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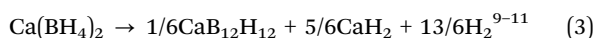
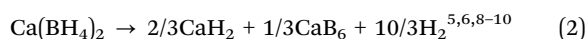
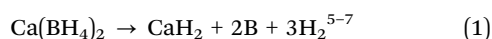
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Ca(BH₄)₂–Mg₂NiH₄: on the pathway to a Ca(BH₄)₂ system with a reversible hydrogen cycle

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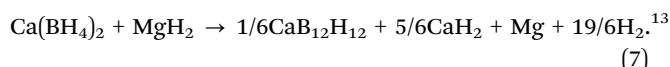
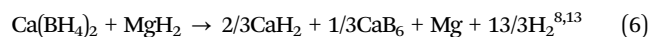
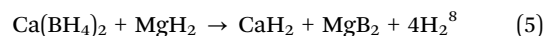
The Ca(BH₄)₂–Mg₂NiH₄ system presented here is, to the best of our knowledge, the first described Ca(BH₄)₂-based hydride composite that reversibly transfers boron from the Ca-based compound(s) to the reaction partner. The ternary boride MgNi_{2.5}B₂ is formed upon dehydrogenation and the formation of Ca(BH₄)₂ upon rehydrogenation is confirmed.

Due to their high gravimetric H₂ density, metal borohydrides¹ are promising candidates for solid state hydrogen storage. However, high thermal stabilities as well as poor reversibility of their decomposition products are the major obstacles to be overcome for technical applications. One of the most promising approaches to solve the reversibility issue of borohydrides is to combine them with selected materials to create reversible reactive compositions with lowered reaction enthalpy, the so-called reactive hydride composites (RHCs).^{2,3} The system that has attracted the most attention in recent years is LiBH₄–MgH₂.⁴ Because of its reduced desorption enthalpy compared to LiBH₄, mixtures of hydrides based on Ca(BH₄)₂ were also investigated intensively. Unfortunately, all systems presented so far have suffered from sluggish hydrogen reaction kinetics and poor reversibility. One reason for the latter finding is the tendency of Ca(BH₄)₂ to form kinetically stable side products upon dehydrogenation that hinder a complete rehydrogenation. In the case of pure Ca(BH₄)₂, several desorption paths are proposed in the literature:



In fact, recent reports have indicated that the decomposition of Ca(BH₄)₂ may follow more than one single reaction path.^{6,12} In these studies, the respective decomposition products and their ratio partially depend on the applied hydrogen back-pressure as well as the dehydrogenation temperature.^{6,12}

Also for the hydride composite Ca(BH₄)₂–MgH₂,^{8,13–16} several possible decomposition pathways are reported in the literature:



For this system, Bonatto-Minella *et al.* demonstrated a reversibility of approximately 55% between subsequent cycles.¹⁵ The authors rule out the possibility that the hydride composite desorbs according to eqn (5). Instead, the formation of CaB₆ was confirmed to be the cause of the partial reversibility (eqn (6)), which was also reported earlier by Kim *et al.*^{8,16} Bonatto-Minella *et al.* suggested that Mg promotes a better reversibility of the composite compared to pure Ca(BH₄)₂ by acting as a nucleation agent for CaB₆ due to the low *d*-value mismatch {111}_{CaB₆}/ {1011}_{Mg} of only 0.6%.¹⁵ Consequently, this mixture cannot be considered as a typical RHC since the overall desorption enthalpy is not lowered by the formation of reaction products between Ca(BH₄)₂ (including its decomposition products) and Mg/MgH₂. The drop in reversible capacity is attributed to the formation of CaB₁₂H₁₂ which has too high kinetic barriers to reversibly form Ca(BH₄)₂ under moderate temperature and hydrogen pressure conditions.¹³ Therefore, this kinetically stable phase acts as a boron sink upon cycling.

In order to obtain complete reversibility for Ca(BH₄)₂-based systems, a reaction partner has to be identified that can reversibly and effectively bind boron, hence preventing the formation of competing stable phases like CaB₁₂H₁₂ or amorphous boron. This compound should be lightweight and preferably store hydrogen itself. Mg₂NiH₄,^{17–20} which has a hydrogen capacity of 3.6 mass%, matches these criteria. Vajo *et al.* showed that a mixture of LiBH₄ and Mg₂NiH₄ forms the ternary boride MgNi_{2.5}B₂ upon desorption

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which can act as boron donor to form LiBH_4 again.^{21,22} Later Afonso *et al.* confirmed a similar reaction mechanism for the composite $\text{NaBH}_4\text{-Mg}_2\text{NiH}_4$.²³

In this work, the dehydrogenation reactions of the system $\text{Ca}(\text{BH}_4)_2\text{-Mg}_2\text{NiH}_4$ have been investigated for the first time. Furthermore, the potential for complete rehydrogenation of the desorbed products is demonstrated. For all experiments shown in this work, an initial mixture of $\text{Ca}(\text{BH}_4)_2$ and Mg_2NiH_4 in a molar ratio of 1 : 2.5 was prepared by 5 hours of ball milling.[†] To investigate the thermal dehydrogenation path, an *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD) experiment was performed applying a temperature ramp of 5 K min^{-1} heating from ambient temperature to $450\text{ }^\circ\text{C}$ at 1 bar H_2 (Fig. 1). The room temperature diffraction pattern exhibits the diffraction peaks of the low-temperature monoclinic phase ($C12/c1$) of Mg_2NiH_4 and its high-temperature cubic phase ($Fm\bar{3}m$) (weight ratio approx. 2.3 : 1). Diffraction peaks of $\text{Ca}(\text{BH}_4)_2$ can be attributed to the α -($F2dd$) and γ -phase ($Pbca$), with a weight ratio of roughly 5 : 1. The first event with rising temperature is the polymorphous change from α -/ γ - $\text{Ca}(\text{BH}_4)_2$ to β - $\text{Ca}(\text{BH}_4)_2$ ($P\bar{4}$), which starts at about $174\text{ }^\circ\text{C}$. The second modification in the diffraction pattern is related to another polymorphous change: the monoclinic Mg_2NiH_4 converts to the cubic phase at approx. $244\text{ }^\circ\text{C}$. At about $318\text{ }^\circ\text{C}$, Mg_2NiH_4 starts to decompose to Mg_2Ni and hydrogen. At slightly higher temperatures, the intensity of $\text{Ca}(\text{BH}_4)_2$ diffraction peaks starts to decrease, while the peaks of four other phases occur and intensify, namely $\text{MgNi}_{2.5}\text{B}_2$, Mg , CaH_2 and an unknown phase. With further temperature increase, the peaks of Mg_2Ni first grow until the maximum intensity is reached at roughly $365\text{ }^\circ\text{C}$, followed by a quick decline of peak intensity. The peaks of $\text{MgNi}_{2.5}\text{B}_2$, Mg and CaH_2 grow during the remaining heating period and the following isothermal region at $450\text{ }^\circ\text{C}$. In contrast, the peaks of the unknown phase only grow until the highest intensity is attained at about

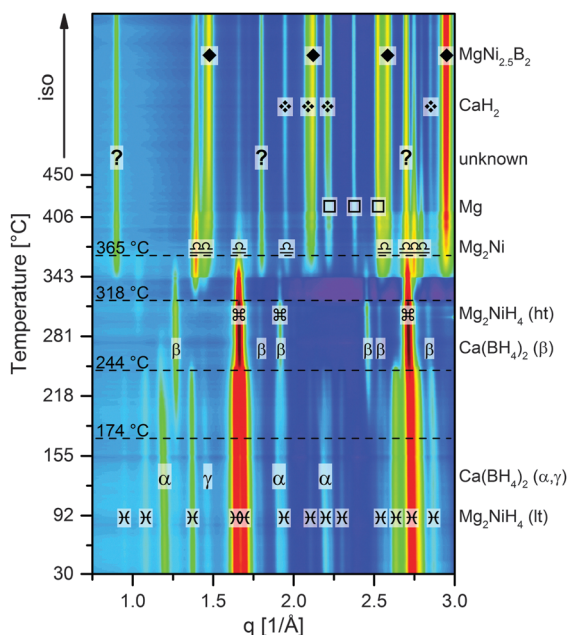


Fig. 1 *In situ* SR-PXD analysis of $\text{Ca}(\text{BH}_4)_2\text{-Mg}_2\text{NiH}_4$, the sample was heated at 5 K min^{-1} from RT to $450\text{ }^\circ\text{C}$ at 1 bar H_2 .

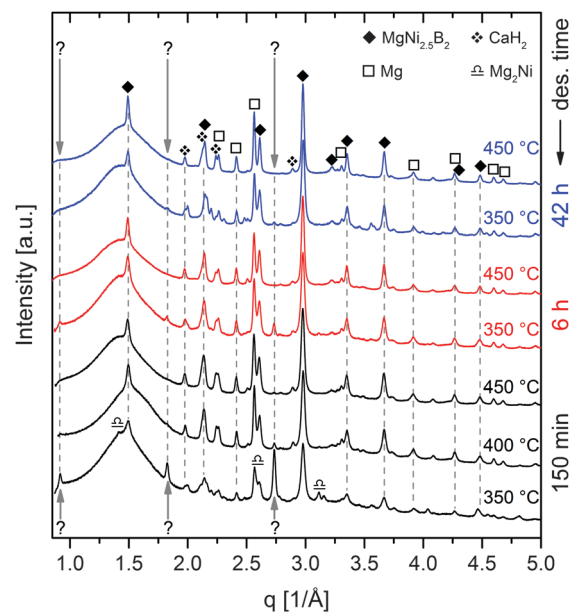


Fig. 2 *Ex situ* PXD pattern of $\text{Ca}(\text{BH}_4)_2\text{-Mg}_2\text{NiH}_4$ desorbed at 1 bar H_2 and different final temperatures and times, respectively.

$410\text{ }^\circ\text{C}$, then the peak intensities reduce much slower than those of Mg_2Ni . Moreover, it must be emphasised that the diffraction peaks of $\text{Ca}(\text{BH}_4)_2$ vanish already at about $365\text{ }^\circ\text{C}$, that is when $\text{MgNi}_{2.5}\text{B}_2$ and the unknown phase, which potentially contains boron, are still growing. This finding strongly suggests the possibility of Mg_2Ni reacting with the decomposition products of $\text{Ca}(\text{BH}_4)_2$, *i.e.* CaB_6 , CaB_xH_y and/or amorphous boron. Furthermore, the sequence of peak intensity changes for the different phases suggests that the unknown phase is a yet unreported Mg–Ni–B-phase. Since the reaction kinetics for the dehydrogenation are too sluggish to monitor the complete process by means of *in situ* SR-PXD, additional material was desorbed at a pressure of 1 bar H_2 in a Sieverts apparatus and then characterised using *ex situ* laboratory Powder X-ray Diffraction (PXD). Fig. 2 shows the diffraction patterns[‡] of seven different samples. All samples were heated to their respective maximum temperatures with 3 K min^{-1} ; subsequently the material was kept under isothermal conditions for different times. Diffractograms with the same colour represent samples with equal total desorption time, *i.e.* the isothermal time was altered in such a manner that the overall time of both, heating period and isotherm, was equal for desorptions of the same set. Diffractograms of samples with a total desorption time of 150 minutes are shown in black. Red and blue diffractograms indicate total desorption times of 6 and 42 hours, respectively. The sample heated up to $350\text{ }^\circ\text{C}$ for 150 min shows the peaks of Mg_2Ni and the unknown phase besides those of $\text{MgNi}_{2.5}\text{B}_2$, Mg and CaH_2 . However, compared to the *in situ* SR-PXD pattern at $350\text{ }^\circ\text{C}$ the ratios of the individual phases are different: Mg_2Ni almost vanished whereas the peaks of the unknown phase are much more pronounced than at any temperature in the *in situ* experiment. Hence, it can be deduced that the reaction path leading to this unknown phase is more dominant at lower temperatures. Nevertheless, looking at the PXD patterns of the material desorbed at $350\text{ }^\circ\text{C}$ with longer isotherms, the peaks of the unknown phase first decline (6 h)

absorption. Consequently, aside from its ability to act as a boron-donor for the formation of LiBH_4 and NaBH_4 , $\text{MgNi}_{2.5}\text{B}_2$ also exchanges boron reversibly with $\text{Ca}(\text{BH}_4)_2$. The ^{11}B spectrum of the reabsorbed material also shows another small resonance peak at -14.7 ppm which cannot be assigned clearly. However, it can be assumed that it belongs to a $(\text{B}_x\text{H}_y)^{z-}$ -phase that could be an intermediate product in $\text{Ca}(\text{BH}_4)_2$ formation. The NMR spectrum indicates a converted fraction to $\text{Ca}(\text{BH}_4)_2$ of roughly one-third. However, the reabsorption did not complete under the applied conditions since there is still a high fraction of $\text{MgNi}_{2.5}\text{B}_2$ present in the absorbed sample. At the moment the reason for this limited reconversion is not clear yet. Since the PXD analysis of the reabsorbed sample (not presented here) only shows very small and broad $\text{Ca}(\text{BH}_4)_2$ reflexes, the $\text{Ca}(\text{BH}_4)_2$ crystallites seem to be rather small. Hence, crystallite growth appears to be restricted. Further studies will have to clarify which microstructure develops and whether the reconversion into the initial hydride is confined in some way. For instance, the reconversion may be restricted to interface areas between the desorbed reactants, and the newly formed $\text{Ca}(\text{BH}_4)_2$ may act as a diffusion barrier, leading to reduced kinetic rates and thus an incomplete rehydrogenation.

In summary, the reactive hydride composite $\text{Ca}(\text{BH}_4)_2$ - Mg_2NiH_4 features a complete boron transfer from $\text{Ca}(\text{BH}_4)_2$ to $\text{MgNi}_{2.5}\text{B}_2$ upon dehydrogenation. No other boron-containing phases were present among the decomposition products; this includes especially the inactive phases amorphous boron and $\text{CaB}_{12}\text{H}_{12}$. Hence, a degradation of the hydrogen storage capacity caused by these boron sinks, as observed in pure $\text{Ca}(\text{BH}_4)_2$ ^{6,7,11} or $\text{Ca}(\text{BH}_4)_2$ - MgH_2 ,^{13–15,24} can be ruled out for this composite. Mg_2NiH_4 destabilises $\text{Ca}(\text{BH}_4)_2$ at a hydrogen pressure of 1 bar resulting in the lowering of desorption temperatures by about 55 K as compared to pure $\text{Ca}(\text{BH}_4)_2$. These dehydrogenation conditions might still be above the desired temperature range for technical applications. However, the absence of boron sinks must be considered as a substantial improvement of $\text{Ca}(\text{BH}_4)_2$ based RHCs. Further optimisation of the material preparation should reduce the desorption temperatures at least down to the level of Mg_2NiH_4 . Although the system did not reabsorb entirely, it was proven that the formation of $\text{Ca}(\text{BH}_4)_2$ starting from $\text{MgNi}_{2.5}\text{B}_2$ as boron-donor is thermodynamically and kinetically possible. Reabsorption conditions have not been optimised yet. Hence, it is likely that rehydrogenation could also be achieved at lower temperatures and pressure. Moreover, no additives were used within this study. Therefore, further improvements of the hydrogen sorption kinetics may be feasible.

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Notes and references

† The milling was performed in a SPEX 8000M Mill using stainless steel milling vials and stainless steel balls with a diameter of 10 mm. A ball-to-powder ratio of 10:1 was employed.

‡ The background of each diffraction pattern has a broad amorphous peak between 1 and 2 \AA^{-1} which is caused by the PMMA sample holder used to protect the material from air.

§ Typically, Mg_2NiH_4 features only one single desorption peak. The presence of the double peak is a kinetic effect. A possible explanation could be a kinetic separation between nucleation and growth of $\text{Mg}_2\text{Ni}^{25}$ as a consequence of the rather low activation energy for desorption and a rather homogeneous particle size distribution after 5 h of ball milling.

¶ Due to absorption and a small leakage the pressure dropped to approx. 180 bar at the end of the synthesis.

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