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Letter

Thermal decomposition behavior of calcium borohydride $Ca(BH_4)_2$

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Abstract

The thermal decomposition behavior of adduct-free $Ca(BH_4)_2$, prepared by heating $Ca(BH_4)_2{\cdot}2THF$ powder under vacuum, was investigated by X-ray diffraction and thermal analyses. It has been found that $Ca(BH_4)_2$ undergoes a polymorphic transformation at 440 K and eventually decomposes in two steps between 620 and 770 K. CaH_2 and an unknown intermediate compound form after the first step, but CaH_2 is the only crystalline phase observed after the second step with a total weight loss of about 9.0 wt.%.

Keywords: Hydrogen storage materials; Phase transitions; Thermochemistry; X-ray diffraction; Thermal analysis

1. Introduction

Hydrogen is one of the most promising clean fuel of the future, particularly for on-board applications for automobiles [1]. As potential hydrogen storage materials, alkali and alkali-earth metal borohydrides such as $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ have high gravimetric and volumetric hydrogen densities [2–18]. $Ca(BH_4)_2$ is least studied among them and very little is known about its thermochemistry, although it has relatively high theoretical hydrogen storage capacity (11.6 wt.%) and allegedly lower decomposition temperature than that of $LiBH_4$ [2,19]. Recently, Miwa et al. [18] have characterized the crystal structure of adduct-free $Ca(BH_4)_2$ by the Rietveld method and confirmed that the diffraction pattern is in good agreement with the previous report [20]. Based on the thermogravimetric analysis together with the results of ab-initio calculations, they proposed that the desorption reaction of $Ca(BH_4)_2$ is

$$Ca(BH_4)_2 \rightarrow 2/3CaH_2 + 1/3CaB_6 + 10/3H_2 \quad (9.6\,wt.\%\,H_2) \tag{1}$$

although they mentioned the existence of an unknown intermediate compound. However, no detailed experimental data on the thermal decomposition of $Ca(BH_4)_2$ have been disclosed so far [19,20].

In this study, we report the results on the thermodynamic properties of adduct-free calcium borohydride $Ca(BH_4)_2$ in detail for the first time. The thermal decomposition behavior of $Ca(BH_4)_2$ has been investigated by means of the thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) coupled with mass spectrometry (MS) and in situ high temperature X-ray diffraction (XRD) as well as room temperature XRD in order to understand the dehydrogenation reaction path.

2. Experimental

The starting material is $Ca(BH_4)_2{\cdot}2THF$ which has been purchased from Aldrich. Adduct-free $Ca(BH_4)_2$ was prepared by heating the commercial powder under vacuum at 473 K for 1 h. All materials were stored and handled in an argon-filled glove box and both the water vapor and oxygen levels inside the glove box were maintained below 1 ppm. The phase compositions and transformations of the $Ca(BH_4)_2$ powders were characterized by XRD (Bruker D8 Advance) and in situ high temperature XRD (PANalytical X'pert PRO MPD) with Cu Kα radiation. The in situ high temperature XRD patterns were obtained every 50 K up to 573 K under vacuum. The thermal decomposition behavior of $Ca(BH_4)_2$ was analyzed by DSC (Netzsch DSC 204 F1) coupled with MS (Netzsch QMS 403 C) and TGA (Netzsch TG 209 F1). The heating rate was fixed at 5 K/min and the flow rate of pure Ar (99.9999%) gas was at 50 ml/min for both DSC/MS and TGA measurements.

3. Results and discussion

Fig. 1 shows an XRD pattern of the vacuum dried and slow cooled $Ca(BH_4)_2$ sample measured at room temperature. Since the diffraction peaks match quite well with those of $Ca(BH_4)_2$

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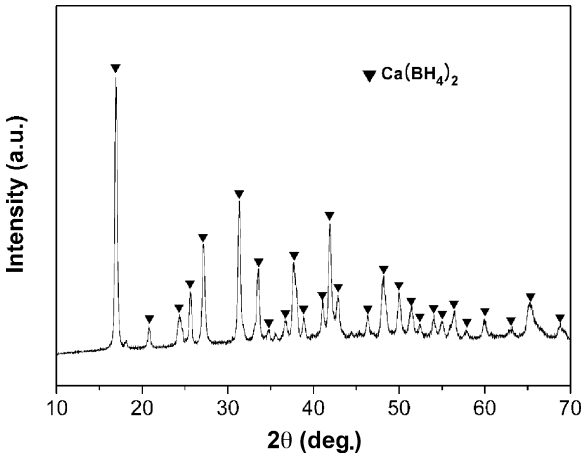

Fig. 1. XRD pattern of the $Ca(BH_4)_2$ sample dried under vacuum.

in the previous studies [18,20], it is thought to be a single phase $Ca(BH_4)_2$ without any THF adduct. Typical DSC/MS curves of this adduct-free $Ca(BH_4)_2$ are presented in Fig. 2(a). A small endothermic peak appears at around 440 K and the second, sharp endothermic peak at 640 K. The third, relatively broad endothermic peak finally appears between 670 and 770 K. According to the MS data, there is no gas evolution at the first endothermic reaction. However, both the second and third are accompanied with hydrogen evolution and no other gas phase is detected by MS. Fig. 2(b) shows a typical TGA curve and the weight loss

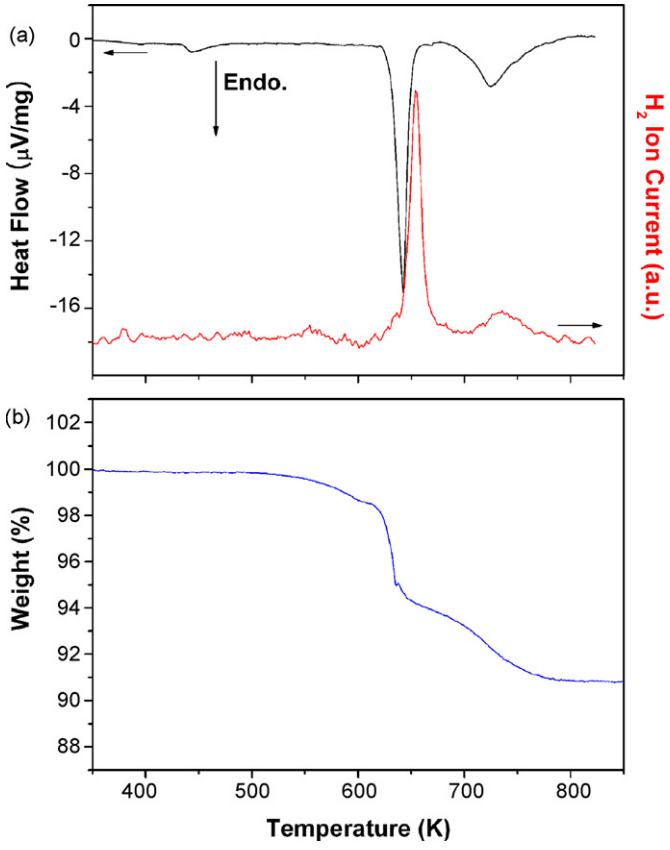

Fig. 2. (a) DSC and MS data ($m/z = 2$), and (b) TGA curve of the $Ca(BH_4)_2$ sample dried under vacuum.

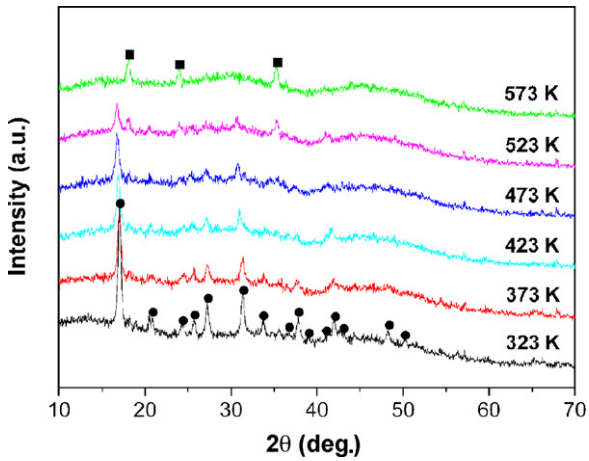

Fig. 3. In situ high temperature XRD patterns of $Ca(BH_4)_2$ during heating. Solid circles and squares indicate low and high temperature phases of $Ca(BH_4)_2$, respectively.

behavior matches quite well with the DSC data, except that there is a slight weight decrease before 600 K. The total weight loss is approximately 9.0% which is lower than that of the theoretical value based on the proposed decomposition reaction (1), but higher than the following reaction:

$$Ca(BH_4)_2 \rightarrow CaH_2 + 2B + 3H_2 \quad (8.7\,\text{wt.\%}\,H_2) \qquad (2)$$

In order to find out the cause of the first endothermic reaction which does not accompany with hydrogen evolution, an in situ high temperature XRD analysis was carried out and the result is presented in Fig. 3. As temperature increases up to 423 K, the intensities of the diffraction peaks for $Ca(BH_4)_2$ gradually decrease. At 473 K, unknown diffraction peaks start to appear and only this unknown phase exists at 573 K. From this result together with those of DSC, MS and TGA, the endothermic reaction around 440 K is believed to be a polymorphic transformation from low to high temperature phase of $Ca(BH_4)_2$. In fact, the diffraction peaks of the high temperature phase were observed together with the low temperature phase in the XRD pattern of the air-cooled sample (not shown here).

Fig. 4 presents the XRD patterns of the $Ca(BH_4)_2$ samples dehydrogenated up to 663 and 753 K under vacuum, together with pure CaH_2 and CaB_6 for comparison. At 663 K, both CaH_2 and another unknown phase are observed. This unknown phase seems to be an intermediate compound consisting of calcium, boron and hydrogen. Similar cases during the dehydrogenation reaction of $LiBH_4$ were reported previously [8–10]. When heated up to 753 K, the unknown peaks disappear and the only CaH_2 phase is observed while no crystalline B or CaB_6 was observed. This indicates that the intermediate compound decomposes into crystalline CaH_2 and amorphous boron and/or amorphous calcium boride. Not like the case of $Zn(BH_4)_2$ [21], no borane gas has been detected by MS during dehydrogenation in the present study.

According to the phase diagram [22], the only intermetallic compound in the Ca–B binary system is CaB_6. Moreover, thermodynamic calculation using the Thermo-Calc program [23] indicates that the products of reaction (1) have Gibbs free energy

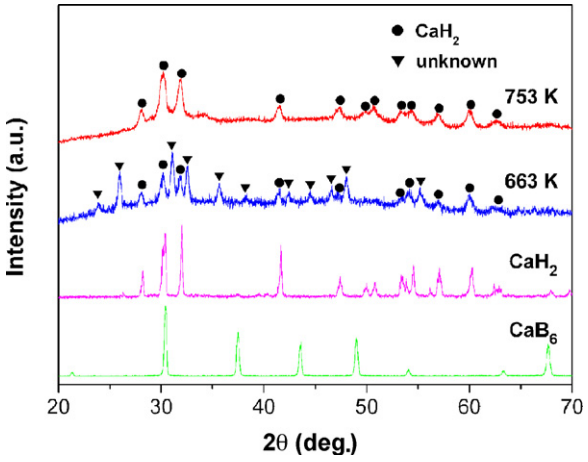

Fig. 4. XRD patterns of the $Ca(BH_4)_2$ samples dehydrogenated at 663 and 753 K. The patterns of commercial CaH_2 and CaB_6 are included for comparison.

lower than that of reaction (2) by about 9 kJ/mol, i.e., crystalline CaB_6 is more stable than either amorphous or crystalline boron. More analytical work has to be done to know the exact form of boron in the dehydrogenated state.

Based on the above results, the thermal decomposition behavior of $Ca(BH_4)_2$ can be described as follows:

1. *Polymorphic transformation*: $Ca(BH_4)_2$ (LT) → $Ca(BH_4)_2$ (HT) at around 440 K.
2. *First decomposition step*: $Ca(BH_4)_2$ → CaH_2 + intermediate compounds at 620–660 K.
3. *Second decomposition step*: intermediate compounds → CaH_2 + a-B and/or a-CaB_6 at 670–770 K.

4. Conclusion

In summary, we have investigated the thermal decomposition behavior of $Ca(BH_4)_2$ and found that $Ca(BH_4)_2$ undergoes a slow polymorphic transformation at around 440 K and eventually decomposes in two steps between 620 and 770 K. CaH_2 and an unknown intermediate compound form after the first step and this intermediate compound finally decomposes into CaH_2 and amorphous B and/or amorphous calcium boride. Further studies on the decomposition reaction mechanism and reversibility (hydrogen absorption) of $Ca(BH_4)_2$ are now in progress.

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