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Ball-milling and AlB_2 addition effects on the hydrogen sorption properties of the $CaH_2 + MgB_2$ system

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ABSTRACT

Among the borohydrides proposed for solid state hydrogen storage, $Ca(BH_4)_2$ is particularly interesting because of its favourable thermodynamics and relatively cheap price. Composite systems, where other species are present in addition to the borohydride, show some advantages in hydrogen sorption properties with respect to the borohydrides alone, despite a reduction of the theoretical storage capacity. We have investigated the milling time influence on the sorption properties of the $CaH_2 + MgB_2$ system from which $Ca(BH_4)_2$ and MgH_2 can be synthesized by hydrogen absorption process. Manometric and calorimetric measurements showed better kinetics for long time milled samples. We found that the total substitution of MgB_2 with AlB_2 in the starting material can improve the sorption properties significantly, while the co-existence of both magnesium and aluminum borides in the starting mixture did not cause any improvement. Rietveld refinements of the X-ray powder diffraction spectra were used to confirm the hypothesized reactions.

1. Introduction

Complex hydrides (above all alanates, amides, and borohydrides) [1] have been intensively studied in recent years because of their higher theoretical hydrogen storage capacity if compared to traditional transition metals hydrides. Calcium borohydride, in particular, has been shown to release about 9.0 wt% of hydrogen if heated up to 550 °C [2]. MgH_2, which releases more than 7 wt% of hydrogen at 300 °C, is the most studied metal hydride and is being investigated for possible practical applications [3–5]. In this framework we decided to focus on the promising $Ca(BH_4)_2 + MgH_2$ reactive hydride composite (RHC) [6–8]. We studied the influence of milling time on the formation of the hydrogenated system from calcium hydride and magnesium boride. In addition, we investigated the effect of the addition of aluminum boride on the kinetic and thermodynamic hydrogen sorption properties.

2. Materials and methods

The starting materials calcium hydride (98%, −10 mesh) and magnesium diboride (−100 mesh) were purchased from Alfa Aesar, while aluminum diboride (≥96%, −325 mesh) was bought from Sigma–Aldrich. The samples were ball milled in a Spex8000M Mixer/Mill for different milling times (from 2 min to 900 min), performing 15 min milling followed by 15 min pause steps to avoid sample heating inside the hardened steel milling vial. All the powders have been handled inside an Ar filled glove box (MBraun) with moisture and oxygen level kept below 1 ppm. Amounts of powder ranging from 0.45 g to 0.65 g were introduced in an automatic manometric Sievert's type gas reaction analyzer, PCTPro-2000 by Setaram. Concerning the absorption tests, the samples were charged with an initial pressure of 120 bar, then a temperature ramp from room temperature to 360 °C was performed at 5 °C/min rate, followed by an isothermal step (lasting 1400 min or 3000 min) at 360 °C. Isothermal dehydrogenation runs were performed on the absorbed samples at 390 °C under static vacuum. Coupled manometric–calorimetric measurements were performed by coupling the manometric instrument with the Sensys DSC instrument (Setaram). 50 mg of the samples hydrogenated in the manometric apparatus were loaded in the high pressure cell of the Sensys apparatus under Ar atmosphere inside the glove box. The cell was inserted in the furnace of the DSC instrument and connected with the manometric instrument by a 1/8′ stainless steel tube. The powders were subjected to a thermal programmed desorption (TPD) measurement performed by heating from room temperature to 580 °C at 2 °C/min with a starting hydrogen pressure of 0.1 bar. The integration of the calorimetric peaks was made by Calisto software (Setaram). X-ray powder diffraction (XRPD) measurements have been performed using a Bruker D8 Advance diffractometer with Bragg–Brentano geometry and Cu Kα radiation. Rietveld refinements on the XRPD profiles have been performed using the software MAUD [9].

3. Results and discussions

3.1. Effect of milling time on $CaH_2 + MgB_2$ samples

Calcium borohydride and magnesium hydride can be obtained from calcium hydride and magnesium boride [8], according to the

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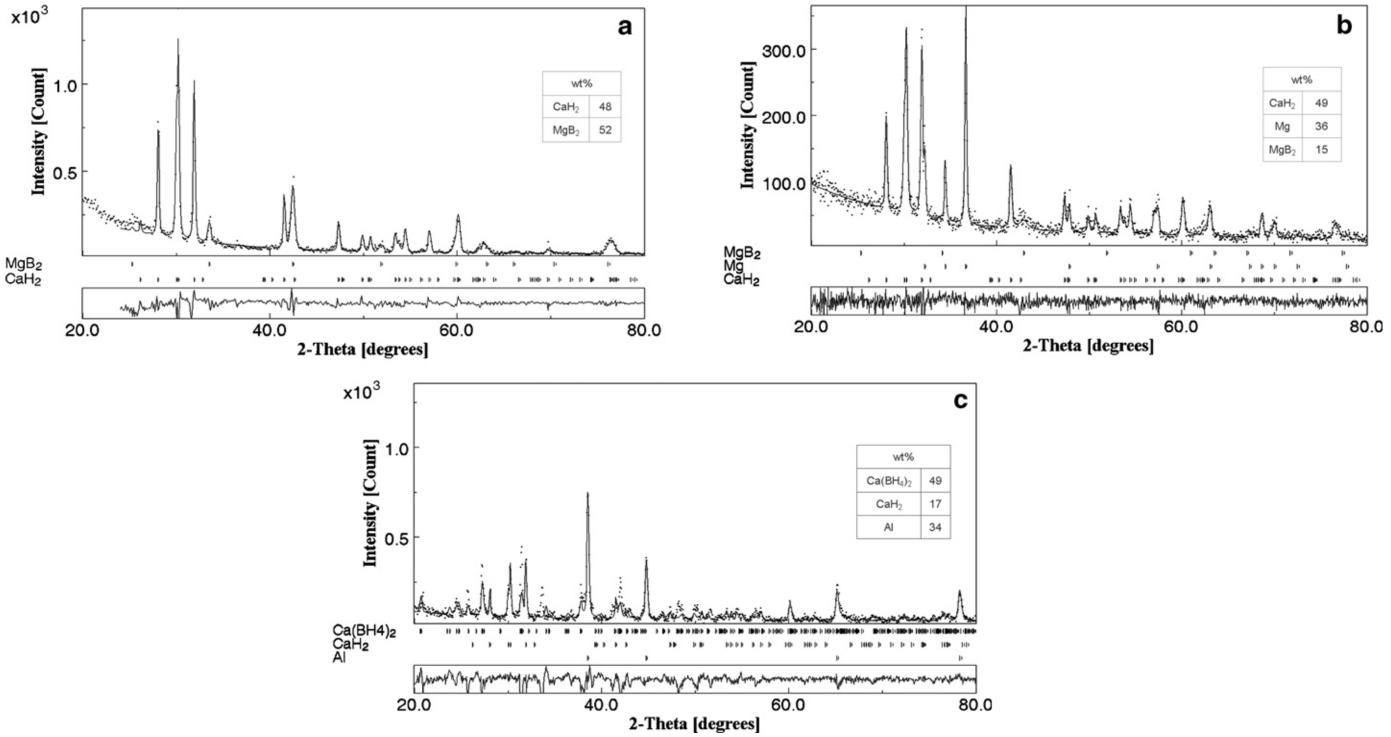

Fig. 1. XRPD patterns for different samples: (a) $CaH_2 + MgB_2$ after milling for 90 min; (b) $CaH_2 + MgB_2$ milled for 90 min, hydrogenated and subsequently desorbed; (c) $CaH_2 + AlB_2$ milled for 90 min and hydrogenated. The insets show calculated weight content of the constituent phases.

reaction:

$$CaH_2 + MgB_2 + 4H_2 \rightarrow Ca(BH_4)_2 + MgH_2 \quad \text{theoretical } H_2 \text{ content} = 8.39\,\text{wt\%} \qquad (1)$$

Four samples of calcium hydride and magnesium boride were prepared by milling for 2, 90, 450 and 900 min, respectively. As shown in Fig. 1(a), milling does not lead to the formation of any new phase, but decreases the crystallites size of the starting hydrides (see Table 1). In Fig. 2 we compare the effect of milling time on the hydrogenation kinetics, and one can observe improved kinetics for the longer time milled samples. It is worth noting that the sample milled for 450 min shows the best kinetics just at the beginning, getting worse with respect to the 900 min milled sample after 0.5 h. XRPD analysis performed on the 90 min milled $CaH_2 + MgB_2$ sample after hydrogenation revealed a strong presence of the intermediate phase $Ca_4Mg_3H_{14}$ [8], together with the desired borohydride, magnesium hydride and some unreacted MgB_2 (Fig. 3), thus indicating that full absorption did not occur.

Fig. 4 shows the absorption and the desorption curves recorded for the 90 min milled sample, which takes 3600 min to reach

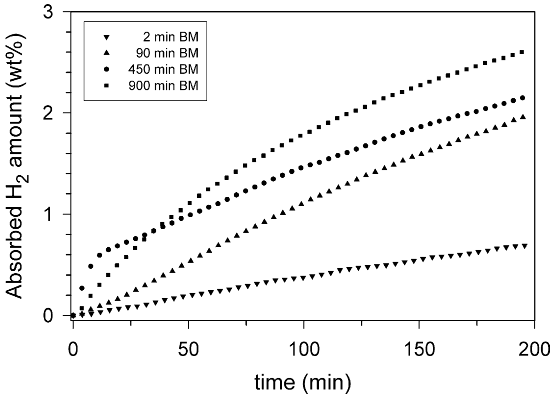

Fig. 2. Effect of milling time on the absorption kinetics (first 200 min) for $CaH_2 + MgB_2$ milled samples. Absorption was performed at 360 °C and starting hydrogen pressure = 120 bar. The crystallite size reduction improves the hydrogenation kinetics as milling time increases. The 450 min milled sample shows the fastest kinetics in the initial part of the charging procedure.

Table 1

Results obtained by XRPD, manometric and coupled manometric-calorimetric measurements on $CaH_2 + MgB_2$ milled samples. Milling time has a clear effect on powder size, hydrogen capacity and release onset temperature. Crystallites size (with estimation error of 5%) for CaH_2 and MgB_2 have been obtained as a result of Rietveld analysis performed on the patterns by the software MAUD [9].

Sample	Crystallites size for the as milled samples (Å)		H_2 desorbed amount after hydrogenation for 1400 min (wt%)	Hydrogen release onset (°C)	ΔH double-peak (kJ/mol H_2)
	CaH_2	MgB_2			
($CaH_2 + MgB_2$) as milled for 2 min	1260	880	3.2	348	49.0
($CaH_2 + MgB_2$) as milled for 90 min	230	360	4.6	346	49.7
($CaH_2 + MgB_2$) as milled for 450 min	160	280	4.9	338	49.5
($CaH_2 + MgB_2$) as milled for 900 min	–	–	5.8	336	50.7

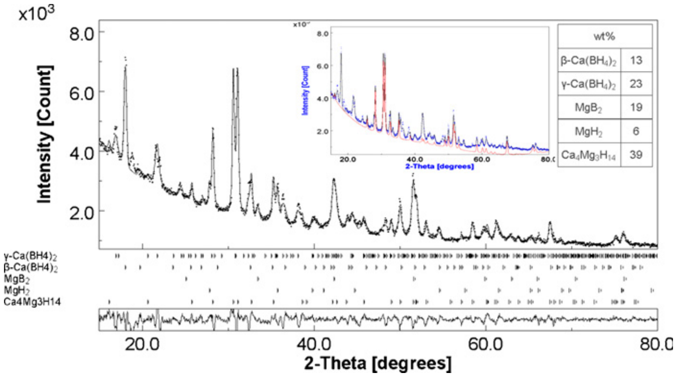

Fig. 3. XRPD pattern for the $CaH_2 + MgB_2$ 90 min milled sample after hydrogenation for 3000 min at 360 °C and initial pressure of 120 bar. The Rietveld analysis shows a strong presence of the intermediated hydrogenated phase $Ca_4Mg_3H_{14}$ (39 wt%), together with the desired hydrated products $Ca(BH_4)_2$ and MgH_2 and some still unreacted MgB_2. The insets show calculated weight content of the detected constituent phases and the calculated partial XRD profile (in red) for the $Ca_4Mg_3H_{14}$ phase. (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

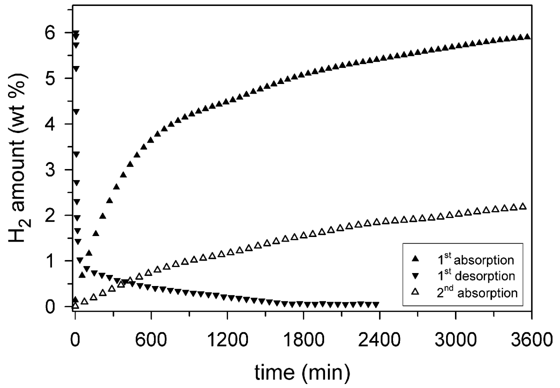

Fig. 4. Sorption kinetics (T = 360 °C) comparison for the $CaH_2 + MgB_2$ 90 min milled sample: desorption is faster than absorption (90% of the total absorbed amount is released in 300 min). Re-hydrogenation curve is also shown, indicating that the system is not fully reversible.

6.0 wt% of hydrogen content, and fully desorbs in 1800 min at 390 °C, with 90% of the hydrogen content released in the first 300 min. The fact that the system fully desorbs was also confirmed by the Rietveld analysis performed on the XRPD spectrum of the same sample after desorption (Fig. 1(b)): there is no presence of any hydrogenated phases, except for the starting compound CaH_2. However, unbound magnesium is also present in addition to the starting boride, thus suggesting the presence of some amorphous boron, not detected by diffraction. Although MgB_2 has a strong negative free energy of formation, so that its presence in the desorbed system is thermodynamically favoured compared to Mg and B alone, actually its formation is probably hindered by a slow kinetics. This in fact entails a not full reversibility of the system.

The second hydrogenation run for the 90 min milled sample after full desorption is also reported in Fig. 4; the re-hydrogenation was performed in the same conditions of the first hydrogenation. It can be seen that the system has a lower capacity than in the first absorption, indicating that full reversibility is not achieved.

Coupled manometric–calorimetric desorption measurements were performed on the samples ball-milled for different times after the first hydrogenation run: in Fig. 5(a) the discharging profile for the 90 min milled sample charged for 1400 min is shown. The amount of hydrogen released by the four $CaH_2 + MgB_2$ milled samples, reported in Table 1, increases by increasing the milling time, so the storage capacity improves with the mechanical treatment.

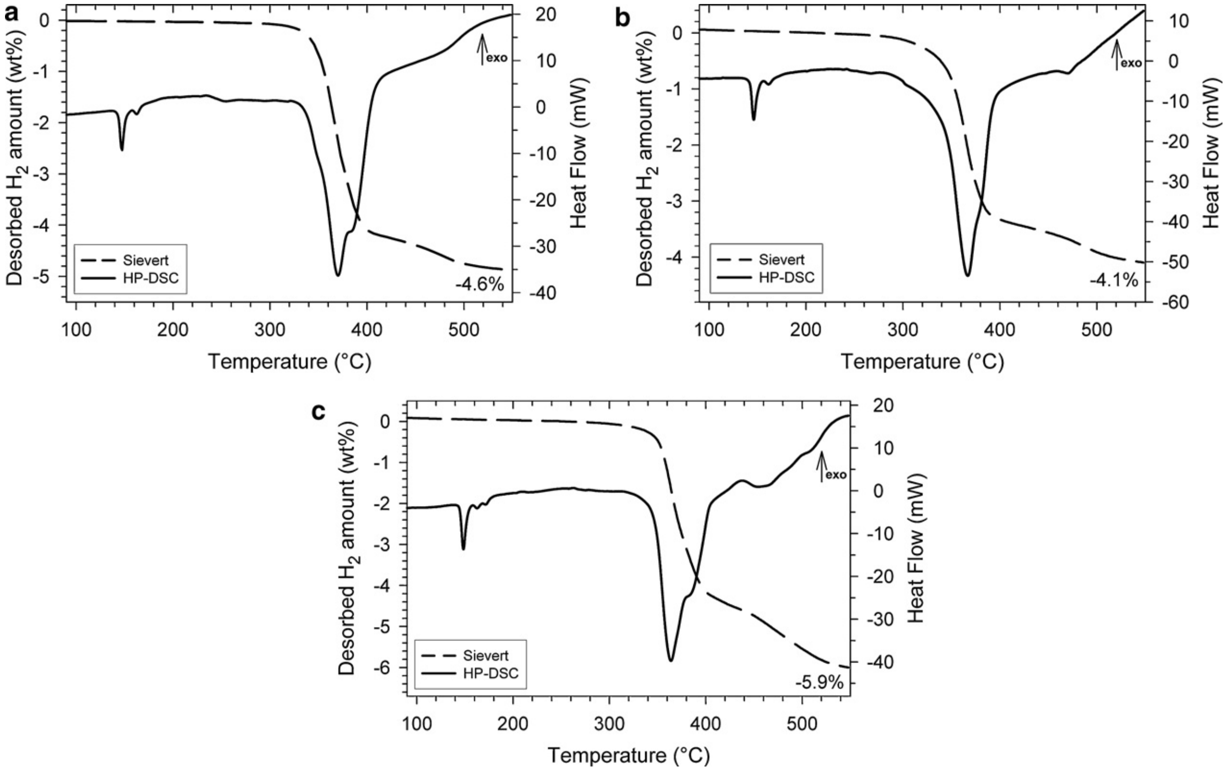

Fig. 5. Temperature programmed desorption (TPD) measurements performed by the coupled manometric (Sievert's)–calorimetric (DSC) system. The figure shows the desorption profiles for 90 min milled samples after a first absorption at 360 °C and 120 bar: (a) $CaH_2 + MgB_2$ after 1400 min absorption; (b) $CaH_2 + (1/2)MgB_2 + (1/2)AlB_2$ after 3000 min absorption; (c) $CaH_2 + AlB_2$ after 3000 min absorption. The comparison of the released hydrogen amounts for the three systems previously absorbed for the same time (3000 min) is reported in Table 2.

Table 2
Comparison between binary and ternary samples containing MgB_2 and AlB_2. The best behaviour is shown by the binary system containing aluminum boride.

Sample	Theoretical hydrogen capacity (wt%)	H_2 released amount after hydrogenation for 3000 min (wt%)	H_2 released amount referred to theoretical capacity	H_2 release onset (°C)	ΔH double-peak (kJ/mol H_2)	H_2 re-absorbed amount referred to theoretical capacity
($CaH_2 + MgB_2$) 90 min milled	8.39	5.8	70%	343	51.4	16%
($CaH_2 + (1/2)MgB_2 + (1/2)AlB_2$) 90 min milled	7.32	4.1	56%	346	58.0	18%
($CaH_2 + AlB_2$) 90 min milled	6.25	5.9	94%	341	45.3	21%

Concerning the calorimetric profile, according to what reported in recent studies [2,8], the first main peak starting at around 130 °C can be attributed to the transition of $Ca(BH_2)_4$ from the α-phase (stable at room temperature) to the β-phase. In the range 150–190 °C other small endothermic features are present, probably indicating other structural changes of the borohydride (γ-phase) or loss of coordination water [10]. In the region between 340 °C and 440 °C a double peak indicates the hydrogen release from the borohydride phase forming the intermediate mixed hydrogenated phase $Ca_4Mg_3H_{14}$ in addition to CaH_2, Mg, B and H_2 (peak on the left) and then CaH_2, Mg, B and H_2 from the mixed phase itself (peak on the right). In our experiments, differently from the cited work [8], there is rather an overlap of these two peaks even if we used the same heating rate, i.e. 2.0 °C/min. It must be noted that no clean peak corresponding to the hydrogen release from MgH_2 appears, as this compound releases hydrogen in a range inside the double peak region [11]. In Table 1 the double peak onset temperature and the desorption enthalpy are reported: the latter remains quite constant (±2 kJ/mol error), thus suggesting that there is no remarkable difference in the chemical nature of the phases present in the samples, while the former confirms a better behaviour of the samples as the milling time increases.

3.2. Addition of AlB_2

We tried to improve the sorption performance of the system, in particular its reversibility, by adding aluminum boride. Aluminum and magnesium form mixed borides [12] that can be prepared by high energy ball milling [13]. The investigation on the effect of AlB_2 on the studied system is justified by the fact that AlB_2 and MgB_2, having the same layered crystal structure, present a lower decomposition temperature (920 °C and 800 °C, respectively) compared to either boron (that melts at 2075 °C without decomposition), or other metal borides (melting point ranging from 1035 °C for NiB to 3245 °C for ZrB_2) [14]. This indicates a lower lattice energy (absolute value) and thus a lower thermodynamic stability. We supposed that the compatibility between Al and Mg could in principle facilitate the formation of borides, rather than unbound boron, during the hydrogen release processes; this could improve the desorption kinetics, as already suggested [15], and make the system more reversible. For this reason we prepared $CaH_2 + (1/2)MgB_2 + (1/2)AlB_2$ and $CaH_2 + AlB_2$ mixtures. For these two samples we suggest the following reactions, respectively:

$$CaH_2 + (1/2)MgB_2 + (1/2)AlB_2 + (7/2)H_2 \rightarrow Ca(BH_4)_2 + (1/2)MgH_2 + (1/2)Al \quad 7.32\,\text{wt\%} \tag{2}$$

$$CaH_2 + AlB_2 + 3H_2 \rightarrow Ca(BH_4)_2 + Al \quad 6.25\,\text{wt\%} \tag{3}$$

in which it is assumed that (a) both borides take part to the formation of the borohydride, (b) all Mg reacts to form MgH_2 and (c) Al does not absorb hydrogen. Both samples were prepared by 90 min ball milling following the same procedure used for the $CaH_2 + MgB_2$ mixture. Hydrogenation at 360 °C with an initial hydrogen pressure of 120 bar was performed for 3000 min on the two samples, as well as on the $CaH_2 + MgB_2$ 90 min milled sample for comparison. Fig. 1(c) shows the XRPD patterns obtained for the $CaH_2 + AlB_2$ sample after absorption: the Rietveld analysis suggested the presence of the borohydride and aluminum together with some unreacted calcium hydride, thus indicating that the assumed reaction (3) occurred and that also in this case full hydrogenation was not achieved. The absence of unreacted AlB_2 seems to suggest a decomposition of the boride before the formation of the borohydride. In Figs. 5(b) and (c) the coupled manometric–calorimetric measurements performed on the two samples containing AlB_2, after a previous absorption run for 3000 min, are shown. If we consider the theoretical capacity referring to reactions (1)–(3), it can be stated that there is a strong increase in the absorption relative percentage for the $CaH_2 + AlB_2$ sample, as it releases the 94% of the full theoretical hydrogen capacity; instead, the actual behaviour of the system with both borides contradicts the initially assumed positive effect of the compatibility between MgB_2 and AlB_2, as this ternary system shows a lower hydrogen content than the system containing only the magnesium boride. What is more, the absolute value of 5.9 wt% denotes an interesting hydrogen capacity for the system $CaH_2 + AlB_2$. A summary of the results obtained on the three samples is given in Table 2: interestingly, a reduction of the specific enthalpy of the desorption process confirms the better behaviour of the $CaH_2 + AlB_2$ system, differently from what calculated by Wolverton et al. [16]. Also the desorption enthalpy value of the ternary system confirms its lower performance.

Desorption runs were also performed at 390 °C and under static vacuum on both the systems containing AlB_2 (data not shown): also in this case the best result was obtained for the binary mixture containing aluminum boride, which released all the previously absorbed hydrogen amount in just 100 min, while the system with the two borides desorbed in twice this time, which is still better than the desorption time needed by the $CaH_2 + MgB_2$ system (see Fig. 2). In addition, a second hydrogenation test showed the better behaviour of the $CaH_2 + AlB_2$ binary system, which was able to restore the highest hydrogen capacity percentage if referred to the theoretical capacities of each system, as reported in Table 2.

4. Conclusions

We performed manometric and coupled manometric–calorimetric measurements to investigate the sorption properties of the $CaH_2 + MgB_2$ system after different ball milling times. The results showed a better kinetics for samples milled for longer time (900 min). The sample could absorb 6.0 wt% of hydrogen at 360 °C and initial hydrogen pressure of 120 bar, but in a long time (60 h). All the absorbed hydrogen could be released at 390 °C, but the system exhibited not full reversibility due to unbound Mg and B formed during the desorption process. The coexistence of MgB_2 and AlB_2 in the starting system gives worse performances with respect to the $CaH_2 + MgB_2$ binary system, while the total substitution of the magnesium boride with aluminum boride revealed very interesting sorption properties. As a matter of fact, the $CaH_2 + AlB_2$ system is able to absorb almost the full theoretical capacity (5.9 wt% vs. 6.3 wt%). Also desorption and re-hydrogenation kinetics resulted quite improved, thus indicating this system as an interesting one to be pursued on with further studies.

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