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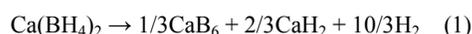
ARTICLE TYPE**A Novel Strategy for Reversible Hydrogen Storage in Ca(BH₄)₂**Yigang Yan,^{ab} Arndt Remhof,^{*ab} Daniel Rentsch,^c Andreas Züttel,^{bd} Santanab Giri^c and Puru Jena^c

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We report that decomposition pathway of Ca(BH₄)₂ can be efficiently controlled by reaction temperature. That is, it decomposes into CaB₆ at a lower temperature range of 320 to 350°C, but into amorphous boron at 400 to 450°C. We identified the formation of CaB₂H₆ as the crucial intermediate step on the way to CaB₆ 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 H₂ for reversible on-board storage. For instance, Ca(BH₄)₂ shows an enthalpy change of 36 ± 4 kJ/mol H₂ in the decomposition reaction into CaB₆ 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 [B₁₂H₁₂]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., AlB₂ and MgB₂) as the final product. For example, using Al or MgH₂ as an additive, the reversibility of LiBH₄ and NaBH₄ was dramatically improved.^{7–10} However, this strategy does not work efficiently for other metal borohydrides such as Ca(BH₄)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 LiBH₄ to 11.4 wt% H for LiBH₄-0.5Al.

A number of studies have been conducted aiming to alter the reaction pathway of Ca(BH₄)₂, including the methods of additive addition,^{13–16} combination with other complex hydrides,^{17–19} nanoconfinement,^{20, 21} application of external H₂ pressure,²² etc. However, all of these methods showed limited effect on avoiding the formation of boron sinks toward full reversibility of Ca(BH₄)₂. The full rehydrogenation to Ca(BH₄)₂ has been considered impossible unless a very high H₂ pressure is applied, i.e. 400 to 700 bar H₂ at 400 to 440°C.^{5, 13, 15, 23–25}

In present study, we identified the formation of CaB₂H₆ as the crucial intermediate step on the way to CaB₆, 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(BH₄)₂ was decomposed in CaB₆ and CaH₂, which facilitate the reversibly absorption of hydrogen under much mild conditions. This study provides new insights into the decomposition mechanism of Ca(BH₄)₂ as well as instructions for further development of Ca(BH₄)₂ as a hydrogen storage material.

The decomposition of Ca(BH₄)₂ was carried out at 320 to 450°C under dynamic vacuum. The ¹¹B 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(BH₄)₂ at –31.0 ppm, an intermediate centered at –14 ppm and newly formed CaB₆ 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 ¹¹B-¹H CP-MAS NMR spectrum. Only the resonance assigned to CaB₆ was observed, indicating the full decomposition of Ca(BH₄)₂ into CaB₆ and CaH₂. Also, approximately 9.3 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 ¹¹B MAS NMR spectra (Figs. 1c and d). These observations indicate an obvious temperature dependence of the decomposition pathway of Ca(BH₄)₂.

Due to the decomposition into CaB₆ at 350°C (20 h), the reversibility of Ca(BH₄)₂ was achieved under relatively moderate conditions (300 to 350 °C, 130 to 185 bar H₂). At 300 °C, Ca(BH₄)₂ was partially recovered, as observed by ¹¹B MAS NMR (Fig. 2). Above 90% of boron was transformed back to Ca(BH₄)₂ at 350 °C and 185 bar H₂. 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(BH₄)₂ was very limited at 350 °C and 185 bar H₂, i.e., approximately 33% of boron can be converted back to Ca(BH₄)₂ (Fig. S2, †ESI). These results support the strategy of improving the reversibility by controlling the decomposition pathway.

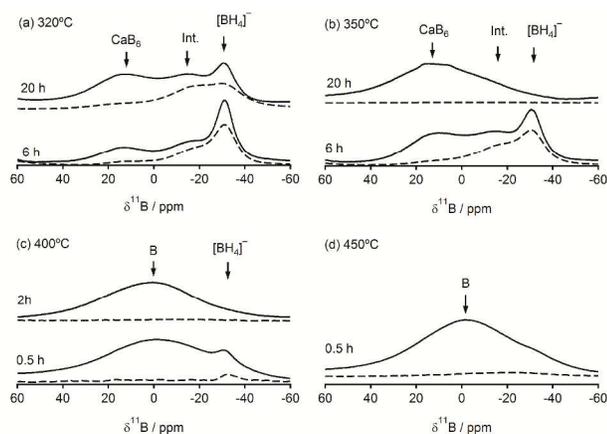


Fig. 1 ^{11}B MAS NMR spectra of $\text{Ca}(\text{BH}_4)_2$ after H_2 desorption under vacuum at 320 to 450°C. In (a) and (b), the resonance centered at -14 ppm indicates the formation of an intermediate (labelled Int.). Dashed lines represent the ^{11}B CP-MAS NMR spectra.

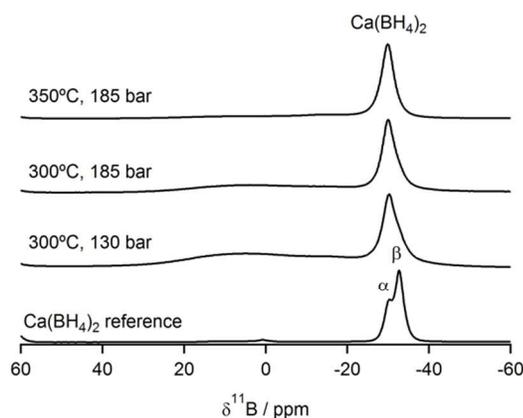


Fig. 2 ^{11}B MAS NMR spectra of the rehydrogenated $\text{Ca}(\text{BH}_4)_2$ at 300 to 350°C under 130 to 185 bar H_2 , referred to the pure $\text{Ca}(\text{BH}_4)_2$. Before rehydrogenation, $\text{Ca}(\text{BH}_4)_2$ was dehydrogenated at 350 °C for 20 h.

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 $\text{CaB}_{12}\text{H}_{12}$ (-15.6 ppm). Thereby this intermediate was tentatively assigned to $\text{CaB}_{12}\text{H}_{12}$ in the previous study.^{22, 26} $\text{CaB}_{12}\text{H}_{12}$ was reported to be a highly stable compound. The self-decomposition of $\text{CaB}_{12}\text{H}_{12}$ or the reaction between $\text{CaB}_{12}\text{H}_{12}$ and CaH_2 requires high temperature such as 600°C.²⁷ Since $\text{Ca}(\text{BH}_4)_2$ could be fully decomposed into CaB_6 at 350°C (Fig. 1b), the resonance at -14 ppm should be assigned to another intermediate such as CaB_2H_x ($2 \leq x \leq 6$) which was proposed based on X-ray diffraction (XRD) results.²⁸ Accordingly, CaB_2H_x were observed by XRD in $\text{Ca}(\text{BH}_4)_2$ 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 $\text{Ca}(\text{BH}_4)_2$, samples of $\text{Ca}(\text{BH}_4)_2$ partially decomposed at 320 to 400°C were dissolved in D_2O and measured by solution-state ^{11}B NMR (Fig. 3). In all the samples investigated, no $[\text{B}_{12}\text{H}_{12}]^{2-}$ species were

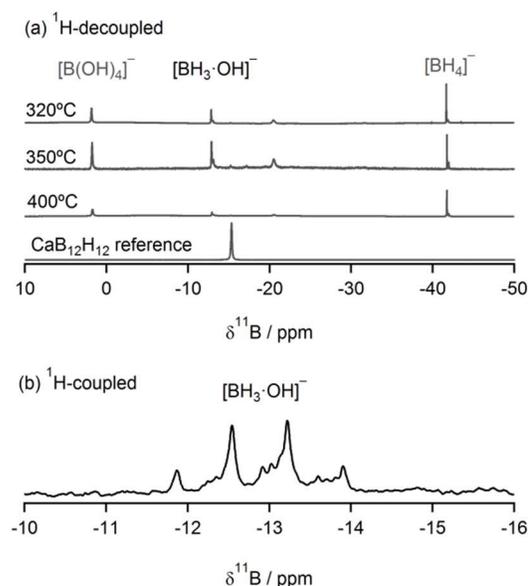


Fig. 3 (a) $^{11}\text{B}\{^1\text{H}\}$ NMR spectra recorded of $\text{Ca}(\text{BH}_4)_2$ (dissolved in D_2O) after decomposition under vacuum at 320°C (6 h), 350°C (6 h) and at 400 °C (0.5 h), respectively. A reference sample of $\text{CaB}_{12}\text{H}_{12}$ shows its resonances at -15.3 ppm. (b) ^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.^{29, 30}

Molecule	Atom	Absolute shielding ($\delta^{11}\text{B}$ / ppm)	Chemical Shift ($\delta^{11}\text{B}$ / 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 ppm³⁰ 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].

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.³¹ The structure of $[\text{BH}_3\cdot\text{OH}]^-$ is shown in Fig. S4(†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

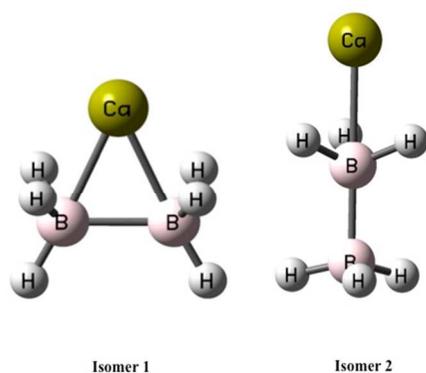
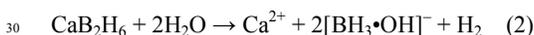


Fig. 4 Two possible isomers of CaB_2H_6 cluster.

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. S5 (†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 differs from the alkaline metal borohydrides, LiBH_4 and NaBH_4 , which do produce $[\text{BH}_3\cdot\text{OH}]^-$ when reacting with D_2O (Fig. S6, †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. S7, †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. S8, †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 an intermediate as observed by ^{11}B MAS NMR (Figs. 1a and 1b) at the chemical shift of -14 ppm.

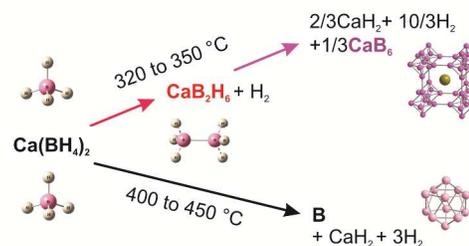
It is known that diborane splits into two $[\text{BH}_3]$ units in organic solvents (e.g., THF). The $[\text{BH}_3\cdot\text{OH}]^-$ species observed in this study are very likely the evidence for the formation of a $[\text{B}_2\text{H}_6]$ compound (i.e., CaB_2H_6), which analogously splits into two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



The formation of CaB_2H_6 as a reaction intermediate is supported by theoretical calculations. That is, within the compounds CaB_2H_x ($2 \leq x \leq 6$), the formation of CaB_2H_6 follows the lowest-energy decomposition pathway.³²

In the previous study, the intermediate CaB_2H_x was assigned to the resonance at around -31 ppm in the solid-state ^{11}B NMR spectra, the same chemical shift to $\text{Ca}(\text{BH}_4)_2$.^{16, 26} However, the first principles cluster calculations predicted that electrons redistribution occur when $\text{Ca}(\text{BH}_4)_2$ converts to CaB_2H_6 (Fig. S10, †ESI). In another word, the chemical environment of boron atoms will change and ^{11}B chemical shift should be different between $\text{Ca}(\text{BH}_4)_2$ and CaB_2H_6 . The ^{11}B chemical shift of $\text{Ca}(\text{BH}_4)_2$ and CaB_2H_6 were calculated (Table 1) based on the cluster structures. The calculated ^{11}B chemical shift of $\text{Ca}(\text{BH}_4)_2$ is -35.1 ppm referred to $\text{B}(\text{OH})_3$, which is close to the experimental values, i.e., -30 and -33 ppm for α and β - $\text{Ca}(\text{BH}_4)_2$, respectively (Fig. 2).

The structure CaB_2H_6 has been predicted to be monoclinic (space group, $C2/c$),³² which shows two arrangements of isomer (Fig. 4). Isomer 1 of CaB_2H_6 contains one type of boron atom



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

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 $\text{B}(\text{OH})_3$. Either of the two arrangements will show a distinct downfield ^{11}B resonance relative to $\text{Ca}(\text{BH}_4)_2$. 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 $\text{Ca}(\text{BH}_4)_2$ and CaB_6 , respectively. The resonance at -14 ppm was reasonably assigned to CaB_2H_6 . The broad feature of the ^{11}B resonance of CaB_2H_6 is owing to the co-existence of these three types of boron atoms.

Above all, we identified CaB_2H_6 as the reaction intermediate and ruled out the formation of $\text{CaB}_{12}\text{H}_{12}$ during the decomposition of $\text{Ca}(\text{BH}_4)_2$ at 320 to 450°C under vacuum. The appearance of CaB_2H_6 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_2H_6 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, 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 $\text{Ca}(\text{BH}_4)_2$ which was reported to melt above 370°C.³³

The $[\text{B}_2\text{H}_6]^{2-}$ anion is isostructural to the C_2H_6 ethane molecule,³⁴ which has been reported as a ligand in some organometallic compounds.³⁵⁻³⁷ Other $[\text{B}_2\text{H}_6]^{2-}$ containing compound such as $\text{K}_2\text{B}_2\text{H}_6$ has been successfully synthesized in THF solution from the reaction of K_2BH_3 and $[\text{BH}_3]$ units.³⁸ MgB_2H_6 has also been discussed,^{36, 37} while the DFT predictions did not support MgB_2H_6 forming as an intermediate for the decomposition of $\text{Mg}(\text{BH}_4)_2$.^{39, 40} On the other hand, octahydroborate, $[\text{B}_3\text{H}_8]^-$ containing compound, has been identified as the intermediate for $\text{Mg}(\text{BH}_4)_2$ and $\text{Y}(\text{BH}_4)_3$.^{41, 42}

Why CaB_2H_6 rather than $\text{Ca}(\text{B}_3\text{H}_8)_2$ and $\text{CaB}_{12}\text{H}_{12}$ forms as the intermediate for $\text{Ca}(\text{BH}_4)_2$ were further investigated by our 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. S10 (†ESI). 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 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, H_2 desorption profiles of $\text{Ca}(\text{BH}_4)_2$ in first two cycles, ^{11}B MAS NMR spectrum of rehydrogenated $\text{Ca}(\text{BH}_4)_2$ (350°C under 185 bar H_2) after desorption at 450°C , XRD of $\text{Ca}(\text{BH}_4)_2$ after partial decomposition under vacuum at 320 to 400°C , optimized Geometries and optimized cartesian coordinates of $[\text{BH}_3\cdot\text{OH}]^-$, ^{11}B 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, 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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