Decomposition Reactions and Reversibility of the LiBH$_4$–Ca(BH$_4$)$_2$ Composite

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Received: May 12, 2009; Revised Manuscript Received: June 21, 2009

LiBH$_4$ is one of the promising candidates for hydrogen storage materials because of its high gravimetric and volumetric hydrogen capacity. However, its high dehydrogenation temperature and limited reversibility has been a hurdle for its use in real applications. In an effort to overcome this barrier and to adjust the thermal stability, we make a composite system LiBH$_4$–Ca(BH$_4$)$_2$. In order to fully characterize this composite system we study xLiBH$_4$ + (1 − x)Ca(BH$_4$)$_2$ for several x values between 0 and 1, using differential scanning calorimetry, in situ synchrotron X-ray diffraction, thermogravimetric analysis, and mass spectrometry. Interestingly, this composite undergoes a eutectic melting at ca. 200 °C in a wide composition range, and the eutectic composition lies between x = 0.6 and 0.8. The decomposition characteristics and the hydrogen capacity of this composite vary with x, and the decomposition temperature is lower than both the pure LiBH$_4$ and Ca(BH$_4$)$_2$ at intermediate compositions, for example, for x ≈ 0.4, decomposition is finished below 400 °C releasing about 10 wt % of hydrogen. Partial reversibility of this system was also confirmed for the first time for the case of a mixed borohydride composite.

1. Introduction

Complex metal hydrides hold a great promise as potential solid state hydrogen storage materials because of their high theoretical hydrogen storage capacity. Within this class of materials, LiBH$_4$ is one of the most studied case since it has a hydrogen content of 18.5 wt % and the following reversible reaction can release as much as 13.9 wt % hydrogen:

LiBH$_4$ ↔ LiH + B + 3/2H$_2$  13.9 wt % H$_2$  (1)

Practical use of LiBH$_4$ however has been hampered due to its high dissociation temperature, and therefore various strategies have been pursued to lower its decomposition temperature such as adding catalysts, confinement in a nanoporous scaffold, and destabilization using metal or metal hydrides. Another route to adjust stability is to mix with less stable metal borohydrides. A systematic study by Nakamori et al. has shown that stability of metal borohydrides can be roughly estimated by the electronegativity of cation; a less electronegative metal can form a more stable metal borohydride. According to this principle, stability of a mixed borohydride LiBH$_4$–M(BH$_4$)$_x$ can be tuned by changing the metal M and the mixing ratio. To our knowledge, M = Zn, Al, Zr, K, and Sc have been investigated so far. Li et al. characterized the thermal decomposition behavior of M = Zn, Al, and Zr. In the case of Zn and Al, separation into the two individual borohydrides occurs upon heating, but the decomposition temperature of ZrLi$_{1−x}$(BH$_4$)$_x$ (m = 5, 6) lies between that of pure Zr(BH$_4$)$_4$ and LiBH$_4$, which could validate this approach as a means of adjusting thermodynamics of complex metal hydride. Nickels et al. reported a similar trend in their recent study on LiK(BH$_4$)$_2$. These previous studies underscore the need for further investigation on multiple-cation borohydrides. However, in order to design novel mixed cation borohydrides, knowledge of the underlying mechanism for the changes in stability due to varying cation composition must be understood. In some of the aforementioned double-cation borohydrides, even the starting phases were not well characterized not to mention the decomposition product; to the best of our knowledge reversibility has never been reported.

Here we pursue a more practical approach inspired by recent studies which have proved the reversibility of the following reactions:

6LiBH$_4$ + CaH$_2$ ↔ 6LiH + CaB$_6$ + 10H$_2$  11.7 wt % H$_2$  (2)

Ca(BH$_4$)$_2$ ↔ 2/3CaH$_2$ + 1/3CaB$_6$ + 3H$_2$  9.6 wt % H$_2$  (3)

Both reaction schemes 2 and 3 promise large hydrogen storage capacity, but even higher in their combination as the following:

4LiBH$_4$ + Ca(BH$_4$)$_2$ ↔ 4LiH + CaB$_6$ + 10H$_2$  12.8 wt % H$_2$  (4)

A pseudobinary system as shown in eq 4 has the potential to form intermediate compounds, solid solution, or can remain as...
a physical mixture of two solids, LiBH₄ and Ca(BH₄)₂. Therefore, a systematic study of the composite xLiBH₄ + (1 − x)Ca(BH₄)₂ was performed. Scanning through wide composition ranges will provide a clear picture of the initial phases. Second, we would like to address whether reaction 4 precedes reactions 2 and 3. In that case, LiBH₄ and Ca(BH₄)₂ would react directly and the composite system would exhibit lower stability than the pure compounds LiBH₄ and Ca(BH₄)₂. Lastly, the reversibility of the composite system will also be discussed.

2. Experimental Section

2.1. Starting Material. LiBH₄ (assay 95%, Acros), Ca(BH₄)₂·2THF (assay 98%, Sigma-Aldrich), and NbF₅ (assay 98%, Sigma-Aldrich) were used as starting materials. Adduct-free Ca(BH₄)₂ was prepared by drying the commercial powder at around 200 °C in vacuum for 20 h, and LiBH₄ and NbF₅ powders were used as-purchased. The powders were handled in an argon-filled glovebox.

Each batch of composite was about 2 g of LiBH₄ and Ca(BH₄)₂ mixture in different molar ratio of x:1−x, x = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.2. The powder composite was placed in a hardened steel bowl with seven 12.7 mm and fourteen 7.9 mm diameter Cr-steel, which was then sealed with a Viton O-ring and a lid. The ball-milling was conducted using a planetary mill (Fritsch P7) at 600 rpm for 4 h. For x = 0.4, 0.4LiBH₄ + 0.6Ca(BH₄)₂ + 0.02NbF₅ (in molar ratio) were prepared in the same manner.

The phase composition of as-milled samples were investigated with laboratory X-ray diffraction (XRD, Bruker D8 with Cu Kα radiation, λ = 1.5418 Å). All laboratory XRD measurements were performed at room temperature. A dome-shaped, vacuum tight, sample holder was used to prevent contact with air during XRD measurement.

2.2. Thermal Analysis. Differential scanning calorimetry (Netzsch DSC 204 F1), thermogravimetric analysis (Netzsch TG 209 F1), and mass spectrometry (Netzsch QMS 403 C) were carried out to analyze the dehydrogenation path of the samples. For differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), ca. 3 mg of sample was used; data were recorded while heating to 500 °C at a scanning rate of 2 °C/min under flowing argon condition ( assay 99.9999%, 50 mL/min).

2.3. In Situ Synchrotron XRD. In situ synchrotron radiation power X-ray diffraction (SR-PXD) measurements were carried out at the synchrotron MAX II, Lund, Sweden, in the research laboratory MAX-Lab at beamline I711 with a MAR165 CCD detector system. The selected X-ray wavelength was 1.09801 Å. The sample cell was specially developed for studies of gas/solid reactions and allows high pressure and temperature to be applied. The samples were mounted in a sapphire single crystal tube (1.09 mm o.d., 0.79 mm i.d., Al₂O₃) in an argon filled glovebox (p(O₂), H₂O) < 0.1 ppm. The temperature was controlled with a thermocouple placed in the sapphire tube next to the sample. A gas supply system was attached to the sample cell, which allows change of gas and pressure via a vacuum pump during X-ray data acquisition. The details of the experimental setup can be found in ref 23. The system was flushed with Ar and evacuated three times before the valve to the sample was opened prior to the X-ray experiment. The X-ray exposure time was 30 s (2 × 15 s) per powder diffraction pattern. All the in situ dehydrogenation experiments were done at a scanning rate of 2 °C/min under ρ(H₂) = 1 bar unless otherwise mentioned. The FIT2D program was used to remove diffraction spots from the sapphire sample holder.

3. Results and Discussion

3.1. Starting Material. Figure 1 shows XRD pattern of two composites (x = 0.8 and 0.4) after milling. All observed reflections are identified as a polymorph of Ca(BH₄)₂ or LiBH₄, and shift in peak positions is only insignificant compared to the two pure borohydrides. Hence we conclude that LiBH₄ or Ca(BH₄)₂ exist as a physical mixture rather than a new compound or a solid solution. Interestingly, ball-milling with LiBH₄ gives a mixture of γ-Ca(BH₄)₂ but no Bragg reflection can be assigned to β-Ca(BH₄)₂ which is usually the majority phase of the Ca(BH₄)₂ powder dried at 200 °C.

3.2. Thermal Analysis. We present in Figure 2 the DSC data of xLiBH₄ + (1 − x)Ca(BH₄)₂ composite at nine different values of x. DSC data verify the XRD data that these two borohydrides remain unaffected by each other in the as-milled samples under the conditions studied. The polymorphic transformation from orthorhombic (α-LiBH₄) to hexagonal (β-LiBH₄) LiBH₄ at ca. 110 °C, and several endothermic peaks around 150 °C related to those of Ca(BH₄)₂ are consistently observed independent of
the composition. However, a thermal event is observed for the composite, an endothermic peak at 200 °C, which is not observed for either pure LiBH₄ or Ca(BH₄)₂. The appearance of this peak accompanies the disappearance of the peak for the melting of LiBH₄ at 280 °C (except for x = 0.9). From a typical phase diagram of pseudobinary system having negligible mutual solubility, we suspect that the endothermic peak at 200 °C would arise from the eutectic melting of LiBH₄ and Ca(BH₄)₂. This hypothesis has been thoroughly investigated by in situ SR-PXD measurements, which is presented in Section 3.3.2.

DSC results raise another interesting point. For composites rich in either LiBH₄ or Ca(BH₄)₂, the decomposition proceeds in multiple steps and occurs above 400 °C, that is, the excess amounts decomposes like pure LiBH₄ or Ca(BH₄)₂. Second, the DSC curves for the intermediate compositions cannot be accounted for by a simple overlap of x = 0 and x = 1, a certain kind of chemical reaction should occur between LiBH₄ and Ca(BH₄)₂ during decomposition. Furthermore, DSC data implies that x = 0.8 is not an optimal composition in order to reduce the decomposition temperature. In fact, the lowest decomposition temperature was achieved at x = 0.4 where a major decomposition ends at only 370 °C. This is in contrast to our expectation from reaction 4.

3.3. In Situ XRD Experiment. 3.3.1. Polymorphic Phase Transition of Ca(BH₄)₂. While structure and transition between different polymorphs of LiBH₄ is well understood, those of Ca(BH₄)₂ seem much more complicated and are still not fully understood. Five different polymorphs of Ca(BH₄)₂ have been reported up to now. At room temperature, mixtures of α-, β-, and γ-Ca(BH₄)₂ are usually found and the proportion of each phase is very sensitive to the preparation condition. Several in situ XRD experiments have shown that α- and γ-Ca(BH₄)₂ transform to β-Ca(BH₄)₂ upon increasing temperature. Theoretical work based on density functional theory supports this experimental observation that α-Ca(BH₄)₂ is stable at low temperatures and β-Ca(BH₄)₂ at elevated temperatures. Majzoub et al. predicted that γ-Ca(BH₄)₂ is metastable, but this point has not been proven experimentally. Another polymorph δ-Ca(BH₄)₂ reported by Riktor et al. appears at higher temperatures than β-Ca(BH₄)₂. No structural information has yet been given for δ-Ca(BH₄)₂. Filinchuk et al. recently identified another polymorph α'-Ca(BH₄)₂ which forms from α-Ca(BH₄)₂ via a second-order phase transition and transforms to β-Ca(BH₄)₂ at elevated temperature.

In our composite system, we clearly observed α-Ca(BH₄)₂ → γ-Ca(BH₄)₂ → β-Ca(BH₄)₂ transition in a narrow temperature range of ca. 30 °C as shown in Figure 3 for x = 0.8. The same sequential phase transition was observed at other x values not presented here. This rapid transition is in contrast to the similar but rather slow transition in the case of pure Ca(BH₄)₂, in which α- to γ-Ca(BH₄)₂ transition has never been reported. This may suggest that a tiny amount of LiBH₄ is dissolved in the Ca(BH₄)₂ lattice and the phase transition is facilitated by the created lattice defects. Our result could tell which polymorph is thermodynamically most stable at a given temperature provided that the presence of LiBH₄ does not affect the relative stability of these three polymorphs.

3.3.2. Eutectic Melting. We performed in situ SR-PXD measurements for x = 0.9, 0.8, 0.6, 0.5, and 0.4. The eutectic melting predicted by DSC data is consistently observed, and the in situ SR-PXD data locate the eutectic composition between x = 0.6 and 0.8. SR-PXD patterns at ca. 200 °C for x = 0.8 and 0.6 are plotted in Figure 4 and Figure 5, respectively. These SR-PXD patterns provide a direct evidence of the eutectic melting; as temperature increases, β-Ca(BH₄)₂ disappears first in Figure 4 whereas h-LiBH₄ disappears first in Figure 5. We provide in Figure 6 a schematic phase diagram of this pseudobinary system for clarity. Two dots in the diagram indicate the temperature at which the remaining solid compound, LiBH₄ or Ca(BH₄)₂, disappears from the SR-PXD pattern and that could be an upper limit of the liquidus temperature (drawn in dashed line). In the case of x = 0.6, β-Ca(BH₄)₂ transforms to δ-Ca(BH₄)₂ almost simultaneously with the eutectic melting, and the temperature marked in Figure 6 corresponds to the temperature at which δ-Ca(BH₄)₂ disappears. Here δ-Ca(BH₄)₂ appears at temperatures at more than 100 °C lower than the case of pure Ca(BH₄)₂, which again hints at a rapid phase transformation in this composite system. In the case of x = 0.8, δ-Ca(BH₄)₂ was not observed probably because Ca(BH₄)₂ melts completely before the β- to δ-Ca(BH₄)₂ transition starts.

3.3.3. Decomposition Process. In situ SR-PXD data reveals the complexity of the decomposition reaction for the composites investigated here, which is clearly illustrated in Figure 7 and Figure 8 for the composites x = 0.8 and 0.6 in the temperature up to 550 °C.
For both composites, a new set of diffraction peaks appear around 230 °C growing from the melt or from remaining $\delta$-Ca(BH$_4$)$_2$. TGA and MS data in Figure 9 show that mass decrease and hydrogen release is associated with the formation of this phase. The same set of peaks are seen in Ca(BH$_4$)$_2$ + 0.02NbF$_5$ system (not presented here). Therefore the new phase is assumed to be partially dissociated Ca(BH$_4$)$_2$. We tentatively call it as “CaB$_m$H$_n$.” It is worth noting that CaH$_2$ is not formed simultaneously with CaB$_m$H$_n$, suggesting that this is different from dodecaborohydride (CaB$_{12}$H$_{12}$) previously described as an intermediate state of dehydrogenated tetraborohydride.

A recent structure analysis of an unknown intermediate phase identified another partially decomposed phase as CaB$_2$H$_2$38,38, which is consistent with our observation that the formation of CaB$_m$H$_n$ is not accompanied by CaH$_2$. However, the ex situ XRD pattern of the partially decomposed Ca(BH$_4$)$_2$33,34,38 is different from that of CaB$_2$H$_2$ observed by in situ SR-PXD in this study. Nevertheless the recent identification of CaB$_2$H$_2$ together with our result leads us to the conclusion that partially decomposed Ca(BH$_4$)$_2$ may have stoichiometry different from CaB$_{12}$H$_{12}$.

Compared to previous investigations of pure Ca(BH$_4$)$_2$, a temperature at which CaB$_m$H$_n$ starts to appear is lower by $\sim$100 °C. In a wide temperature range, this phase is the only crystalline phase observed in this study.
phase detected by XRD since LiBH$_4$ and Ca(BH$_4$)$_2$ exist in a melt. The new phase CaB$_6$H$_4$ forms at ca. 230 °C and the intensity of the Bragg reflections appear to remain constant upon further heating. TGA and MS data (Figure 9) show a similar trend; there is no gradual weight loss or hydrogen release upon further heating of the sample. In a thermodynamic point of view, increasing temperatures should favor the formation of CaB$_6$H$_4$ and Ca(BH$_4$)$_2$, and CaB$_6$H$_4$ should not coexist. One may argue that Ca(BH$_4$)$_2$ could have transformed completely to CaB$_6$H$_4$ and only LiBH$_4$ would remain in the melt. However, XRD data in Figure 8 show that the intensity of the CaB$_6$H$_4$ peaks remain almost constant when the intensity of the CaH$_2$ peaks increase abruptly. This suggest that CaH$_2$ is mainly formed from a decomposition of Ca(BH$_4$)$_2$ remaining as a melt as shown in reaction scheme 3. Therefore, apparently Ca(BH$_4$)$_2$ only partially transforms to CaB$_6$H$_4$, which tends to suggest that the free energy change involved in the formation of CaB$_6$H$_4$ might be almost zero and the activation barrier might be high, so that the experimental conditions are different from the thermodynamic equilibrium condition. Structural disorder introduced by the melting process may provide a decomposition pathway with a lower activation energy, thereby assisting the formation of CaB$_6$H$_4$ at around the melting point.

For $x = 0.6$ (Figure 8), CaH$_2$ peaks appear around 320 °C but shrink rapidly upon the formation of CaB$_6$. It is natural to think that the reaction 2 immediately follows the reaction 3, that is, Ca(BH$_4$)$_2$ dissociates first and the product CaH$_2$ reverts with LiBH$_4$ forming LiH and CaB$_6$. LiH though is not observed in SR-PXD patterns, possibly due to its weak scattering efficiency. The composite system at $x = 0.8$ (Figure 7) behaves slightly different, that is, no clear signature of CaH$_2$ is observed. It could be that the lower activity of Ca(BH$_4$)$_2$ at $x = 0.8$ raises the temperature of the reaction 3, resulting in reaction 2 and 3 or in reaction 4 occurring almost at the same time. It is difficult to know whether the overall dissociation proceeded in two steps or in a single step.

In both cases, there are some unidentified diffraction peaks in the final product, which indicate the presence of more than one unidentified phase since these sets of peaks are different for $x = 0.8$ and $x = 0.6$. Second, compounds like LiB$_6$H$_4$ and other unidentified phases that are not easily detected by XRD may form. The formation of unidentified phases and CaB$_6$H$_4$ results in a decomposition route different from the ideal reaction scheme 4. Since CaB$_6$H$_4$ appear to have higher thermal stability than Ca(BH$_4$)$_2$, the amount of CaH$_2$ presumably would not be sufficient to react completely with LiBH$_4$ when $x = 0.8$. Even at $x = 0.6$, CaH$_2$ appears to be completely consumed by LiBH$_4$, which means that an even larger amount of Ca(BH$_4$)$_2$ would be required for complete dissociation of LiBH$_4$ through the reaction 2. Lastly, we would like to note that our system has never reached a thermodynamic equilibrium, which is always the case when an experiment is done under continuous heating condition. Since each reaction scheme has different activation barrier, one may find a different reaction sequence when slower or faster heating rate is applied.

3.4. Hydrogen Storage Capacity. The theoretical limit for the hydrogen capacity can be calculated by the combination of two reactions when intermediate compounds are excluded. The lower boundary is set by a linear combination of the reactions 1 and 3; the upper boundary is set by a linear combination of reactions 2 and 3. In the inset of Figure 9, the calculated hydrogen capacity for each limit is drawn in red and blue line for the upper and the lower bound, respectively. This can be taken as a rough estimate, since we in this work show that the decomposition of the composite system is more complex. But, in fact the measured hydrogen storage capacities (TGA, see Figure 9) compare well with the theoretical limits and about 10 wt % of hydrogen are released below 400 °C for $x = 0.4$ and 0.6. This places the composite $x$LiBH$_4$+(1-$x$)Ca(BH$_4$)$_2$ among the materials with the highest hydrogen storage capacities.

3.5. Reversibility. We have tested reversibility for the composite 0.4LiBH$_4$ + 0.6Ca(BH$_4$)$_2$, which decomposes at relatively low temperature compared to other compositions. It has been found previously that the reactions 2 and 3 are difficult to reverse without the presence of a catalyst. Therefore, the catalytic additive NbF$_3$ was added in order to promote the kinetics of release and uptake of hydrogen. Initially, the sample 0.4LiBH$_4$ + 0.6Ca(BH$_4$)$_2$ + 0.02NbF$_3$ was heated to 400 °C (heating rate 5 °C/min) and kept at 400 °C for two hours at $p$(H$_2$) = 1 bar in order to complete the dehydrogenation. In situ SR-PXD patterns were collected and are shown in Figure 10. In this case, no unknown phases were observed after decomposition in contrast to the other two compositions $x = 0.8$ and 0.6. The temperature was still kept constant at 400 °C but the hydrogen pressure was raised to 120 bar in order to study the rehydrogenation in situ as shown in Figure 11. In the beginning, the major phases are CaH$_2$, CaB$_6$H$_4$, and CaO. Gradually, the intensity of the CaH$_2$ peaks decreases due to hydrogen uptake, but neither LiBH$_4$ nor Ca(BH$_4$)$_2$ appears since they form a melt. The rehydrogenation at prolonged time also induces particle growth, that is, the broad peaks of CaB$_6$H$_4$ become visible after a few hours. A TGA-MS experiment was also performed under similar conditions as used above for in situ SR-PXD (see Figure 12). The regenerated α-LiBH$_4$ and α-Ca(BH$_4$)$_2$ prove that this composite system is partially reversible. To our knowledge, this is the first case of reversible mixed cation borohydride system at moderate conditions, 400 °C and $p$(H$_2$) = 90 bar. TGA data in the inset in Figure 12 shows that about 40% of the hydrogen content is reversibly absorbed after one cycling. The mixing ratio, catalyst, and de/rehydrogenation condition need to be further optimized in order to achieve better performance.
LiBH$_4$–Ca(BH$_4$)$_2$ Composite

Figure 11. In situ SR-PXD patterns of 0.4LiBH$_4$ + 0.6Ca(BH$_4$)$_2$ + 0.02NbF$_5$ at 400 °C, $p$(H$_2$) = 120 bar. Diffraction from CaH$_2$ shrinks during the process, but no new peaks appear, suggesting that LiBH$_4$ and Ca(BH$_4$)$_2$ directly form in the melt. CaB$_6$ becomes more visible after few hours.

Figure 12. XRD pattern of a 0.4LiBH$_4$ + 0.6Ca(BH$_4$)$_2$ + 0.02NbF$_5$, which was dehydrogenated at 400 °C for 2 h under static vacuum and then rehydrogenated at 400 °C, $p$(H$_2$) = 90 bar for 20 h. The rehydrogenation was not complete, but the formation of α-LiBH$_4$ and α-Ca(BH$_4$)$_2$ clearly proves that this composite system is thermodynamically reversible. TGA data of the as-milled and the rehydrogenated samples are shown in the inset.

4. Conclusions

A systematic study has been carried out on a mixed cation borohydride system, xLiBH$_4$ + (1 − x)Ca(BH$_4$)$_2$. The two borohydrides do not react when mixed by a ball-milling but exist as a physical mixture. This mixture exhibits eutectic melting as similar to other pseudobinary systems which have limited mutual solubility in solid state. The eutectic composition lies between x = 0.6 and 0.8. The decomposition proceeds in multiple steps and the major reactions are identified by in situ SR-PXD. Right above the eutectic melting point, Ca(BH$_4$)$_2$ decomposes partially to an unidentified new material CaB$_6$. At higher temperatures the remaining Ca(BH$_4$)$_2$ dissociates forming CaH$_2$, which reacts with molten LiBH$_4$. Hence, hydrogen release does not occur in a single step through a direct reaction between LiBH$_4$ and Ca(BH$_4$)$_2$ as originally envisioned, but at a certain composition (x ≈ 0.4) the mixture releases hydrogen at lower temperatures as compared to the individual borohydrides, highlighting the need for further in-depth investigation of this interesting system. Partial reversibility of the composite is confirmed, which is the first case of mixed cation borohydride systems. In addition, phase transition sequence between the four different Ca(BH$_4$)$_2$ polymorphs, α → γ → β → δ, is clearly observed in this in situ SR-PXD study.

Acknowledgment. The authors at KIST acknowledge financial support from the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Programs funded by the Ministry of Education, Science, and Technology of Korea. D.R. and T.J. thank the Danish Natural Science Research Council under the program DanScatt and the Carlsberg Foundation for financial support.

References and Notes