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Supporting Information for "A Hydride Composite Featuring Mutual Destabilisation and Reversible Boron Exchange: Ca(BH$_4$)$_2$-Mg$_2$NiH$_4$"

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### Results of X-ray Raman Scattering experiments

In order to complement the data provided by X-ray diffraction and nuclear magnetic resonance (NMR), we performed a complementary study of the environment of calcium with X-ray Raman Spectroscopy (XRS), which yields similar spectra as soft x-ray absorption spectroscopy (XAS) but in a bulk-sensitive fashion. Details concerning the technique are available in literature [1].

The XRS experiment was performed using the 72-element X-ray Raman spectrometer on the beamline ID20/UPBL6 of the European Synchrotron Radiation Facility (ESRF) [2]. The beam was monochromated using a Si(111) double crystal and Si(311) channel-cut monochromators, and focused to a spot size of 20 x 20 µm. The spectrometer employs Si(660) analysers that reflect X-rays with a fixed photon energy of 9.69 keV with an energy resolution of 0.6 eV. Spectra were collected at room temperature. A suitable background was subtracted from the spectra and they were normalized over the whole edge intensity to a fixed area in the range 345–360 eV.

Figure SI1 shows the Ca L$_{2,3}$ edges of Ca(BH$_4$)$_2$-Mg$_2$NiH$_4$ decomposed under two different conditions, namely 350°C for 150 minutes and 450°C for 42 hours. Two broad peaks are evident at the energies of 348.5 and 352 eV, corresponding to the transitions from 2p$_{3/2}$ and 2p$_{1/2}$ states, respectively. The spectra are rather similar but there is a small shift toward

lower excitation energies with higher level of decomposition. We analysed the spectra with a multi-component fitting of these Ca L$_{2,3}$ edges performed with the shown reference compounds. This is an established method for the quantitative evaluation of phase fractions [3]. The best fit is obtained with the scenario that the Ca(BH$_4$)$_2$ decomposes according to the partial reaction: Ca(BH$_4$)$_2$ -> a CaH$_2$ + b CaB$_6$ /Ca(BH$_4$)$_2$ + c Ca-free boron compounds + d H$_2$.

Figure SI1: (Upper panel) Ca L$_{2,3}$ edges of Ca(BH$_4$)$_2$-MgNi$_{2.5}$B$_2$ decomposed in different thermodynamic conditions (continuous lines) and their multi component fitting (dashed lines). (Lower panel) Ca L$_{2,3}$ edges of reference materials.
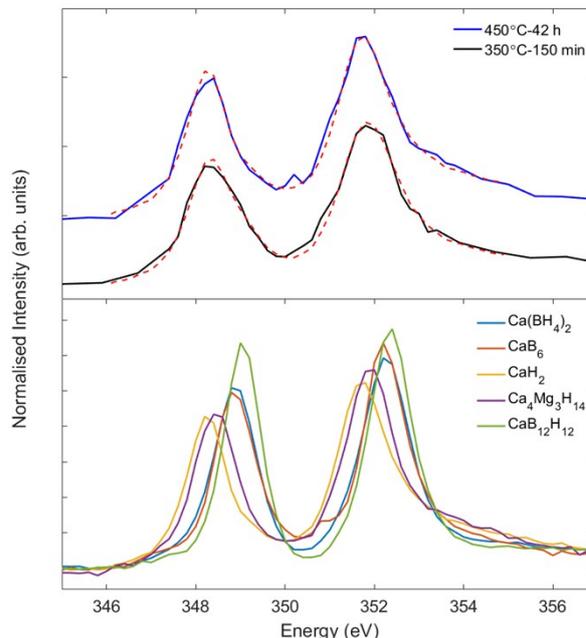
Since Ca(BH$_4$)$_2$ and CaB$_6$ have absorption edges at the same energies, our XRS results are not able to distinguish between these components. Furthermore, our best fit is obtained when neglecting contributions of CaB$_{12}$H$_{12}$, thus supporting the results of the complementary techniques, which tend to minimize the formation of CaB$_{12}$H$_{12}$ as a stable product.

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At 350°C, a=0.78 and b=0.22, providing an amount of free, elemental boron, corresponding to a stoichiometry of c=0.68. At 450°C, the reaction further progresses with a=0.96 and b=0.04, resulting in c=1.76.

Calcium hydride (CaH_2) is the best fit for the main product and its overall stoichiometry depends on the reaction conditions. A minor fraction of the side product CaB_6 is clearly produced, at the decomposition of the composite material, most likely for all the reported reaction conditions as suggested by NMR.

Boron is progressively released while the reaction advances: most of it is released as $MgNi_{2.5}B_2$ directly and in minor amounts as CaB_6, $CaB_{12}H_{12}$ and elemental boron that are then further consumed for the formation of $MgNi_{2.5}B_2$. The amount of boron in the dehydrogenation products increases with the increasing time, namely at 450°C after 42 hours.

We also collected x-ray absorption near edge spectra (XANES) at the Ni K edge in order to explore the products from the perspective of the local environment of nickel atoms. We collected these XANES data on the beamline ID20/UPBL6 at the ESRF while using the previously described beamline setup together with Si-drift detector. Results are shown in Figure SI2.
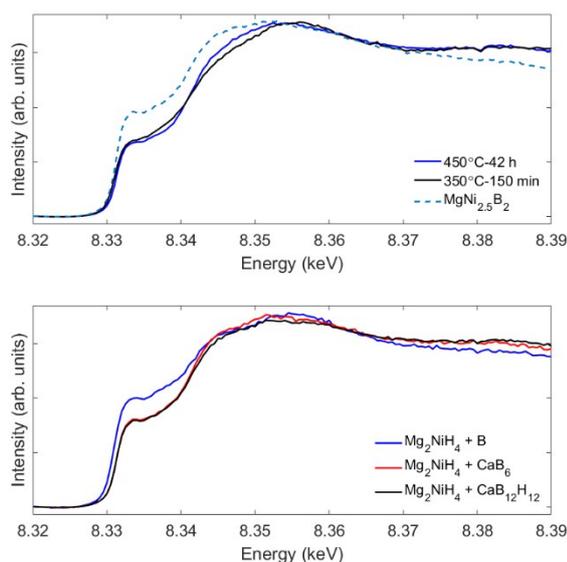

Figure SI2: (Upper panel) XANES spectra of the Ni K edge of the composite $Ca(BH_4)_2$-$MgNiH_4$ decomposed in two different thermodynamic conditions and of the reference material $MgNi_{2.5}B_2$. (Lower panel) XANES spectra of the products of the reactions between $MgNiH_4$ and B, CaB_6 and $CaB_{12}H_{12}$.

Spectra are composed of a pre-peak at the energy of 8.332 keV and of a broad, main-peak region at 8.35 keV. The former feature is due to the sum of the contributions of the dipole allowed $1s$-$4p$ transition and $1s$-$3d$ transition happening as a consequence of the partial p-type character of nickel $3d$ states due to their hybridization with boron $2p$ states [4]. The latter feature, namely the main edge, is due to the absorption process involved in the dipole-allowed transition between $1s$-$4p$ states.

Normalizing the spectra to the area in the plotted range, the pristine $MgNi_{2.5}B_2$ exhibits a stronger pre-peak region intensity than the decomposed samples.

We compare the spectra with those of the products of the reactions between $MgNiH_4$, B, CaB_6 and $CaB_{12}H_{12}$, shown in the lower panel of figure SI2. These results are also complementary to PXRD and NMR data in the Figures 4 and 5 of the manuscript.

The reactions between $MgNiH_4$ and either CaB_6 or $CaB_{12}H_{12}$ produce XANES spectra comparable to the ones of the decomposed mixture of hydrides, while after the reaction between $MgNiH_4$ and B, the Ni K edge features stronger pre-edge peak and weaker EXAFS region.

From the analysis of these three reactions (detailed in Figure 4 and related paragraph in the manuscript), we know that both CaB_6 and $CaB_{12}H_{12}$ promote an almost complete transfer of boron to $MgNi_{2.5}B_2$ (96 and 97%, respectively), while the reaction with B transfers a fraction leaving unreacted elemental boron available (~28%) and a portion of the unknown phase.

In addition, the fraction of $MgNi_{2.5}B_2$ in the absorbed samples shown in figure 10 appears to suffer from a deficiency in the stoichiometry of boron.

We may conclude that such effect is mirrored in the local environment of nickel (and of its electronic structure), in particular affecting the availability of $3d$ low energy states in the conduction band that become available for the transition of the electron from the core level.

The difference that we see in the spectra corresponding to the reactions between Mg_2NiH_4, B, CaB_6 and $CaB_{12}H_{12}$, is comparable to the one that we observe between the spectra of the decomposed composite $Ca(BH_4)_2$-Mg_2NiH_4 and of the reference $MgNi_{2.5}B_2$. The weaker pre-edge features that we observe in the decomposed samples, arguably suggest that the decomposition process promotes a variable transfer of boron that happens to be more complete in the $MgNi_{2.5}B_2$ produced from the mixture $Ca(BH_4)_2$-Mg_2NiH_4 than the one in pure $MgNi_{2.5}B_2$.

Obtaining a quantitative description of this effect is not within the possibilities of our data, as SR-PXRD shown in Figure 6 does not exclude that the decomposition of $MgNiH_4$ also produces elemental Mg and Mg_2Ni that can coexist for temperatures higher than 450°C.

Nevertheless, the picture presented by XRS and XANES spectra is in agreement with the SR-PXRD and NMR results and strongly supports the conclusions of the manuscript, namely confirming the progress of the decomposition reaction as shown in equation (3) and providing strong hints of the mobility of boron within $MgNi_{2.5}B_2$.

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