Effects of Ball Milling and TiF$_3$ Addition on the Dehydrogenation Temperature of Ca(BH$_4$)$_2$ Polymorphs

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Received: 19 August 2020; Accepted: 10 September 2020; Published: 15 September 2020

Abstract: The changes introduced by both ball milling and the addition of small amounts of TiF$_3$ in the kinetics of the hydrogen desorption of three different Ca(BH$_4$)$_2$ polymorphs ($\alpha$, $\beta$ and $\gamma$) have been systematically investigated. The samples with different polymorphic contents, before and after the addition of TiF$_3$, were characterized by powder X-ray diffraction and vibrational spectroscopy. The hydrogen desorption reaction pathways were monitored by differential scanning calorimetry. The hydrogen desorption of Ca(BH$_4$)$_2$ depends strongly on the amount of coexistent $\alpha$, $\beta$ and $\gamma$ polymorphs as well as additional ball milling and added TiF$_3$ to the sample. The addition of TiF$_3$ increased the hydrogen desorption rate without significant dissociation of the fluoride. The combination of an $\alpha$-Ca(BH$_4$)$_2$ rich sample with 10 mol% of TiF$_3$ and 8 h of milling led to up to 27 °C decrease of the hydrogen desorption peak temperature.

Keywords: calcium borohydride; hydrogen storage; powder X-ray diffraction; ball milling; additives; kinetics of the hydrogen desorption; polymorphs; vibrational spectroscopy; reaction pathways; differential scanning calorimetry

1. Introduction

The alkali earth metal calcium borohydride, Ca(BH$_4$)$_2$, possesses 11.6 wt.% gravimetric and 130 kgm$^{-3}$ volumetric hydrogen densities, respectively, and therefore it is often considered an attractive hydrogen storage system either alone or in composites [1–7]. Moreover, its calculated low reaction enthalpy, 32 kJmol$^{-1}$H$_2$ for equation

$$3\text{Ca} (\text{BH}_4)_2 \rightarrow \text{CaB}_6 + 2\text{CaH}_2 + 10\text{H}_2,$$

that leads to a 9.6 wt.% H$_2$ yield [8–12] and its possible reversibility at moderate conditions [2,13–16], make Ca(BH$_4$)$_2$ a particularly attractive hydrogen storage candidate.

However, this is a complicated borohydride to control. There are four known polymorphs of Ca(BH$_4$)$_2$. Three of them are referred to as low-temperature phases, $\alpha$, $\alpha'$, and $\gamma$-Ca(BH$_4$)$_2$, while only one high-temperature modification, $\beta$-Ca(BH$_4$)$_2$, has been identified [1,10,17].
Their crystal structures have been assigned to orthorhombic space groups in the cases of \( \alpha \) - \((F\overline{dd} [8,18])\) or \( F\overline{2}d\) \([17]\) and \( \gamma \)-Ca(BH\(_4\))\(_2\) \((Pbc\alpha [18])\), and to tetragonal space groups for \( \alpha' \) - \((I-42d [17])\) and \( \beta \)-Ca(BH\(_4\))\(_2\) \((P4_2/m [19]\) or \( P-4 [17]\)\). Most transitions between the polymorphs are of first-order \([20]\), with the \( \alpha' \)-\( \alpha \) transition being of second order \([17]\). Because of the small enthalpy differences between the various polymorphs \( \Delta H(\alpha-\beta) = 13.03 \text{ kJmol}^{-1}\text{H}_2\), \( \Delta H(\alpha-\gamma) = 6.08 \text{ kJmol}^{-1}\text{H}_2\) \([19]\); or \( \Delta H(\alpha-\beta) = 8.59 \text{ kJmol}^{-1}\text{H}_2\), \( \Delta H(\alpha-\gamma) = 3.38 \text{ kJmol}^{-1}\text{H}_2\) \([20]\)), it is common that they appear mixed in different ratios in batches produced by the same synthesis method. This fact complicates the characterization of the thermodynamics and kinetics of Ca(BH\(_4\))\(_2\) and the future reproducibility for practical applications \([1]\).

The complete dehydrogenation of Ca(BH\(_4\))\(_2\) takes place between room temperature (RT) and 600 °C \([1,10,21]\). The process leads to three main endothermic events that can be assigned to the reversible \( \alpha \) to \( \beta \), low-temperature-to-high-temperature polymorphic transformation (between 160 and 250 °C), the decomposition of the high- temperature polymorph \( \beta \) (above 350 °C), and the decomposition of intermediates formed from metastable phases (CaB\(_2\)H\(_4\)) has been proposed \([22]\). The temperatures at which these events occur depend strongly on experimental conditions such as type of gas flow, heating rate, et cetera, but also on the partial content of the different Ca(BH\(_4\))\(_2\) polymorphs in the sample \([1]\). In particular, our previous detailed study of the role of Ca(BH\(_4\))\(_2\) polymorphs showed increases of the decomposition temperature of up to 15 °C in samples containing \( \gamma \)-Ca(BH\(_4\))\(_2\) compared to a purer \( \alpha \)-Ca(BH\(_4\))\(_2\), and of about 6 °C lower decomposition temperatures for a pure \( \beta \)-Ca(BH\(_4\))\(_2\) sample synthesized by a solvent free method compared to the high-temperature \( \beta \) modification obtained via the polymorphic transformation of \( \alpha \)-Ca(BH\(_4\))\(_2\). The polymorphic content was also found to affect the amount of hydrogen released in each of the decomposition steps, with an increase of the mass loss for samples containing more of the \( \alpha \)-Ca(BH\(_4\))\(_2\) polymorph \([1]\). These results confirm that the pure Ca(BH\(_4\))\(_2\) polymorphs have different kinetic barriers and that the polymorphic content of a sample determines the decomposition kinetics \([1]\).

On the other hand, it is known that the decomposition temperature of Ca(BH\(_4\))\(_2\) is decreased both by ball milling and by the addition of additives in small amounts \([2,15,21]\). Recently, similar effects have been observed in other light metal borohydrides such as NaBH\(_4\) \([23–26]\) and Mg(BH\(_4\))\(_2\) \([27–29]\), and on reactive composites like the Ca(BH\(_4\))\(_2\)-MgH\(_2\) system \([6]\). Moreover, fluoride additives such as TiF\(_3\) and NbF\(_5\) not only have shown that the reversibility of Ca(BH\(_4\))\(_2\) is possible under moderate conditions (140 bar and near RT), but also that they significantly decrease the decomposition temperature of the borohydride when compared to chlorides \([14,15,27,30]\). However, the mechanisms by which the improvement happens are not yet known.

Based on these previous works, we present here a study on the effects on the dehydrogenation temperature of the three most common polymorphs of Ca(BH\(_4\))\(_2\), \( \alpha \), \( \beta \) and \( \gamma \), by both ball milling and the addition of small amounts of TiF\(_3\).

2. Results and Discussion

2.1. Milling Effects on As-Received Ca(BH\(_4\))\(_2\)

Before analyzing the influence of TiF\(_3\) on the decomposition properties of Ca(BH\(_4\))\(_2\) polymorphs, the effects of ball milling on the as-received \( \alpha, \beta \), and \( \gamma \)-Ca(BH\(_4\))\(_2\) were studied (Table 1 and Figure 1). Due to the lack of enough original material these milling experiments were not performed on pure \( \beta \)-Ca(BH\(_4\))\(_2\).
In addition to the broadening of the diffraction peaks seen for all the milled samples when compared to the as-received material, the PXD analysis (top of Figure 1) also shows an increase of the $\beta$-Ca(BH$_4$)$_2$ content with increased milling time in the case of the $\alpha \beta \gamma$ sample. This indicates that the temperatures achieved in the vials during the milling process are enough to induce a phase transformation from the low temperature $\alpha$- to the high temperature $\beta$-Ca(BH$_4$)$_2$. The transition temperature is about 167 °C under a helium gas flow and with a heating rate of 5 °C/min [1]. This behavior is in agreement with the fact that $\beta$-Ca(BH$_4$)$_2$ becomes more stable compared to $\alpha$-Ca(BH$_4$)$_2$ with increasing temperature [19]. The Differential scanning calorimetry (DSC) curves (bottom of Figure 1) show a small decrease of the decomposition temperature of the samples with milling time, from approximately the 357 °C of the 1 h milled sample to the 353 °C of the 8 h sample, and thus indicates that the $\beta$-Ca(BH$_4$)$_2$ formed during milling is less stable that the same phase formed during heating. This could be related to smaller crystallites in the milling case. No big changes in the polymorphic ratio with milling time are observed in the PXD patterns of the $\gamma$ sample (Figure 1b), leading to no shift of the decomposition temperatures in the DSC curves (Figure 1d). The lack of change in this case agrees with the gradual and broad temperature range in which the $\gamma$ to $\beta$ transformation occurs [31] and the fact that $\gamma$-Ca(BH$_4$)$_2$ is metastable in the whole temperature range below the
decomposition temperature of the high temperature β polymorph [19]. Thus, it seems that under the ball milling conditions used in this work, the γ to β transformation is less probable than the α to β transformation. The behavior is reproducible and indicates that not only the as-received Ca(BH$_4$)$_2$ polymorphs have different decomposition temperatures [1], but that ball milling effects also depend on the polymorphic composition of the samples.

2.2. Milling Effects on Ca(BH$_4$)$_2$ with TiF$_3$

PXD patterns of the samples containing 1.6 and 10 mol% of TiF$_3$ show that no new species are formed during the milling with Ca(BH$_4$)$_2$ (Figure 2). In particular, no cation or anion substitutions, such as those found for NaBH$_4$ [24], are observed. In all the cases, Ca(BH$_4$)$_2$ and TiF$_3$ in the crystalline form are still present in the milled material. The broadening of the Bragg peaks and the loss of signal to noise ratio of the measurements are an indication of the finer crystallite size introduced by ball milling.

![Figure 2](image)

Figure 2. PXD results on ball milled α$_{β4}$ (up, (a,b)) and γ (middle, (c,d)) with 1.6 mol% (left-hand side, (a,c)) and 10 mol% (right-hand side, (b,d)) of TiF$_3$. Bottom: PXD results on ball milled β$_{64}$ (left-hand side, (e)) and β$_{92}$ (right-hand side, (f)) with 10 mol% of TiF$_3$. Samples were taken from the vials after 1, 2, 4 and 8 h milling. The pattern of the as-received sample is included for comparison.
The PXD results are confirmed by IR spectroscopy (Figures 3 and 4), where the only differences between the as-received and the samples with TiF$_3$ are observed in the 400–1000 cm$^{-1}$ range. In particular, the samples with additive show a prominent feature at approximately 554 cm$^{-1}$, which increases with additive amount.

![Figure 3](image3.png)

**Figure 3.** Infrared (IR) spectra for $\alpha_{\beta\gamma}$-Ca(BH$_4$)$_2$ samples with additive. External modes corresponding to lattice vibrations in TiF$_3$ are marked with a red box. The spectrum of a sample prepared by milling $\alpha_{\beta\gamma}$ + 50 mol% TiF$_3$ is also included.

![Figure 4](image4.png)

**Figure 4.** IR spectra for as-received (upper panel) and $\alpha_{\beta\gamma}$, $\beta_{92}$ and $\gamma$ with 10 mol% of TiF$_3$. External modes corresponding to lattice vibrations in TiF$_3$ are marked with a red box.

According to symmetry selection rules, the two IR active vibrational modes in borohydrides are the $\nu$BH stretching and $\delta$HBH bending modes at 2200–2300 cm$^{-1}$ and 1100 cm$^{-1}$, respectively. Other bands corresponding to overtones and combinations are also seen experimentally [1]. Below 1000 cm$^{-1}$, external and librational modes between BH$_4^-$ and Ca$^{2+}$ can be distinguished in the IR spectra [1].

The addition of TiF$_3$ changes the decomposition behavior of the samples after milling compared to the as-received materials. Thus, while $\alpha$-Ca(BH$_4$)$_2$ + 1.6 mol% TiF$_3$ (Figure 2a) transforms into
**Activation Energies**

Sample α, containing 98% of the α-Ca(BH₄)₂ polymorph (Table 1), was ball milled for 8 h without stop, with and without 10 mol% TiF₃. The milling products were separated in smaller samples and then heated at different heating rates in order to calculate their activation energies from a generalization of the Kissinger equation [33]:

\[
\ln(\beta / T_{\text{max}}^2) = -E_a / RT_{\text{max}},
\]

where \( \beta \) is the heating rate and \( T_{\text{max}} \) is the temperature of the endothermic peak at its maximum; \( R \) is the gas constant and \( E_a \) is the activation energy. Activation energies calculated from the graphical representation of this equation lead to values of 199 ± 3 and 204 ± 1 kJmol⁻¹ for the samples with additive and without additive, respectively (Figure 8). The small difference indicates some success by TiF₃ to destabilize Ca(BH₄)₂, in agreement with the observed decomposition behavior.
Figure 5. Corresponding DSC curves of ball milled αβγ (top, (a,b)) and γ (middle, (c,d)), with 1.6 mol% (left-hand side, (a,c)) and 10 mol% (right-hand side, (b,d)) of TiF₃, respectively. Bottom: Corresponding DSC curves of the ball milled β₆₄ (left-hand side, (e)) and β₉₂ (right-hand side, (f)) with 10 mol% of TiF₃. Only the main decomposition region between 330 and 380 °C is shown. Measurements were done under dynamic conditions in protective Ar flow, with 2 °C/min heating rates. The curves have been shifted to show the peak trend.
Figure 6. Position of the decomposition peaks as observed by DSC. The lowest decomposition temperature corresponds to $\alpha + 10\text{ mol}\% \text{ TiF}_3$ milled for 8 h and is marked by a red circle. 0 h means the sample was measured as-received.

Figure 7. PXD (left-hand panel, (a)) and DSC (right-hand panel, (b)) results of ball milled $\alpha$ with 10, 20 and 50 mol% of TiF$_3$ after 8 h continuous milling. The results for the as-received material are included for comparison.
Figure 8. Kissinger plot corresponding to as-received \( \alpha \) and \( \alpha + 10 \) mol\% TiF\(_3\) milled for 8 h.

3. Materials and Methods

The present study was performed on Ca(BH\(_4\))\(_2\) samples containing different amounts of the \( \alpha \), \( \beta \), and \( \gamma \) polymorphs (Table 1). All polymorphs were crystalline and stable at room temperature (RT). Samples \( \alpha_{\beta\gamma} \) and \( \alpha \) were prepared from commercial Ca(BH\(_4\))\(_2\).2THF by heating in vacuum up to 160 °C for 1 h, while \( \gamma \) was synthesized by wet chemistry of CaH\(_2\) + 2Et\(_3\)N.BH\(_3\). The \( \beta_{64} \) and \( \beta_{92} \) samples containing 64 and 92 mol\% of \( \beta \) phase, respectively, were synthesized by a solvent-free method based on the reaction of metal hydrides with diborane and subsequent ball milling. The details of the synthesis methods are described elsewhere [8,34–36]. Sample handling was carried out in MBraun Unilab glove boxes filled with purified argon (<1 ppm O\(_2\), H\(_2\)O) and transportable glove bags filled with Ar.

Milling with and without additive was carried out in Ar using a Fritsch Pulverisette 7 (P7) planetary mill at 505 rpm. Steel balls 10 mm in diameter and tempered steel vials were used. Small amounts of milled material were extracted from the vials after 1, 2, 4, and 8 h, always keeping the ball-to-powder ratio constant to 50:1. TiF\(_3\) powder (Aldrich, 99%) was added to the different polymorphs in 1.6, 5, 10, 20 and 50 mol\% amounts (Table 2). Tests with 5 mol\% of ScH\(_2\) and AlF\(_3\) showed little effect on the decomposition temperature of Ca(BH\(_4\))\(_2\) and are not discussed here. As shown by Llamas et al. [24], stoichiometric mixtures may lead to new compounds that alter the decomposition path (thermodynamics) of a borohydride. In this study, only kinetic effects were investigated.

Table 1. Sample list. Phase fractions were obtained from PXD patterns using F2dd [17], Pbcn [18] and P-4 [17] for \( \alpha \), \( \gamma \) and \( \beta \)-Ca(BH\(_4\))\(_2\), respectively. Other phases, except for CaH\(_2\) and FeNi\(_3\) in \( \beta_{92} \), where not taken into account.

| Sample Name | Highest Content Polymorph | Phase Fraction \( \alpha / \beta / \gamma \) (mol\%) | Synthesis Method |
|-------------|---------------------------|--------------------------------------------------|------------------|
| \( \alpha_{\beta\gamma} \) | \( \alpha \) | 67/23/10 | from Ca(BH\(_4\))\(_2\).2THF \( \text{a} \) |
| \( \alpha \) | \( \alpha \) | 98/–/2 | from Ca(BH\(_4\))\(_2\).2THF \( \text{a} \) |
| \( \gamma \) | \( \gamma \) | 8/–/92 | from CaH\(_2\) + 2Et\(_3\)N.BH\(_3\) \( \text{b} \) |
| \( \beta_{64} \) | \( \beta \) | \( \sim 64/–/– \text{d} \) | reactive milling in B\(_2\)H\(_6\) \( \text{c} \) |
| \( \beta_{92} \) | \( \beta \) | \( \sim 92/–/– \text{d} \) | reactive milling in B\(_2\)H\(_6\) \( \text{c} \) |

\( \text{a} \) Reference [8,34]; \( \text{b} \) Reference [35]; \( \text{c} \) Reference [36]; \( \text{d} \) also containing Ca\(_3\)(BH\(_4\))\(_3\)(BO\(_3\)).
Table 2. Sample preparation conditions.

| Sample Name | Highest Content Polymorph | Milling Time / h | TiF<sub>3</sub> Content / mol% |
|-------------|---------------------------|------------------|-------------------------------|
| α<sub>β,γ</sub> | α | 1, 2, 4, 8 | 0, 1.6, 5, 10 |
| α | α | 8, 24 | 10, 20, 50 |
| γ | γ | 1, 2, 4, 8 | 0, 1.6, 5, 10 |
| β<sub>64</sub> | β | 1, 2, 4, 8 | 10 |
| β<sub>92</sub> | β | 1, 2, 4, 8 | 10 |

Powder X-ray diffraction (PXD) patterns were collected in transmission mode using CuKα radiation (\(\lambda = 1.5418 \text{ Å}\)) in a Bruker AXS D8 Advance Diffractometer equipped with a Göbbel mirror and a LynxEye\textsuperscript{TM} 1D strip detector. Diffraction patterns were obtained at RT in rotating boron containing glass capillaries (0.8 mm φ) filled and sealed under Ar atmosphere. Data acquisition was restricted to 2θ = 5 – 80°, with Δ2θ = 0.02° and 2 s/step scanning rates. The phase fraction of the different samples was obtained from the PXD patterns using GSAS \[37\].

Differential scanning calorimetry (DSC) was carried out between RT and 500 °C in Al crucibles with pierced lid using a Setaram Sensys DSC. Additional DSC measurements were carried out in a STA449F3 Jupiter from NETZSCH using corundum (\(\text{Al}_2\text{O}_3\)) crucibles and pierced lids. In both cases measurements were done under dynamic conditions in protective Ar flow with 2 °C/min heating rates. Additional heating rates of 5 and 10 °C/min were used in the STA449F3 Jupiter to determine sample activation energies. Approximately 30 mg of fresh material was used in every case.

Infrared (IR) spectroscopy was carried out in a Bruker IFS 66v spectrometer with a DTGS detector. The samples were embedded in KBr pellets (7 mm φ), with a 0.5% mass concentration. The transmission spectra of the KBr pellets were recorded in the 400–8000 cm\(^{-1}\) region, with a 4 cm\(^{-1}\) resolution. Scattering contribution to the spectra due to the pellets was considered to be negligible at these wavenumbers. Mass absorption coefficients (κ) were calculated from the transmission (T) data as:

\[
κ = -ln(T/A/m),
\]

where \(A\) is the area of the pellet in cm\(^2\), and \(m\) is the mass of the absorbing sample in g \[38\]. The spectroscopic curves were further normalized to the strongest peak in both the bending and the stretching regions to allow a better visualization of the peak shifts introduced by the different samples. Peak analysis was carried out in Origin 7.5 using Gaussian curves.

4. Conclusions

The hydrogen desorption peak temperature of Ca(BH\(_4\))\(_2\) depends strongly on the composition of the coexistent α, β and γ polymorphs, which is determined by the synthesis method. Additional ball milling affects the kinetics of the material and leads to a lowering of the peak temperature, which is more pronounced by increasing the content of the α polymorph in the sample. The kinetic effect is further decreased by the addition of TiF\(_3\) to the sample, that is, TiF\(_3\) increases the hydrogen desorption rate. The improved kinetics by the addition of TiF\(_3\) was observed without significant dissociation of TiF\(_3\) and, therefore, must be related to the reduction of all the crystallite sizes (including those of TiF\(_3\)) due to the ball milling process.

Author Contributions: Conceptualization and methodology for this article as well as experimental investigation, validation, formal analysis, data curation, project administration, provision of materials, supervision, visualization and writing of original draft was carried out by I.L.J., O.F., M.F. and E.G.B. provided samples, while A.Z. and B.C.H. reviewed the original manuscript. Overall resources and funding acquisition by B.C.H. All authors have read and agreed to the published version of the manuscript.

Funding: Financial support from the Research Council of Norway, the FLYHY project (contract no. 226943) and the ERA-NET project Hy-CO (grant#0327791) under the FP7 Program in the European Commission are also gratefully acknowledged.
Acknowledgments: The authors acknowledge the contributions of Claus Nielsen at the Chemistry Department of the University of Oslo for IR spectroscopy and the project team at the SNBL Beam Line, ESRF, Grenoble.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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