Effect of additives on the synthesis and reversibility of Ca(BH₄)₂

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Metal borohydrides are potential materials for solid-state hydrogen due to their high gravimetric and volumetric hydrogen densities. Among them, Ca(BH₄)₂ is particularly interesting because of the predicted suitable thermodynamic properties. In this work, we investigate a new synthesis route using high-pressure reactive ball milling. Starting from CaH₂ and CaB₆, with a TiCl₃ or TiF₃ as additive, a reaction yield of 19% is obtained after 24 h milling at room temperature and 140 bar H₂. The presence of Ca(BH₄)₂ is confirmed by the presence of the stretching mode of the [BH₄]⁻ group in the infrared spectra of the as-milled samples. Using in situ XRD, we observe the recrystallisation of a poorly crystallised Ca(BH₄)₂ phase present after milling. The reversible decomposition/formation of Ca(BH₄)₂ is obtained with higher yield (57%) using higher temperature and TiF₃ as additive but not with TiCl₃ despite its similar electronic structure. The differences observed using different additives and the influence of the anion are discussed.

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1. Introduction

Hydrogen as energy carrier, combined with fuel cells or for direct combustion, is one solution for the future energy challenge of our society [1]. In order to build a “hydrogen economy”, safe and reliable storage is needed. Solid-state storage in hydrides appears to be a valuable alternative, in particular for mobile applications [1].

Metal borohydrides M(BH₄)ₓ, with M a light cation, are of particular interest. For example, LiBH₄ contains 18.4 wt% of hydrogen but its thermodynamic properties do not enable the release of hydrogen at temperatures required for application (100–150 °C) [2]. More suitable performances can be achieved with Ca(BH₄)₂, hydrogen content 11.6 wt%, because of significantly lower predicted enthalpy of reaction. Miwa et al. [3] have proposed Eq. (1) as the decomposition reaction and calculated an enthalpy of reaction of 32 kJ mol⁻¹ H₂.

3Ca(BH₄)₂ ⇌ 2CaH₂ + CaB₆ + 10H₂ (1)

The total hydrogen release for this reaction is theoretically 9.6 wt%. Later, Siegel et al. [4] have reported a value of 41.4 kJ mol⁻¹ H₂ for the enthalpy of reaction (1) based on first principle calculations. The values reported for the enthalpy of reaction are similar and lie in the range of interest for hydrogen storage applications.

The lower decomposition temperature of Ca(BH₄)₂ compared to LiBH₄ has also been predicted by Nakamori et al. [5], as shown in their plot of the decomposition temperature vs. the electronegativity of the different cations.

Different polymorphs of Ca(BH₄)₂ are observed depending on the synthesis method or heat treatment. The first calculated structure of Ca(BH₄)₂, which is observed experimentally at room temperature, is an orthorhombic Pmmm structure [3,6,7] and is called α phase. Another space group P2₁2₁2₁ has been proposed for the α phase more recently [8,9] based on synchrotron analysis. This structure fits better the overall diffraction pattern of the pure α phase but the main diffraction peaks are the same as previously reported. Another polymorph named β-Ca(BH₄)₂ is also observed with a tetragonal P42/m structure [7,10,11]. This phase is obtained at room temperature [12] but is also formed by transformation of the α phase upon heating [13]. For this β phase also, a different space group P-4 has been reported [8,14]. Again, the main diffraction peaks are similar to the previous structure and only minor diffraction peaks differ. Additional polymorphs α', γ and δ (high-temperature phase) have been proposed/observed in the last years by different groups [8,11–14] and can be obtained depending on the synthesis method.

The overall decomposition reaction described in Eq. (1) has been confirmed by recent works [15,16]. The reaction is more complex than described by Eq. (1) and proceeds in two steps as observed for other borohydrides. It has been reported that the first step of decomposition leads to the formation of CaH₂ and an intermediate phase and the second to the decomposition of the intermediate compound into CaH₂ and CaB₆ (or “amorphous” B) [15,17,18]. The
exact nature of this intermediate phase is not known yet. Riktor et al. [19] have proposed a CaB₂H₄ compound as intermediate, however, the appearance of this phase has been found to depend on the heating treatment and analysis techniques. The use of TiF₃, TiCl₃, NbF₅ or NbC₅ leads to a decrease of the decomposition temperature [20,21], however, the same decrease of temperature is obtained by ball milling Ca(BH₄)₂ only. Nevertheless, the use of appropriate additives is necessary to facilitate the re-absorption reaction. Best results have been obtained using NbF₅: 5 wt% H₂ (50–60% reaction yield) is absorbed with the highest rate under 90 bar H₂ and 350 °C for 24 h [21]. The better kinetics obtained may be related to the low melting point of NbF₅ (77 °C), implying its melting during milling, that allows a better dispersion in Ca(BH₄)₂ during milling because of the liquid state. The formation of CaH₂·Fx phases during decomposition may also play a role in the enhancement of the sorption properties.

One of the first methods used is a metathesis reaction [22] from LiBH₄ (or NaBH₄) and CaCl₂. Nevertheless, LiCl is formed as a by-product and should be separated from the borohydride in a second step. Another method is by wet chemical synthesis but this necessitates the use of large quantity of solvent, which has to be removed in additional purification steps [23]. Rönnbøe and Majzoub [16] have demonstrated the possibility to synthesise Ca(BH₄)₂ by hydrogénation of CaH₂ and CaB₆. They have used conditions at 700 bar H₂ and 440 °C for 48 h. The reaction proceeds only when adding a mixture of TiCl₃ and Pd; with 8 wt% of these additives, the reaction yields 60% of Ca(BH₄)₂.

In this study, we show that the synthesis of Ca(BH₄)₂ is possible by reactive ball milling of CaH₂ and CaB₆ under mild conditions. The mechano-chemical synthesis method has already been successfully used to prepare novel rare earth intermetallics [24] and various complex hydrides [25–27]. Different characterisation techniques are combined to obtain a clear picture about the reaction products. In particular, Raman and infrared (IR) spectroscopy give complementary information about the composition of the samples analysed. The importance of the additive for hydrogen absorption will also be discussed. Up to now, the effect of the additive has only been considered for the decomposition reaction, for the re-absorption reaction, it is only stated that the use of additive is necessary [21]. In this paper, more information about Ca(BH₄)₂ and corresponding reaction paths is obtained by investigating thoroughly the synthesis reaction and the effect of different additives in detail.

2. Experimental

2.1. Sample preparation

Reactive ball milling is used for the synthesis of Ca(BH₄)₂ through reaction (1) from CaH₂ (99.999%, Sigma–Aldrich) and CaB₆ (99.5%, Alfa Aesar) with 2:1 mol ratio to avoid the formation of by-products. For mechano-chemical synthesis, we used a stainless steel vial designed for milling under high-pressure (max 150 bar). In addition, temperature and pressure sensors are installed in the lid of the vial and can be used to monitor the reaction in situ during milling (exo-magnetics). The addition of NaBH₄ to the starting mixture was done to promote the reaction kinetics. Two compositions were used with two different additives. The choice of TiCl₃ (99.999%, Sigma–Aldrich) was guided by the very good efficiency of sodium alanate [25]. It has already been used for Ca(BH₄)₂ [16,20]. TiF₃ (Sigma–Aldrich) has been proposed more recently [21] and has a positive effect during decomposition of Ca(BH₄)₂. It is expected that this effect can also help the reverse reaction. A limited contamination by iron was detected in the samples originating from the vial walls and balls. However, the presence of iron is likely to be identical in the samples prepared with TiCl₃ or TiF₃, and should not hamper the comparison between the effect of both additives. The vial with 2 g of starting mixture and 37 stainless steel balls (10 mm, ball-to-powder ratio 75:1) was pressurised with 140 bar H₂ and then milled for 24 h without interruption in a Fritsch Pulverisette 6 planetary mill. Cycling was done using a Sieverts’ type apparatus (Hy-Energy PCTPro 2000). Around 200 mg of loose powder was loaded in a stainless steel cylinder with glass wool on top to avoid powder escape. This cylinder was then installed in a stainless steel sample holder with packing material to reduce the free volume as much as possible. The sample holder is heated through an external heating jacket. Temperature of the sample is recorded by a thermocouple placed close to the bottom of the vial. For each samples using TiCl₃ or TiF₃ as additive, one cycle was performed at 350 °C in static vacuum for desorption, and then in 90 bar H₂ for absorption. The sample temperature was elevated to 350 °C during the first desorption step and then kept constant for 10 h during desorption and for the all absorption step following. Powder handling is done under Ar atmosphere in a glove box with H₂O and O₂ contents less than 1 ppm.

2.2. Characterisation

Room temperature X-ray diffraction (XRD) analysis was performed using a STADI-MP diffractometer (Mo Kα, radiation). The measurements were done in transmission geometry using a Debye–Scherrer geometry and a Position Sensitive Detector (PSD). In situ XRD measurements during heating were performed on a Brucker D8 Advance apparatus with Cu Kα radiation. For both type of measurement, the powder was filled in a glass capillary (0.7 mm external diameter) prepared in the glove box and protected by paraffin. The capillary is then sealed by melting the end of the capillary. For in situ XRD, the capillary is inside a MRR (Materials Research Instruments) high-temperature capillary furnace.

To allow a direct comparison of the XRD patterns measured at different wavelengths, the diffracted intensities are plotted as a function of the wave vector Q rather than the angle 2θ. The wave vector is defined by:

\[ Q = \frac{2 \pi}{\lambda} \]

where λ is the interplanar distance obtained from the Bragg’s law.

Raman spectroscopy was performed at room temperature using a Renishaw microscope 2000 (Renishaw plc, Gloucestershire, U.K.) with a spectral resolution of 1 cm⁻¹. The 633 nm line of the HeNe laser was focused on the sample through the magnifying objective (50 ×) of the microscope. Around 10 mg of sample were placed in a Linkam THMS500 cell (Linkam Scientific Instruments, U.K.) directly adapted to the microscope of the instrument. The cell allows the use of controlled atmosphere and temperature. The glass window of the cell is 0.1 mm thick. The samples were placed under a small Ar flow to avoid contamination during measurement.

For infrared (IR) measurements, all samples were handled in a nitrogen filled glove box. The samples were introduced in a Specac Golden Gate ATR cell. The IR spectra were recorded at room temperature using BIO-RAD EXALBUR spectrometer with 1 cm⁻¹ of resolution.

Pure CaH₂, CaB₆ and Ca(BH₄)₂ were also analysed in the same conditions for comparison. For Raman measurement, the Ca(BH₄)₂ reference compound (Aldrich, dry powder) is composed mainly of the β phase with presence of small quantity of the α phase. For IR measurement, the Ca(BH₄)₂ is composed mainly of the α phase (from drying Ca(BH₄)₂ 2THF, Aldrich).

3. Results and discussion

3.1. Synthesis by high-pressure reactive milling

The evolution of the temperature and the pressure recorded during the milling of the mixture 2 CaH₂ + CaB₆ + 0.08 TiCl₃ are given in Fig. 1a and from these values the hydrogen content in the vial is calculated using the ideal gas law and shown in Fig. 1b. Note that thorough external controls were performed during the complete process to ensure that no hydrogen leak occurred. The variation of hydrogen pressure measured during milling is only related to the reaction taking place inside the vial. It has already been shown for NaBH₄ that the variation of H₂ pressure inside the vial gives reliable information on the reaction completion [28,29]. High-pressure of 140 bar is used for milling to obtain the highest driving force possible for the reaction [28,30]. A high number of balls and high rotational speed are also used to increase the energy of the milling [28,31] and improve the effectiveness of the process. At the beginning of the process, we observe an increase of the temperature due to the friction between the balls and to the vial walls that leads to an increase of the H₂ pressure. A maximum temperature of 55 °C is measured in the vial lid and is reached after 5 h milling. Note that the real temperature upon powder particle collision and the temperature of the surrounding gas are higher than the recorded temperature in the lid. This could lead to an overestimation of the decrease of H₂ determined from the pressure drop in the vial, especially at the beginning of the process when the temperature and pressure change because of the mechanical activation and of the
exothermic absorption of hydrogen by the mixture. The variation of the quantity of H2 should be then seen as a qualitative view of the H2 absorption during the milling process. After 25 h, the rate of hydrogen absorption determined from the pressure decrease is very low and the milling is stopped to analyse the compound(s) formed. Considering the initial and final pressure in the vial (at room temperature), we obtain a consumption of 0.0186 mol H2. The total H2 amount consumed for reaction (1) would be 0.0992 mol, considering the starting quantity of reactants, indicating that a reaction yield of 19% can be obtained during milling. Although small, this yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]). Similar behaviour is obtained for the sample prepared with TiCl3 (not shown). From this first experiment, the additives seem to have little influence on the synthesis reaction. The reaction yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]). Similar behaviour is obtained for the sample prepared with TiCl3 (not shown). From this first experiment, the additives seem to have little influence on the synthesis reaction. Considering the initial and final pressure in the vial (at room temperature), we obtain a consumption of 0.0186 mol H2. The total H2 amount consumed for reaction (1) would be 0.0992 mol, considering the starting quantity of reactants, indicating that a reaction yield of 19% can be obtained during milling. Although small, this yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]). Similar behaviour is obtained for the sample prepared with TiCl3 (not shown). From this first experiment, the additives seem to have little influence on the synthesis reaction. Considering the initial and final pressure in the vial (at room temperature), we obtain a consumption of 0.0186 mol H2. The total H2 amount consumed for reaction (1) would be 0.0992 mol, considering the starting quantity of reactants, indicating that a reaction yield of 19% can be obtained during milling. Although small, this yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]). Similar behaviour is obtained for the sample prepared with TiCl3 (not shown). From this first experiment, the additives seem to have little influence on the synthesis reaction. Considering the initial and final pressure in the vial (at room temperature), we obtain a consumption of 0.0186 mol H2. The total H2 amount consumed for reaction (1) would be 0.0992 mol, considering the starting quantity of reactants, indicating that a reaction yield of 19% can be obtained during milling. Although small, this yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]). Similar behaviour is obtained for the sample prepared with TiCl3 (not shown). From this first experiment, the additives seem to have little influence on the synthesis reaction. Considering the initial and final pressure in the vial (at room temperature), we obtain a consumption of 0.0186 mol H2. The total H2 amount consumed for reaction (1) would be 0.0992 mol, considering the starting quantity of reactants, indicating that a reaction yield of 19% can be obtained during milling. Although small, this yield is quite encouraging considering that the reaction takes place at low temperature (60% was previously obtained at 700 bar and 440 ºC, after 48 h [16]).

The XRD patterns of the milled powders are very similar whatever the additive used and show mainly peaks related to CaH2 and CaB6 (Fig. 2). For the sample milled with TiCl3 (Fig. 2a), the peaks related to CaH2 are very weak and the low intensities observed can also be related to a large broadening due to crystallite size reduction during milling. No other hydride phase formed during milling can be detected, it is likely very disordered or poorly crystallised and cannot be seen by XRD. For the sake of clarity in the following discussion, we call it amorphous hydride phase. In addition, no trace of the additive itself is found in the patterns despite they are present in relatively large amount in the starting mixture. There is also no compound found that could originate from the decomposition of the additive TiCl3. On the other hand, a small amount of CaF2 can be detected from the XRD pattern of the as-milled sample with TiF3. This phase may be formed by the decomposition of TiF3 by reaction with CaH2. Other CaF2–H6 compounds with similar structure as CaF2 have been reported by Kim et al. [21], however, from the XRD pattern, we do not detect the additional diffraction peaks (compared to CaF2) of such phases (Fig. 2b); therefore, we only consider the formation of CaF2 for the following discussion. In general, the additive itself or any compound formed from it should be finely distributed in the powder (nanocomposite) or with a highly disordered structure, so hardly detectable by XRD.

The borohydrides compounds are often difficult to analyse by XRD because of their complex structures and sometime disordered/amorphous state, especially after milling. For example, Agresti and Khandelwal [32] have evidenced by XRD the formation of LiBH4 from milling of LiH and B only after removing un-reacted compounds using a solvent and heating the products. Raman spectroscopy is often used as an additional characterisation technique for these types of compounds [33–35], especially to detect the presence of borohydride phases while they cannot be identified in XRD patterns [5,16]. Interestingly, it is possible to distinguish the different polymorphs of Ca(BH4)2 by Raman spectroscopy [10]. Raman spectroscopy is sensitive to the vibrations of the molecules. Infrared (IR) spectroscopy is also sensitive to the vibrations of molecules and shows comparable spectra. However, the principles and selection rules are different for both techniques meaning that they give complementary information on a sample [36]. The Raman effect is based on a change of the polarisability of the molecule whereas the IR spectroscopy is sensitive to the change of the dipole moment of the molecule. These different criterions imply that different compounds and bonding are detected by each technique.

The Raman spectrum of pure CaBH4 (Fig. 3a) is composed mainly of vibration modes arising around 2300 cm−1 that corresponds [10] to the stretching modes of the B–H bonding in [BH4]−. The corresponding bending modes appear in the 1000–1400 cm−1 range. For CaH2, different lines arise at low wave numbers [37]: 130, 180, 206 cm−1 and we observe additional lines at 727 and 1000 cm−1 in Fig. 3b. For pure CaB6, the spectrum [16,38] is composed of three lines at 755, 1117 and 1259 cm−1 (Fig. 3c). The Raman spectra obtained for the samples prepared with TiCl3 or TiF3 (Fig. 3d and e) show mainly the presence of CaB6 with the three vibration lines as observed for the pure compound. No vibration line corresponding to CaH2 is observed for the sample containing TiCl3, while there might be a small contribution from CaH2 in the spectrum of the sample milled with TiF3 (see ca. 150 cm−1). There is also no trace of another vibration mode. It is not possible to identify the hydride phase formed during milling. Infrared spectroscopy is therefore used because of its higher sensitivity (higher cross section) that can be beneficial in the case of a small amount of compound as it is the case. The results of IR measurements on the as-milled samples
Fig. 3. Raman spectra for reference compounds Ca(BH₄)₂ (a), CaH₂ (b), CaB₆ (c) and for the as-milled samples with TiCl₃ (d) or TiF₃ (e) as additive.

are given in Fig. 4.

The IR spectrum obtained for pure Ca(BH₄)₂ (Fig. 4a) can be compared with the Raman spectrum in Fig. 3a. There are two main regions of vibrations, around 2300 cm⁻¹ for the stretching modes and for 1000–1300 cm⁻¹ for the bending modes. The peak observed at ca. 1600 cm⁻¹ is related to a contamination by water. On the other hand, the spectrum obtained for CaH₂ (Fig. 4b) is different with only a large feature around 1000 cm⁻¹. The spectrum of pure CaB₆ (Fig. 4c) does not show any vibration in contrast with Raman spectroscopy. The bands observed around 2330–2370 cm⁻¹ are related to gaseous CO₂ contamination. Similar IR spectra are obtained for the both as-milled samples (Fig. 4d and e). We only observe two broad components around 1000 and 2200 cm⁻¹. Comparing with the spectrum obtained for pure CaH₂, it is clear that the component observed around 1000 cm⁻¹ is related to this compound. The broad peak around 2200 cm⁻¹ may correspond to the vibration in the stretching mode of the B–H bonding in [BH₄]⁻, which is observed in the spectrum of pure Ca(BH₄)₂. Note that the wavelengths of the vibrations for the stretching modes are independent of the Ca(BH₄)₂ polymorphs. It is therefore not possible to determine which structure has been formed during milling. In the 1000–1500 cm⁻¹ range, it is also possible to observe smaller features which may be related to the bending mode of B–H (besides CaH₂ contribution). Considering the little amount of borohydride expected from the quantity of hydrogen absorbed during milling (19%), it is not surprising that the signal detected is very low. The very broad peaks obtained can reasonably be ascribed to amorphous/disordered Ca(BH₄)₂. The formation of another borohydride is unlikely since Ca based compounds are the main starting products. The formation of Ti[BH₄]₃ by reaction with the additive [39] cannot be excluded (presence of CaF₂). However, this compound is very unstable and would have decomposed immediately during milling. In addition, the formation of Ti[BH₄]₃ is reported only by reaction between a borohydride and a Ti-based compound, not from the “elements”. By combining different characterisation techniques, we can have a good indication that part of the milled samples is Ca(BH₄)₂.

In situ XRD measurements were performed on both samples prepared with Ti-based additives to analyse the behaviour of the phases formed during heating to 300 °C (before decomposition). The patterns obtained at different temperatures are given in Fig. 5. At low temperatures, the patterns are similar to the one obtained after milling with the presence of CaH₂ and CaB₆ mainly (Fig. 2). For the sample milled with TiCl₃ (Fig. 5a), it is possible to see small

Fig. 5. In situ XRD measurements upon heating from samples milled with (a) TiCl₃ and (b) TiF₃. The hump centred on 1.5 Å⁻¹ is related to the diffraction of the glass capillary. The phases present are: CaH₂ (■), CaB₆ (○), CaF₂ (×) and β-Ca(BH₄)₂ (β).
peaks arising which correspond to β-Ca(BH$_4$)$_2$ (high-temperature phase) at 240 °C. For the sample milled with TiF$_3$, these peaks arise at 210 °C (Fig. 5b). These peaks are growing when the temperature increases. The appearance of the β phase is in agreement with previous reports on phase transformations in Ca(BH$_4$)$_2$ which show that the room temperature polymorphs α or γ transform into the β phase above 200 and 270 °C, respectively [13]. The growth of the β-Ca(BH$_4$)$_2$ phase in our sample above 200 °C is therefore not surprising and confirms that a Ca(BH$_4$)$_2$ phase is already present in the milled sample. The presence of an intermediate phase in the milled sample, which transforms to Ca(BH$_4$)$_2$, is unlikely since the samples were heated under Ar in the capillary. To form Ca(BH$_4$)$_2$ from any intermediate phase, the presence of H$_2$ is required (and probably higher temperature). This observation together with the results of IR spectroscopy are a reasonable proof of the formation of Ca(BH$_4$)$_2$ during milling.

To summarise this part, reactive ball milling under high hydrogen pressures leads to the formation of Ca(BH$_4$)$_2$ in small quantity. The combination of different characterisation techniques allows its unambiguous identification, hardly possible by XRD only since it is poorly crystallised. This result indicates that the quantity of hydrogen absorbed during milling is used for the formation of Ca(BH$_4$)$_2$ with a reaction yield of 19% and no difference is observed between the additives that show similar influence on the milling process.

3.2. Cycling capability

As a next step, we have performed one cycle desorption/absorption in a Sieverts’ type apparatus in order to study the reversibility of the reaction. In addition, the formation of an ordered Ca(BH$_4$)$_2$ phase should be more favourable at high temperature (350 °C) as seen from in situ XRD measurements. The first desorption steps leads to similar results for both samples (Fig. 6a) with a release of ca. 1.6 wt% of hydrogen in agreement with the amount of gas absorbed during milling. The decomposition started at 270–300 °C for both samples during the heating ramp to 350 °C (hydrogen backpressure of about 0.2 bar). The release of H$_2$ is slightly slower and proceeds in two steps for the sample milled with TiF$_3$. The results of the following absorption step are shown in Fig. 6b. For both samples, we observe a first part (t<2 h) with fast hydrogen absorption and then a continuous and slow increase of the hydrogen uptake for the remaining time. For the sample with TiF$_3$, a capacity of 4.8 wt% H$_2$ is achieved after 24 h whereas only 2.8 wt% H$_2$ is reached in the sample containing TiCl$_3$. The capacity obtained using TiCl$_3$ remains far from the theoretical value of 9 wt% H$_2$ taking into account the weight of the additive (8.8 wt% if we consider that TiCl$_3$ has entirely reacted with CaH$_2$ to form CaCl$_2$). For longer absorption time (not shown), the maximum capacity of the sample containing TiF$_3$ obtained is 5.3 wt% H$_2$ after 40 h, corresponding to a reversibility yield of 57% considering the weight of the additive (60% considering the maximum possible weight of by-product CaF$_2$ from the reaction between CaH$_2$ and TiF$_3$). This value is in agreement with the reversible absorption of hydrogen obtained by Kim et al. [21] in similar conditions but directly from the decomposition products of pure Ca(BH$_4$)$_2$. To understand the difference observed between the two additives, structural characterisation is performed by XRD and IR spectroscopy.

Significant different phases are observed in the XRD patterns depending on the additive used (Fig. 7). For both samples, we observe un-reacted CaH$_2$ and CaB$_6$ in agreement with the non-completion of the reaction observed during kinetic measurements (Fig. 6b). In addition, it is possible to observe the formation of CaCl$_2$ or CaF$_2$ from the reaction of the additive with CaH$_2$. The CaCl$_2$ phase fraction is difficult to evaluate because the peaks indicated by ▲ in Fig. 7a, at position expected for CaCl$_2$, are very high relative intensities; it is therefore very likely that there is overlapping with peaks of other compounds. The main difference between the samples prepared with TiCl$_3$ or TiF$_3$ is the clear appearance of the α and β phases of Ca(BH$_4$)$_2$ in the sample milled with TiF$_3$ whereas in the sample with TiCl$_3$, we obtain only a weak peak related to α-Ca(BH$_4$)$_2$ and other more important peaks (indicated with question marks in Fig. 7a) that could not be indexed. These new peaks do not correspond to any intermediate phases [17,19] reported for the decomposition of Ca(BH$_4$)$_2$ or any polymorphs for Ca(BH$_4$)$_2$ itself. The formation of CaHCl was found in additional samples prepared by millings with TiCl$_3$ and performed in different conditions (not shown). Therefore, the un-indexed XRD peaks may be related to a similar Ca-H-Cl(-B?) phase, as suggested by
Kim et al. [20] after ball milling Ca(BH$_4$)$_2$ that is consistent with the weak peaks of CaH$_2$ and the overlap with the CaCl$_2$ peaks. The formation of this unknown phase limits the formation of Ca(BH$_4$)$_2$ during absorption. Note also that no intermediate phase for the formation of Ca(BH$_4$)$_2$ in sample with TiF$_3$ is detected even though the reaction is not complete. We also cannot detect any phase with Ti from the decomposed additives.

IR spectroscopy is performed to check for phases not detected by XRD (Fig. 8). The IR spectrum of the sample with TiCl$_3$ shows weak features related to CaH$_2$ (Fig. 8d), while Ca(BH$_4$)$_2$ vibration lines appear clearly for the sample with TiF$_3$ (Fig. 8e). This is a confirmation that after cycling, no or little Ca(BH$_4$)$_2$ is formed in the sample with TiCl$_3$. The phase formed in this case may be a Ca-H-Cl(-B?) phase as already supposed from the XRD measurement: the small peaks around 1200 cm$^{-1}$ observed in the IR spectrum (Fig. 8d) might be its IR sign. Also, that no intermediate phase for the formation of Ca(BH$_4$)$_2$ in sample with TiF$_3$ is detected even though the reaction is not complete. We also cannot detect any phase with Ti from the decomposed additives.

Fig. 8. IR spectra for reference compounds Ca(BH$_4$)$_2$ (a), CaH$_2$ (b), CaB$_6$ (c) and for the cycled samples with TiCl$_3$ (d) or TiF$_3$ (e) as additive.

The weak features related to CaH$_2$ and overlap with the CaCl$_2$ peaks. The formation of this unknown phase limits the formation of Ca(BH$_4$)$_2$ during absorption. Note also that no intermediate phase for the formation of Ca(BH$_4$)$_2$ in sample with TiF$_3$ is detected even though the reaction is not complete. We also cannot detect any phase with Ti from the decomposed additives.

The formation of this unknown phase limits the formation of Ca(BH$_4$)$_2$ during absorption. Note also that no intermediate phase for the formation of Ca(BH$_4$)$_2$ in sample with TiF$_3$ is detected even though the reaction is not complete. We also cannot detect any phase with Ti from the decomposed additives.

**4. Conclusion**

Ca(BH$_4$)$_2$ can be synthesised by reactive ball milling of its decomposition products CaH$_2$ and CaB$_6$ under 140 bar H$_2$ near room temperature. The reaction yield is 15% after milling which is promising since the process is done at low temperature and 60% yield can be achieved during re-hydrogenation. The compound is in a poorly crystallised state. The combination of Raman and IR spectroscopy with in situ XRD is therefore necessary for a complete analysis of the samples. The comparison of the cycling behaviour of TiCl$_3$ and TiF$_3$-doped Ca(BH$_4$)$_2$ reveals that TiF$_3$ is a better additive. The use of TiCl$_3$ does not allow the reversible formation of Ca(BH$_4$)$_2$ while by cycling the sample milled with TiF$_3$, Ca(BH$_4$)$_2$ is obtained already at mild hydrogenation conditions. The enhanced reversibility can originate from a purely catalytic effect from Ti-based compounds or CaF$_2$-doped Ca(BH$_4$)$_2$ phases and/or be related to the partial substitution of H by F in Ca(BH$_4$)$_2$ changing the stability of the hydride phase. Further investigations are needed to clarify the chemical state of the additive and the location of F atoms that should help to understand the H$_2$ sorption and doping mechanisms in Ca(BH$_4$)$_2$.

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References