



## A comparative study of the hydrogen storage properties of LiBH<sub>4</sub> doping with CaHCl and CaH<sub>2</sub>

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### ABSTRACT

In the present work, CaHCl was synthesized as an additive for the LiBH<sub>4</sub> complex hydride. The hydrogen storage properties of LiBH<sub>4</sub> doping with CaHCl was firstly investigated and compared to LiBH<sub>4</sub> doping with CaH<sub>2</sub>. It is found that LiBH<sub>4</sub> doping with CaHCl exhibits more promising catalytic properties than that of CaH<sub>2</sub>: doping with CaHCl can decrease the thermodynamic stability of LiBH<sub>4</sub> and improve the low temperature dehydrogenation kinetics of LiBH<sub>4</sub> greater than CaH<sub>2</sub> do. The activation energy of the dehydriding step of LiBH<sub>4</sub> decreases from 160.11 kJ/mol in 6LiBH<sub>4</sub> + CaH<sub>2</sub> system to 112.39 kJ/mol in 6LiBH<sub>4</sub> + CaHCl system. The dehydrogenation scheme of 6LiBH<sub>4</sub> + CaHCl system is different from 6LiBH<sub>4</sub> + CaH<sub>2</sub> system, and its dehydrogenation reaction is 6LiBH<sub>4</sub> + CaHCl → 5LiH + LiCl + CaB<sub>6</sub> + 10H<sub>2</sub>↑. However, due to the stable LiCl formed after dehydrogenation, the rehydrogenation route of 6LiBH<sub>4</sub> + CaHCl system is the same as 6LiBH<sub>4</sub> + CaH<sub>2</sub> system to regenerate LiBH<sub>4</sub> and CaH<sub>2</sub> (in molar ratio of 6:1), which indicates that 6LiBH<sub>4</sub> + CaHCl system cannot be fully rehydrogenated. It is also observed that 6LiBH<sub>4</sub> + CaHCl system has more stable cyclic dehydrogenation properties than 6LiBH<sub>4</sub> + CaH<sub>2</sub> system.

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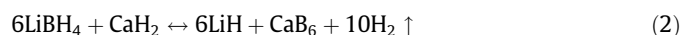
### 1. Introduction

Borohydrides are some potential candidates as hydrogen storage materials for automobile on-board application because of their high gravimetric and volumetric hydrogen densities [1–7]. In particular, LiBH<sub>4</sub> with a theoretical gravimetric hydrogen density of 18.4% is being widely and intensely investigated [6–9]. Dehydriding reaction of LiBH<sub>4</sub> has been expressed as the following Eq. (1), releasing 13.8 wt.% of hydrogen



However, the very strongly bound hydrogen of LiBH<sub>4</sub> resulted in the high dehydrogenation temperature of LiBH<sub>4</sub>. Moreover, the rehydrogenation condition of LiBH<sub>4</sub> is extremely hard, restraining its practical applications.

Vajo et al. [10,11] demonstrated the “destabilization concept” in the LiBH<sub>4</sub>–MgH<sub>2</sub> system, forming the more stable MgB<sub>2</sub> phase to significantly decrease the dehydrogenation temperature relative to pure LiBH<sub>4</sub>. Since then, the other destabilized reaction 6LiBH<sub>4</sub> + CaH<sub>2</sub> system has received much attention and been investigated experimentally [12–18]. This system can reversibly store 11.7 wt.% hydrogen through the Eq. (2):



Jin et al. [13] and Pinkerton et al. [15] reported that 6LiBH<sub>4</sub> + CaH<sub>2</sub> with TiCl<sub>3</sub> as a catalytic additive can reversible re/dehydriding of about 9 wt.% hydrogen. Lim et al. [14,17] investigated the dehydrogenation and rehydrogenation behaviors of 6LiBH<sub>4</sub> + CaH<sub>2</sub> with NbF<sub>5</sub>. It is demonstrated that about 6 wt.% hydrogen storage capacity is achieved at 10th cycle with 15% NbF<sub>5</sub>.

On the other hand, Cl-substitution in the borohydrides has been investigated by mechanochemical reactions between M(BH<sub>4</sub>)<sub>n</sub> and MCl<sub>n</sub> (M = Li, Na, Ca) [19–21]. Arnberg et al. provided a direct evidence of dissolution of LiCl into LiBH<sub>4</sub>, and formation the solid solution Li(BH<sub>4</sub>)<sub>1-x</sub>Cl<sub>x</sub> [19]. Na(BH<sub>4</sub>)<sub>1-y</sub>Cl<sub>y</sub> have also been synthesized and investigated by Olsen et al. [20]. Rongeat et al. [21] reported that effect of the presence of chlorides on the synthesis and decomposition of Ca(BH<sub>4</sub>)<sub>2</sub>, and found that by ball-milling 2LiBH<sub>4</sub> + CaCl<sub>2</sub>, the final products are a combination of Ca(BH<sub>4</sub>)<sub>2-y</sub>Cl<sub>y</sub> and Li(BH<sub>4</sub>)<sub>1-x</sub>Cl<sub>x</sub> which have the lower dehydrogenation temperature than pure LiBH<sub>4</sub>. Lee et al. [22] explored the hydrogen storage properties of CaCl<sub>2</sub> doped Ca(BH<sub>4</sub>)<sub>2</sub>, and reported that during the dehydrogenation of the mixture Ca(BH<sub>4</sub>)<sub>2</sub>–CaCl<sub>2</sub>, the formation of CaHCl through Eq. (3) provided a thermodynamic driving force to the decomposition of Ca(BH<sub>4</sub>)<sub>2</sub> into CaH<sub>2</sub>:



Through the discussion above, the formation of CaB<sub>6</sub> which is more stable than B, and the solid solution M(BH<sub>4</sub>)<sub>n-x</sub>Cl<sub>x</sub> formed

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by Cl-substitution can both improve the hydrogen storage properties of  $\text{LiBH}_4$ . Therefore, in this work, we investigated the effect of CaHCl doping on the hydrogen storage properties of  $\text{LiBH}_4$ , identified the de/rehydrogenated products, and discussed the possible de/rehydrogenation routes.

## 2. Experimental

$\text{LiBH}_4$  (assay 95%, Acrös),  $\text{CaH}_2$  (assay 95%, Alfa Aesar) and  $\text{CaCl}_2$  (assay 96%, Alfa Aesar) were used as starting materials. CaHCl was synthesized by ball-milling the mixture  $\text{CaH}_2$  and  $\text{CaCl}_2$  (molar ratio of 1:1) for 10 h and then heat treating at 450 °C for 12 h under 1 MPa of  $\text{H}_2$  pressure. 1 g mixture of  $\text{LiBH}_4$  and CaHCl in a molar ratio of 6:1 was put into a stainless steel vial with a ball-to-powder ratio of 40:1. The ball-milling process was carried out on a planetary ball mill (QM-3SP4, Nanjing, China) under 1 MPa hydrogen pressure at a speed of 400 rpm for 4 h. The milling process was paused 0.1 h for every 0.4 h to avoid an increase of temperature in the sample during the ball-milling.

The dehydrogenation and rehydrogenation properties of the synthesized products were conducted by a manually controlled temperature program desorption (TPD) apparatus. Before testing, this Sievert-type TPD apparatus was adjusted by a HyEnergy PCT Pro 2000 automated instrument. About 150 mg products were used to carry out the TPD measurement which was performed under vacuum condition from room temperature to 500 °C with a heating rate of 2 or 5 °C/min and maintained at 500 °C for 2 h. All samples prior to rehydrogenation were completely dehydrogenated according to the same conditions as TPD measurements above. The isothermal rehydrogenation was done under different  $\text{H}_2$  pressure (80, 100 MPa) at 450 or 500 °C for 10 h.

The powder X-ray diffraction measurements were performed on an X'Pert PRO (PANalytical) X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. A special container which was fully filled with high purity Ar was prepared to keep the samples from air exposure during sample transferring and testing. The sample window was covered by a layer of transparent tape film that did not show a particular peak. The FTIR spectra were acquired at ambient condition in air by using a Bruker Tensor 27 FTIR spectrometer. The differential scanning calorimetry, thermogravimetric and mass spectrometry (DSC–TG–MS) measurements were performed on a Netzsch DSC 449F3 coupled with a Netzsch Q430C mass spectrometry at different heating rates from room temperature to 550 °C at a heating rate of 5 °C/min under flowing argon condition (high purity, 50 mL/min).

All materials and samples were handled in an argon-filled glove box where water vapor and oxygen levels were kept below 1 ppm.

## 3. Results and discussion

### 3.1. Synthesis of CaHCl

The XRD pattern of the product synthesized by ball-milling the mixture of  $\text{CaH}_2 + \text{CaCl}_2$  (molar ratio 1:1) and heat-treating at 450 °C for 12 h under 1 MPa hydrogen pressure is shown in Fig. 1. Except the few peaks of CaO which come from the air

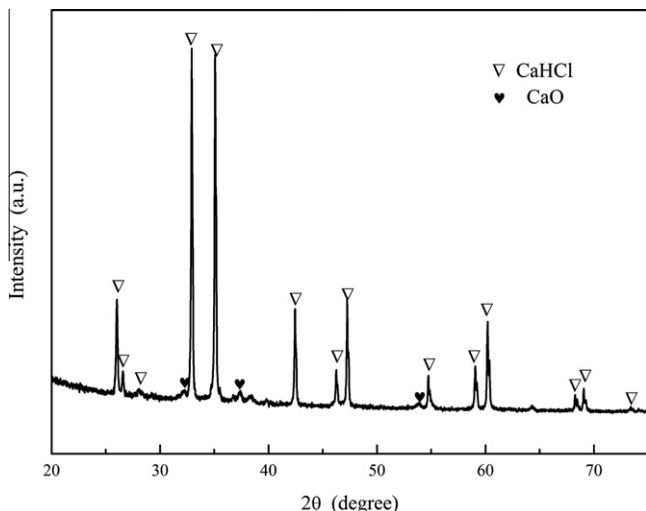


Fig. 1. XRD pattern of the product synthesized by ball-milling the mixture of  $\text{CaH}_2 + \text{CaCl}_2$  and heat-treating at 450 °C for 12 h under 1 MPa hydrogen pressure.

contamination of the sample [14], the other peaks are all assigned to CaHCl. It indicates that CaHCl was totally formed by ball-milling and heat treating the mixture of  $\text{CaH}_2$  and  $\text{CaCl}_2$ . The thermodynamic stability of CaHCl synthesized in our experiment is tested by DSC–TG measurement.

From the results of DSC–TG measurement shown in Fig. 2, it is found that CaHCl is still stable even the temperature increased to 550 °C.

### 3.2. Thermodynamics and kinetics properties of $6\text{LiBH}_4 + \text{CaHCl}$ system

In order to investigate the dehydrogenation properties of  $6\text{LiBH}_4 + \text{CaHCl}$  system, the pristine  $\text{LiBH}_4$ , and  $6\text{LiBH}_4 + \text{CaH}_2$  system are used for drawing a comparison.

First of all, the DSC and MS profiles of  $\text{LiBH}_4$ ,  $6\text{LiBH}_4 + \text{CaHCl}$  and  $6\text{LiBH}_4 + \text{CaH}_2$  systems at a heating rate of 5 °C/min are shown in Fig. 3. The dehydrogenation process of  $6\text{LiBH}_4 + \text{CaH}_2$  system involves three steps, corresponding to the three endothermic peaks of which the peak temperature are 416.6, 468.5, and 480.2 °C, excluding the structural transition and melting peaks of  $\text{LiBH}_4$  at approximately 110 and 280 °C. Meanwhile, the decomposition process of  $6\text{LiBH}_4 + \text{CaHCl}$  system mainly involves four steps of which the peak temperature are 400.8, 455.7, 474.0, 485.1 °C, respectively. The first step dehydrogenation of  $6\text{LiBH}_4 + \text{CaHCl}$  system not only is ahead of  $6\text{LiBH}_4 + \text{CaH}_2$  system, but also releases more hydrogen than  $6\text{LiBH}_4 + \text{CaH}_2$  system.

The similar phenomenon observed in the dehydrogenation kinetics curves of  $6\text{LiBH}_4 + \text{CaHCl}$  system and  $6\text{LiBH}_4 + \text{CaH}_2$  system is shown in Fig. 4 (at a heating rate of 5 °C/min). From the above results, it can be seen that  $6\text{LiBH}_4 + \text{CaHCl}$  system starts to release hydrogen earlier than  $6\text{LiBH}_4 + \text{CaH}_2$  system. Before the first half of dehydrogenation process, the dehydrogenation rate and hydrogen desorption mass of  $6\text{LiBH}_4 + \text{CaHCl}$  system are superior to those of  $6\text{LiBH}_4 + \text{CaH}_2$  system. Although the theoretical hydrogen capacity of  $6\text{LiBH}_4 + \text{CaHCl}$  system is lower than  $6\text{LiBH}_4 + \text{CaH}_2$  system,  $\text{LiBH}_4$  doping with CaHCl can decrease the thermodynamic stability of  $\text{LiBH}_4$  and improve the low temperature dehydrogenation kinetics of  $\text{LiBH}_4$  greater than that of  $\text{CaH}_2$  do.

Following, we calculate the activation energy of  $\text{LiBH}_4$  dehydrogenation in  $6\text{LiBH}_4 + \text{CaHCl}$  and  $6\text{LiBH}_4 + \text{CaH}_2$  system according to the Kissinger equation [23].

$$\ln(\beta/T_m^2) = -E_a/RT_m + \ln(AR/E_a) \quad (4)$$

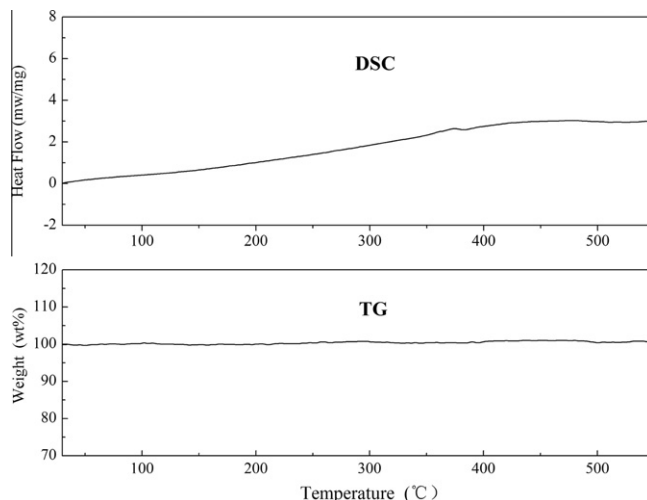


Fig. 2. DSC–MS curves of CaHCl synthesized by ball-milling the mixture of  $\text{CaH}_2 + \text{CaCl}_2$  and heat-treating at 450 °C for 12 h under 1 MPa hydrogen pressure.

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