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A Novel Strategy for Reversible Hydrogen Storage in Ca(BH$_4$)$_2$

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We report that decomposition pathway of Ca(BH$_4$)$_2$ can be efficiently controlled by reaction temperature. That is, it decomposes into CaB$_6$ at a lower temperature range of 320 to 350°C, but into amorphous boron at 400 to 450°C. We identified the formation of CaB$_2$H$_6$ as the crucial intermediate step on the way to CaB$_6$ that only forms at 320 to 350°C.

Hydrogen is considered an ideal synthetic energy carrier to replace the limited fossil fuels. Wide utilization of hydrogen as a fuel strongly relies on its safe and efficient storage and transport, particularly for mobile applications.$^{5,2}$ Light-weight metal borohydrides display high hydrogen densities and thereby offer hope to overcome the challenges associated with solid hydrogen storage.$^3$ In particular, some borohydrides display an enthalpy change in the decomposition reaction within the targeted window of 20-45 kJ/mol H$_2$ for reversible on-board storage. For instance, Ca(BH$_4$)$_2$ shows an enthalpy change of 36 ± 4 kJ/mol H$_2$ in the decomposition reaction into CaB$_6$ according to Eq. 1.$^{4,6}$

\[
\text{Ca(BH}_4\text{)}_2 \rightarrow 1/3\text{CaB}_6 + 2/3\text{CaH}_2 + 10/3\text{H}_2 \quad (1)
\]

One of the main obstacles for metal borohydrides to be utilized as hydrogen storage materials is their poor reversibility. It is generally believed that boron sinks (i.e., amorphous B and/or [B$_2$H$_6$]$^{2-}$ phases) form during the decomposition and hinder rehydrogenation. One strategy to avoid the formation of boron sinks is the addition of additives such as metals or metal hydrides to bind the boron in the form of a metal boride (e.g., AlB$_3$ and MgB$_2$) as the final product. For example, using Al or MgH$_2$ as an additive, the reversibility of LiBH$_4$ and NaBH$_4$ was dramatically improved.$^{7-10}$ However, this strategy does not work efficiently for other metal borohydrides such as Ca(BH$_4$)$_2$.$^{5,11,12}$ Also, the introduction of metal or metal hydrides will unavoidably lower the hydrogen capacity of the system, e.g., from 18.4 wt% H for LiBH$_4$ to 11.4 wt% H for LiBH$_4$-0.5Al.

A number of studies have been conducted aiming to alter the reaction pathway of Ca(BH$_4$)$_2$, including the methods of additive addition,$^{13-16}$ combination with other complex hydrides,$^{17,19}$ nanoconfinement,$^{20,21}$ application of external H$_2$ pressure,$^{22}$ etc. However, all of these methods showed limited effect on avoiding the formation of boron sinks toward full reversibility of Ca(BH$_4$)$_2$.

The full rehydrogenation to Ca(BH$_4$)$_2$ has been considered impossible unless a very high H$_2$ pressure is applied, i.e. 400 to 700 bar H$_2$ at 400 to 440°C.$^5,13,15,23-25$

In present study, we identified the formation of CaB$_2$H$_6$ as the crucial intermediate step on the way to CaB$_6$, which only forms below 370°C. Thereby by controlling the decomposition temperature at 320 to 350°C, the formation of boron sinks such as amorphous boron was efficiently avoided and Ca(BH$_4$)$_2$ was decomposed in CaB$_6$ and CaH$_2$, which facilitate the reversibly absorption of hydrogen under much mild conditions. This study provides new insights into the decomposition mechanism of Ca(BH$_4$)$_2$ as well as instructions for further development of Ca(BH$_4$)$_2$ as a hydrogen storage material.

The decomposition of Ca(BH$_4$)$_2$ was carried out at 320 to 450°C under dynamic vacuum. The $^{1}$B MAS NMR spectra of the solid residue after decomposition are shown in Fig. 1. After dehydrogenation at 320°C for 6 to 20 h and 350°C for 6 h, three resonances were observed, i.e., undecomposed Ca(BH$_4$)$_2$ at −31.0 ppm, an intermediate centered at −14 ppm and newly formed CaB$_6$ centered at 11 ppm.$^{24}$ In the sample dehydrogenated at 350°C for 20 h, all B-H species disappeared where no B-H signal was detected in the $^{1}$B-$^{1}$H CP-MAS NMR spectrum. Only the resonance assigned to CaB$_6$ was observed, indicating the full decomposition of Ca(BH$_4$)$_2$ into CaB$_6$ and CaH$_2$. Also, approximately 9.3 wt% of released hydrogen was recorded during the dehydrogenation process at 350°C for 20 h in agreement with Eq. 1. In contrast, in the samples decomposed at 400 and 450°C, only broad resonances centered at 0 ppm, which is assigned to amorphous boron, were observed in the $^{1}$B MAS NMR spectra (Figs. 1c and d). These observations indicate an obvious temperature dependence of the decomposition pathway of Ca(BH$_4$)$_2$.

Due to the decomposition into CaB$_6$, at 350°C (20 h), the reversibility of Ca(BH$_4$)$_2$ was achieved under relatively moderate conditions (300 to 350 °C, 130 to 185 bar H$_2$). At 300 °C, Ca(BH$_4$)$_2$ was partially recovered, as observed by $^{11}$B MAS NMR (Fig. 2). Above 90% of boron was transformed back to Ca(BH$_4$)$_2$ at 350 °C and 185 bar H$_2$. The reversible hydrogen sorption was further confirmed by temperature-programmed-desorption measurements (Fig. S1, †ESI). In contrast, owing to the formation of amorphous boron as the major product at 450°C (0.5 h), the reformation of Ca(BH$_4$)$_2$ was very limited at 350 °C and 185 bar H$_2$, i.e., approximately 33% of boron can be converted back to Ca(BH$_4$)$_2$ (Fig. S2, †ESI). These results support the strategy of improving the reversibility by controlling the decomposition pathway.
Note that the intermediate was only observed at 320 and 350 °C (Figs. 1a and 1b), which shows a chemical shift at -14 ppm close to that of CaB\textsubscript{2}H\textsubscript{12} (-15.6 ppm). For this reason, this intermediate was tentatively assigned to CaB\textsubscript{2}H\textsubscript{12} in the previous study.\textsuperscript{22, 26} CaB\textsubscript{2}H\textsubscript{12} was reported to be a highly stable compound. The self-decomposition of CaB\textsubscript{2}H\textsubscript{12} or the reaction between CaB\textsubscript{2}H\textsubscript{12} and CaH\textsubscript{2} requires high temperature such as 600 °C.\textsuperscript{27} Since CaB\textsubscript{2}H\textsubscript{12} could be fully decomposed into CaB\textsubscript{2}H\textsubscript{12} at 350 °C (Fig. 1b), the resonance at -14 ppm should be assigned to another intermediate such as CaB\textsubscript{2}H\textsubscript{2} (2 ≤ x ≤ 6) which was proposed based on X-ray diffraction (XRD) results.\textsuperscript{28} Accordingly, CaB\textsubscript{2}H\textsubscript{x} were observed by XRD in CaB\textsubscript{H}\textsubscript{2} after partial decomposition at 320 and 350 °C, which were not observed when the decomposition occurred at 400 °C (Fig. S3).

To further identify the reaction intermediate for CaB\textsubscript{H}\textsubscript{2}, samples of CaB\textsubscript{H}\textsubscript{2} partially decomposed at 320 to 400 °C were dissolved in D\textsubscript{2}O and measured by solution-state \textsuperscript{11}B NMR (Fig. 3). In all the samples investigated, no [B\textsubscript{2}H\textsubscript{12}]\textsuperscript{x} species were observed. Instead, a new resonance at -13.0 ppm was observed when CaB\textsubscript{H}\textsubscript{2} decomposed 320 to 350 °C. It displayed a quartet splitting with a coupling constant J\textsubscript{B,H} of 87 Hz (Fig. 3b), indicating the presence of [B\textsubscript{2}H\textsubscript{12}OH] in aqueous solution.\textsuperscript{31} The structure of [B\textsubscript{2}H\textsubscript{12}OH] is shown in Fig. S4(†ESI) and the chemical shift of [B\textsubscript{2}H\textsubscript{12}OH] was calculated to be -12.9 ppm (Table 1), in agreement with the experimental value.

To verify whether the formation of [B\textsubscript{2}H\textsubscript{12}OH] results from the hydrolysis of undecomposed CaB\textsubscript{H}\textsubscript{2} in water or indicates the presence of a new intermediate, several control experiments were conducted. First, we investigated the hydrolysis of pure CaB\textsubscript{H}\textsubscript{2}. Since the presence of CaH\textsubscript{2} in the decomposition...
products of Ca(BH$_4$)$_2$ will produce alkaline solutions when it reacts with water, we dissolves pure Ca(BH$_4$)$_2$ in aqueous solutions with pH values from 7 to 14. As shown in Fig. S5, no [BH$_4$H]$^-$ was observed in the aqueous solutions of Ca(BH$_4$)$_2$, regardless of pH values of the solution. This behavior differs from the alkaline metal borohydrides, LiBH$_4$ and NaBH$_4$, which do produce [BH$_3$OH]$^-$ when reacting with D$_2$O (Fig. S6, †ESI).

Furthermore, in the alkaline solution (pH = 14) of the partially decomposed Ca(BH$_4$)$_2$ (350°C, vacuum, 6 h), the [BH$_3$OH]$^-$ species faded with time and converted to [B(OH)]$_2$ (Fig. S7, †ESI). In contrast, no obvious decay of [BH$_4$H]$^-$ was observed within 20 h. Also, the reaction of CaB$_6$ with D$_2$O (pH = 7 to 14) at room temperature does not lead to any formation of [BH$_4$] species (Fig. S8, †ESI). Therefore, the [BH$_3$OH]$^-$ species did not result from the hydrolysis of Ca(BH$_4$)$_2$ or CaB$_6$, and must originate from an intermediate as observed by $^{11}$B MAS NMR (Figs. 1a and 1b) at the chemical shift of −14 ppm.

It is known that diboron splits into two [BH$_3$] units in organic solvents (e.g., THF). The [BH$_3$OH]$^-$ species observed in this study are very likely the evidence for the formation of a [BH$_3$] compound (i.e., CaB$_6$H), which analogously splits into two [BH$_3$] moieties in water. This process can be expressed by the following equation:

$$\text{CaB}_6\text{H}_4 + 2\text{H}_2\text{O} \rightarrow \text{Ca}^2+ + 2[\text{BH}_3\text{OH}]^+ + \text{H}_2$$ (2)

The formation of CaB$_6$H$_4$ as a reaction intermediate is supported by theoretical calculations. That is, within the compounds CaB$_6$H$_x$ (2 ≤ x ≤ 6), the formation of CaB$_6$H$_6$ follows the lowest-energy decomposition pathway.  

In the previous study, the intermediate CaB$_6$H$_4$ was assigned to the resonance at around −31 ppm in the solid-state $^{11}$B NMR spectra, the same chemical shift to Ca(BH$_4$)$_2$. However, the first principles cluster calculations predicted that electrons redistribution occur when Ca(BH$_4$)$_2$ converts to CaB$_6$H$_4$ (Fig. S10, †ESI). In another word, the chemical environment of boron atoms will change and $^{11}$B chemical shift should be different between Ca(BH$_4$)$_2$ and CaB$_6$H$_4$. The $^{11}$B chemical shift of Ca(BH$_4$)$_2$ and CaB$_6$H$_4$ were calculated (Table 1) based on the cluster structures. The calculated $^{11}$B chemical shift of CaB$_6$H$_4$ is around −35.1 ppm referred to B(OH)$_3$, which is close to the experimental values, i.e., −30 and −33 ppm for α and β-CaB$_6$H$_4$, respectively (Fig. 2).

The structure CaB$_6$H$_4$ has been predicted to be monoclinic (space group, C2/c), which shows two arrangements of isomer (Fig. 4). Isomer 1 of CaB$_6$H$_4$ contains one type of boron atom showing a $^{11}$B chemical shift at −4.0 ppm, and isomer 2 contains two types of boron atoms showing chemical shifts at 9.3 and 24.5 ppm, referred to B(OH)$_3$. Either of the two arrangements will show a distinct downfield $^{11}$B resonance relative to CaB$_6$H$_4$. Experimentally, $^{11}$B MAS NMR spectra in Figs. 1a and 1b show three resonances, whereby the two at −31 and 11 ppm were unambiguously attributed to Ca(BH$_4$)$_2$ and CaB$_6$H$_4$ respectively. The resonance at −14 ppm was reasonably assigned to CaB$_6$H$_4$. The broad feature of the $^{11}$B resonance of CaB$_6$H$_4$ is owing to the co-existence of these three types of boron atoms.

Above all, we identified CaB$_6$H$_4$ as the reaction intermediate and ruled out the formation of CaB$_2$H$_2$ during the decomposition of Ca(BH$_4$)$_2$ at 320 to 450°C under vacuum. The appearance of CaB$_6$H$_4$ is closely related to the formation of CaB$_6$, and thereby is considered as the crucial intermediate step on the way to CaB$_6$. Furthermore, CaB$_6$H$_4$ only forms at 320 to 350°C. This selective formation allows controlling decomposition of Ca(BH$_4$)$_2$ by reaction temperature, as shown in Scheme 1. As a result, the decomposition of Ca(BH$_4$)$_2$ at 320 to 350°C circumvents the formation of boron sinks such as amorphous boron, facilitating the reversibly absorption of hydrogen under much mild conditions. The two distinct decomposition behavior at 320 to 350°C and at 400 to 450°C may be related to different physical states of Ca(BH$_4$)$_2$ which was reported to melt above 370°C.  

The [B$_2$H$_4$]$^{2-}$ anion is isostructural to the C$_2$H$_6$ ethane molecule, which has been reported as a ligand in some organometallic compounds. Other [B$_2$H$_4$]$^{2-}$ containing compound such as K$_2$B$_2$H$_6$ has been successfully synthesized in THF solution from the reaction of K$_2$B$_2$H$_6$ and [B$_4$H$_8$] units. MgB$_2$H$_4$ has also been discussed, while the DFT predictions did not support MgB$_2$H$_4$ forming as an intermediate for the decomposition of Mg(BH$_4$)$_2$. On the other hand, octahydroborate, [B$_6$H$_3$] containing compound, has been identified as the intermediate for Mg(BH$_4$)$_2$ and Y(BH$_4$)$_2$.

Why CaB$_6$H$_4$ rather than Ca(BH$_4$)$_2$ and CaB$_6$H$_2$ forms as the intermediate for Ca(BH$_4$)$_2$ were further investigated by out first principles cluster calculations. The geometries of the Ca salts including Ca(BH$_4$)$_2$, CaB$_6$H$_4$, Ca(BH$_4$)$_2$, and CaB$_6$H$_2$ are shown in Fig. S10 (†ESI). We found that among all Ca salts, CaB$_6$H$_4$ is the most strongly bound salt followed by Ca(BH$_4$)$_2$, Ca(BH$_4$)$_2$, and CaB$_6$H$_2$ (Table S2, †ESI). This suggests that during the decomposition of Ca(BH$_4$)$_2$, the most preferred intermediate phase is CaB$_6$H$_4$ (Table S3, †ESI).

In summary, we reported a simple and efficient route to close the hydrogen sorption cycle for pure Ca(BH$_4$)$_2$ under moderate conditions. Namely, Ca(BH$_4$)$_2$ releases 9.5 wt% H at 320 to 350°C via decomposition into CaB$_6$ and CaH$_2$ without formation of boron sinks such as amorphous boron and CaB$_2$H$_2$, and rehydrogenation is achieved at the same temperatures and under 130 to 185 bar H$_2$. This affirms that Ca(BH$_4$)$_2$ is still a promising candidate for reversible hydrogen storage. No additives or...
catalysts were used in the present study, leaving enough room for further improvement of the hydrogen sorption performance of Ca(BH$_4$)$_2$ for practical applications.

Notes and references

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6. Electronic Supplementary Information (ESI) available: Methods, H$_2$ desorption profiles of [BH$_4$]$_2$ in first two cycles, $^1$B MAS NMR spectrum of rehydrogenated Ca(BH$_4$)$_2$ (350°C under 185 bar H$_2$) after desorption at 450°C, XRD of Ca(BH$_4$)$_2$ after partial decomposition under vacuum at 320 to 400°C, optimized Geometries and optimized cartesian coordinates of [BH$_4$]-OH, $^1$B NMR spectra of hydrolysis products of Ca(BH$_4$)$_2$, NaBH$_4$, LiBH$_4$, and CaH$_2$ in aqueous solutions with different pH values, decay of [BH$_4$]-OH in alkaline solution, calculated IR of Ca(BH$_4$)$_2$ isomers compared to experimental IR observations, first principles cluster calculations. See DOI: 10.1039/b000000x/