A Novel Strategy for Reversible Hydrogen Storage in $\text{Ca}(\text{BH}_4)_2$

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We found that decomposition pathway of $\text{Ca}(\text{BH}_4)_2$ can be 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_2H_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.^{1, 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, $\text{Ca}(\text{BH}_4)_2$ shows an enthalpy change of 36 ± 4 kJ/mol H_2 in the decomposition reaction into CaB_6 according to Eq. 1.⁴⁻⁶

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 $[\text{B}_{12}\text{H}_{12}]^{2-}$ 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_2 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 $\text{Ca}(\text{BH}_4)_2$.^{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 $\text{LiBH}_4\text{-0.5Al}$.

A number of studies have been conducted aiming to alter the reaction pathway of $\text{Ca}(\text{BH}_4)_2$, 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 $\text{Ca}(\text{BH}_4)_2$. The full rehydrogenation to $\text{Ca}(\text{BH}_4)_2$ 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_2H_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 $\text{Ca}(\text{BH}_4)_2$ was decomposed in CaB_6 and CaH_2 , which facilitate the reversibly absorption of hydrogen under much mild conditions. This study provides new insides into the decomposition mechanism of $\text{Ca}(\text{BH}_4)_2$ as well as instructions for further development of $\text{Ca}(\text{BH}_4)_2$ as a hydrogen storage material.

The decomposition of $\text{Ca}(\text{BH}_4)_2$ was carried out at 320 to 450°C under dynamic vacuum. The ^{11}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 $\text{Ca}(\text{BH}_4)_2$ 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 ^{11}B - ^1H CP-MAS NMR spectrum. Only the resonance assigned to CaB_6 was observed, indicating the full decomposition of $\text{Ca}(\text{BH}_4)_2$ into CaB_6 and CaH_2 . Also, 9.5 wt% of released hydrogen was recorded during the dehydrogenation process at 350°C for 20 h and 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 ^{11}B MAS NMR spectra (Figs. 1c and d). These observations reveal an obvious temperature dependence of the decomposition pathway of $\text{Ca}(\text{BH}_4)_2$.

Due to the full decomposition into CaB_6 at 350°C (20 h), the reversibility of $\text{Ca}(\text{BH}_4)_2$ was achieved under relatively moderate conditions (300 to 350 °C, 130 to 185 bar H_2). At 300 °C, $\text{Ca}(\text{BH}_4)_2$ was partially recovered, as observed by ^{11}B MAS NMR (Fig. 2). Almost all the boron was transformed back to $\text{Ca}(\text{BH}_4)_2$ at 350 °C. This is a major breakthrough compared to the necessary temperatures (400 to 440°C) and pressures (400 to 700 bar) reported in the past.^{17,25} The rehydrogenation conditions for $\text{Ca}(\text{BH}_4)_2$ are also much more favorable than the those for LiBH_4 and $\text{Mg}(\text{BH}_4)_2$, where the rehydrogenation from the dehydrogenation products requires 600°C and 155 to 350 bar H_2 ,^{26,27} and 400°C and 950 bar H_2 ,²⁸ respectively.

Fig. 1 ^{11}B MAS NMR spectra of $\text{Ca}(\text{BH}_4)_2$ after H_2 desorption under vacuum at 320 to 450°C. In (a) and (b), the resonance centered at -14 ppm indicates the formation of an intermediate (labelled Int.). Dashed lines represent the ^{11}B CP-MAS NMR spectra.

Fig. 2 ^{11}B MAS NMR spectra of rehydrogenated $\text{Ca}(\text{BH}_4)_2$ at 300 to 350°C under 130 to 185 bar H_2 . Before rehydrogenation, $\text{Ca}(\text{BH}_4)_2$ was fully dehydrogenated at 350 °C for 20 h.

To investigate the temperature dependence of the decomposition reaction, samples of $\text{Ca}(\text{BH}_4)_2$ partially decomposed at 320 to 400°C were dissolved in D_2O , in order to identify the reaction intermediates by solution-state ^{11}B NMR (Fig. 3). In all the samples decomposed, the widely discussed intermediate, the $[\text{B}_{12}\text{H}_{12}]^{2-}$ species, were not observed. Instead, a new resonance at -13.0 ppm was observed when $\text{Ca}(\text{BH}_4)_2$ decomposed 320 to 350°C. It displayed a quartet splitting with a coupling constant $J_{\text{B-H}}$ of 87 Hz (Fig. 3b), indicating the presence of $[\text{BH}_3]$ units as $[\text{BH}_3\cdot\text{OH}]^-$ in aqueous solution.²⁹ The structure of $[\text{BH}_3\cdot\text{OH}]^-$ is shown in Fig. S1(†ESI) and the chemical shift of $[\text{BH}_3\cdot\text{OH}]^-$ was calculated to be -12.9 to -13.5 ppm (Table 1), in agreement with the experimental value.

To verify whether the formation of $[\text{BH}_3\cdot\text{OH}]^-$ results from the hydrolysis of undecomposed $\text{Ca}(\text{BH}_4)_2$ in water or indicates the presence of a new intermediate, several control experiments were carried out. First, we investigated the hydrolysis of pure $\text{Ca}(\text{BH}_4)_2$. Since the presence of CaH_2 in the decomposition products of $\text{Ca}(\text{BH}_4)_2$ will produce alkaline solutions when it reacts with water, we dissolved pure $\text{Ca}(\text{BH}_4)_2$ in aqueous solutions with pH values from 7 to 14. As shown in Fig. S2(†ESI), no $[\text{BH}_3\cdot\text{OH}]^-$ was observed in the aqueous solutions of $\text{Ca}(\text{BH}_4)_2$, regardless of pH values of the solution. This behavior

Fig. 3 (a) $^{11}\text{B}\{^1\text{H}\}$ NMR spectra recorded of $\text{Ca}(\text{BH}_4)_2$ (dissolved in D_2O) after decomposition under vacuum at 320°C (6 h), 350°C (6 h) and at 400 °C (0.5 h), respectively. A reference sample of $\text{CaB}_{12}\text{H}_{12}$ shows its resonances at -15.3 ppm. (b) ^1H -coupled ^{11}B NMR spectra of the resonance at -13 ppm in (a), displaying a quartet splitting of $[\text{BH}_3]$ unit ($J_{\text{B-H}}$ of 87 Hz).

Table 1. Absolute magnetic shielding values (ppm) and Chemical Shift (ppm) for different boron complexes calculated at B3LYP/6-311+G(2d,p) level of theory.^{30, 31}

Molecule	Atom	Absolute shielding ($\delta^1\text{B}$ / ppm)	Chemical Shift ($\delta^1\text{B}$ / ppm)	
			Referred to B_2H_6	Referred to $\text{B}(\text{OH})_3$
B_2H_6	B	83.6	-	-
$\text{B}(\text{OH})_3$	B	81.4	-	-
$\text{Ca}(\text{BH}_4)_2$	B1, B2	136.1	-34.5	-35.1 (-30.9 ^[a])
$[\text{B}_2\text{H}_6]^{2-}$	B1, B2	138.5	-36.9	-37.5 (-31.4 ^[b])
$[\text{BH}_3\cdot\text{OH}]^-$	B	114.5	-12.9	-13.5 (-13.0 ^[a])
CaB_2H_6				
Isomer 1	B1, B2	105.0	-3.4	-4.0
Isomer 2	B1, B2	91.7 & 125.5	9.9 & -23.9	9.3 & -24.5

The chemical shift of B_2H_6 is 18 ppm³¹ and that of $\text{B}(\text{OH})_3$ is 19.6 ppm (measured in this work). In brackets we show the experimental value in this work [a] and calculated value at “MP2/6-31G*” level in ref 16 [b].

differs from the alkline metal borohydrides, LiBH_4 and NaBH_4 , which do produce $[\text{BH}_3\cdot\text{OH}]^-$ when reacting with D_2O (Fig. S3, †ESI).

Furthermore, in the alkaline solution (pH = 14) of the partially decomposed $\text{Ca}(\text{BH}_4)_2$ (350°C, vacuum, 6 h), the $[\text{BH}_3\cdot\text{OH}]^-$ species faded with time and converted to $[\text{B}(\text{OH})_4]^-$ (Fig. S4, †ESI). In contrast, no obvious decay of $[\text{BH}_4]^-$ was observed within 20 h. Also, the reaction of CaB_6 with D_2O (pH = 7 to 14) at room temperature does not lead to any formation of $[\text{BH}_3]$ species (Fig. S5, †ESI). Therefore, the $[\text{BH}_3\cdot\text{OH}]^-$ species did not result from the hydrolysis of $\text{Ca}(\text{BH}_4)_2$ or CaB_6 , and must originate from another intermediate formed from the decomposition of $\text{Ca}(\text{BH}_4)_2$. On the other hand, in the partially

Fig. 4 Two possible isomers of CaB_2H_6 cluster.

decomposed $\text{Ca}(\text{BH}_4)_2$ at 400°C (Fig. 2), only traces of $[\text{BH}_3\cdot\text{OH}]^-$ was detected, indicating a different decomposition process. A more detailed study of the decomposition process at 400°C was carried out including the hydrogen back-pressures from 0 to 50 bar (Fig. S6, †ESI). Under these conditions, amorphous boron was found to be the main decomposition product (Fig. S6a, †ESI). Other species including $[\text{BH}_3\cdot\text{OH}]^-$ were found only in traces (Fig. S6b, †ESI).

It is known that diborane splits into two $[\text{BH}_3]$ units in organic solvents (e.g., THF). The $[\text{BH}_3\cdot\text{OH}]^-$ species observed in this study are very likely evidence for the formation of a $[\text{B}_2\text{H}_6]$ compound (i.e., CaB_2H_6), which analogously splits into two $[\text{BH}_3]$ moieties in water. This process can be expressed by the below equation:

The $[\text{B}_2\text{H}_6]^{2-}$ anion is isostructural to the C_2H_6 ethane molecule,³² which has been reported as a ligand in some organometallic compounds.^{33–35} $\text{K}_2\text{B}_2\text{H}_6$ was successfully synthesized in THF solution from the reaction of K_2BH_3 and $[\text{BH}_3]$ units.³⁶ Recently, MgB_2H_6 has also been discussed, while the DFT predictions did not support MgB_2H_6 forming as an intermediate for the decomposition of $\text{Mg}(\text{BH}_4)_2$.^{37–39}

CaB_2H_6 has been predicted to be a stable compound with a monoclinic crystal structure (space group, $C2/c$),³⁹ which shows two arrangements of isomer (Fig. 4). The ^{11}B chemical shift of CaB_2H_6 were calculated (Table 1). Isomer 1 of CaB_2H_6 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 $\text{B}(\text{OH})_3$. The co-existence of these three types of boron atoms would result in a broad ^{11}B resonance. Experimentally, a new broad resonance centered at -14 ppm was observed by ^{11}B MAS NMR in the partially decomposed $\text{Ca}(\text{BH}_4)_2$ at 320 and 350°C (Figs. 1a and b), which was not found when $\text{Ca}(\text{BH}_4)_2$ decomposed at 400 and 450°C (Figs. 1c and d). Since $\text{CaB}_{12}\text{H}_{12}$, with a chemical shift of -15 ppm, was ruled out as a reaction intermediate by solution-state ^{11}B NMR measurement (Fig. 2), this new resonance was reasonably assigned to CaB_2H_6 .

Based on the structures shown in Fig. 4, the IR spectra of CaB_2H_6 isomers were calculated (Fig. S7, †ESI). The internal B-H vibrations of CaB_2H_6 , i.e. stretching modes mainly at 2000 to 2500 cm^{-1} and bending modes at around 1100 cm^{-1} , are close to those of $\text{Ca}(\text{BH}_4)_2$. Accordingly, in the samples of $\text{Ca}(\text{BH}_4)_2$ decomposed at 350°C for 2 to 6 h, we observed broad resonances by FT-IR at around 2200 and 1100 cm^{-1} which are possibly from the combination of $[\text{BH}_4]$ and $[\text{B}_2\text{H}_6]$. Furthermore, vibration

Scheme 1. Temperature-dependent decomposition pathway of $\text{Ca}(\text{BH}_4)_2$.

modes around 600 to 800 cm^{-1} observed by FTIR (Fig. S7, †ESI) are identified with the predicted B-B stretching modes of $[\text{B}_2\text{H}_6]$.

Above all, we identified the formation of CaB_2H_6 as the crucial intermediate step on the way to CaB_6 , which only forms at 320 to 350°C . This selective formation allows controlling decomposition of $\text{Ca}(\text{BH}_4)_2$ by reaction temperature, as shown in Scheme 1. As a result, the decomposition of $\text{Ca}(\text{BH}_4)_2$ at 320 to 350°C circumvents the formation of boron sinks such as amorphous boron, which facilitates 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 $\text{Ca}(\text{BH}_4)_2$ which was reported to melt above 370°C .⁴⁰

To further understand the formation of CaB_2H_6 as an intermediate of $\text{Ca}(\text{BH}_4)_2$ from an energetic viewpoint, we carried out first principles cluster calculations. The geometries of the Ca salts including $\text{Ca}(\text{BH}_4)_2$, CaB_2H_6 , $\text{Ca}(\text{B}_3\text{H}_8)_2$ and $\text{CaB}_{12}\text{H}_{12}$ are shown in Fig. S9 (†ESI). In all these CaB_xH_y salts, there are two different types of H atoms, one being positive while the other being negative. For example, in the gas phase $\text{Ca}(\text{BH}_4)_2$ cluster forms a linear chain with the Ca^{2+} being inserted between two $[\text{BH}_4]^-$ units. One type of H atoms carries a charge of -0.08 and the other $+0.21\text{e}$. It is expected that in $\text{Ca}(\text{BH}_4)_2$, the two oppositely charged H atoms will combine and desorb as a H_2 molecule forming CaB_2H_6 . Furthermore, we found that among all Ca salts, CaB_2H_6 is the most strongly bound salt followed by $\text{Ca}(\text{BH}_4)_2$, $\text{Ca}(\text{B}_3\text{H}_8)_2$ and $\text{CaB}_{12}\text{H}_{12}$ (Table S2, †ESI). This suggests that during the decomposition of $\text{Ca}(\text{BH}_4)_2$, the most preferred intermediate phase is CaB_2H_6 (Table S3, †ESI).

In summary, we reported a simple and efficient route to close the hydrogen sorption cycle for pure $\text{Ca}(\text{BH}_4)_2$ under moderate conditions. Namely, $\text{Ca}(\text{BH}_4)_2$ releases $9.5\text{ wt}\%$ H at 320 to 350°C via decomposition into CaB_6 and CaH_2 without formation of boron sinks such as amorphous boron and $\text{CaB}_{12}\text{H}_{12}$, and rehydrogenation is achieved at the same temperatures and under 130 to 185 bar H_2 . This affirms that $\text{Ca}(\text{BH}_4)_2$ 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 $\text{Ca}(\text{BH}_4)_2$ for practical applications.

Notes and references

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† Electronic Supplementary Information (ESI) available: Methods, optimized Geometries and optimized cartesian coordinates of $[\text{BH}_3\cdot\text{OH}]^-$, ¹¹B NMR spectra of hydrolysis products of $\text{Ca}(\text{BH}_4)_2$, NaBH_4 , LiBH_4 and CaB_6 in aqueous solutions with different pH values, decay of $[\text{BH}_3\cdot\text{OH}]^-$ in alkaline solution, ¹¹B NMR spectra of $\text{Ca}(\text{BH}_4)_2$ decomposed at 400°C under different H_2 external pressures, calculated IR of CaB_2H_6 isomers compared to experimental IR observations, first principles cluster calculations. See DOI: 10.1039/b000000x/

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