**Experimental evidence of Na2[B12H12] and Na formation in the desorption pathway of the 2NaBH4 + MgH2 system**

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Experimental evidence of Na$_2$[B$_{12}$H$_{12}$] and Na formation in the desorption pathway of the 2NaBH$_4$ + MgH$_2$ system

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ABSTRACT: We report in the present work the desorption pathway of the $2\text{NaBH}_4 + \text{MgH}_2$ system. Measurements on samples heat treated up to 450 °C for different times have been performed by ex-situ X-ray powder diffraction (XRPD) and solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR). Ex-situ X-ray powder diffraction experiments conducted on full desorbed samples allowed to identify nanocrystalline MgB$_2$ and metallic Na as dehydrogenation products. $^{11}\text{B}$ and $^{23}\text{Na}$ NMR analyses have been also carried out in order to evaluate the structural evolution of decomposed materials. Our measurements show that the local structure of MgB$_2$ was influenced by the replace of Mg with Na atoms in the Mg sites. Moreover, amorphous Na$_2$[B$_{12}$H$_{12}$] was detected in the partially desorbed sample and in the final products of the decomposition reaction. The presence of the [B$_{12}$H$_{12}$]$^2^-$ anion was confirmed by both direct comparison with the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of pure Na$_2$[B$_{12}$H$_{12}$] and dynamic Cross Polarization experiments.

KEYWORDS: Hydrogen Storage, NaBH$_4$, MgH$_2$, Na$_2$[B$_{12}$H$_{12}$], Reactive Hydride Composites RHC, Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR), X-ray Powder Diffraction XRPD.
**11B NMR**

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INTRODUCTION: Light-weight and compact hydrogen storage is both a scientific and technological challenge. To store hydrogen in metal hydrides, thermodynamic and kinetic limitations associated with the hydrogen sorption process must be overcome \(^1\), \(^2\). Complex borohydrides represent a class of promising materials for hydrogen storage applications due to their high volumetric hydrogen density and gravimetric capacity \(^3\). In particular the alkaline and alkaline-earth borohydrides, as NaBH\(_4\), LiBH\(_4\), Mg(BH\(_4\))\(_2\) and Ca(BH\(_4\))\(_2\), have recently received considerable attention as potential hydrogen storage materials \(^4\)-\(^7\). The drawback is that in these materials B and H form strong covalent bonds. This leads to very thermodynamically stable hydrides (e.g. NaBH\(_4\), \(\Delta H_f = -191.4\) kJ/mol \(^8\)) and the high negative values of the formation enthalpies result in the high temperatures required for the dehydrogenation step.

Thermodynamic destabilization is an approach introduced by Reilly and Wiswall in the 1960s, where the basic concept was to use alloys in order to make the hydrides thermodynamically less stable \(^9\). A classical example is the Mg\(_2\)Ni alloy, which can be hydrogenated to Mg\(_2\)NiH\(_4\), with a modest reduction in the thermodynamic stability. Indeed, the addition of non-hydrogen-containing elements/compounds produces a significant loss in hydrogen capacity and this is a typical problem for the destabilization of a single phase hydride.

Recently, a large number of very promising mixed systems with suitable thermodynamic properties has been predicted by Alapati et al. \(^10\). Multi-component hydrogen storage systems (also referred to in the literature as Reactive Hydride Composites), for example, comprise more than one phase in the hydrogen charged state in order to decrease the dehydrogenation and hydrogenation temperature and, at the same time, keep the high gravimetric capacity of the system \(^10\). Typically, one of the phases in the system is a complex borohydride, thanks to the already quoted high hydrogen gravimetric and volumetric capacity of this class of materials. The other phase is a metal hydride such as MgH\(_2\) (e.g. 2NaBH\(_4\)+MgH\(_2\); LiBH\(_4\)+MgH\(_2\)), but the addition of other metal hydride phases was also tried (e.g. TiH\(_2\)) \(^12\)-\(^14\).
The NaBH₄/MgH₂ multi-component system has a high gravimetric capacity, high volumetric hydrogen density and a rather low dehydrogenation temperature compared to the single borohydride compound. Moreover, its resistance to moisture and low price (< 1€/g) make this system an optimal model for the more attractive Ca(BH₄)₂/MgH₂ and LiBH₄/MgH₂ reactive hydride composites.

For the NaBH₄/MgH₂ system a considerable number of papers are present in the literature. These works concern the investigation of several aspects, as the influence of different additives on the kinetic sorption performance, the reversibility, the thermodynamic properties, and the dehydrogenation-rehydrogenation mechanism. Regarding the desorption mechanism, the decomposition of the 2NaBH₄ + MgH₂ system occurs, in a first step, via the dehydrogenation of MgH₂ to Mg and, subsequently, when the decomposition of NaBH₄ takes place, with the formation of the destabilizing MgB₂ compound. Structural investigation on the desorption pathway of the 2NaBH₄ + MgH₂ mixture by in-situ Synchrotron X-ray and Neutron powder diffraction analysis confirmed that the process follows a multi-step reaction. Moreover, the formation of Na₂[B₁₂H₁₂] is also proposed during the intermediate step in the desorption process of the 2NaBH₄ + MgH₂ system. However, the Na₂[B₁₂H₁₂] formation has not been confirmed yet by any structural probe. The same applies for the formation of metallic sodium.

Recent theoretical and experimental studies demonstrated the presence of the [B₁₂H₁₂]²⁻ anion in the partially decomposed single borohydrides of Li, Mg, and Ca. On the other hand, the formation of the [B₁₂H₁₂] specie is not found in the multi-component systems based on borohydrides, as reported by Leon L. Shaw et al., and U. Bösenberg et al., for the 2LiBH₄ + MgH₂ system.

Solid-state ¹¹B NMR experiments have been conducted to identify the reaction intermediates and products formed in the amorphous phase during the thermal hydrogen desorption of metal tetrahydroborates. Since identification of these closo-dodecahydrododecaborates is severely hampered by the absence of clearly discernible X-ray or neutron diffraction peaks from dehydrogenated samples, solid-state NMR spectroscopy represents a powerful tool to identify such phases.
In this work, new results on the evolution of the phases upon desorption of the $2\text{NaBH}_4+\text{MgH}_2$ system are obtained by *ex-situ* solid-state NMR and XRPD experiments. Interestingly, the two techniques gave a tangible evidence of the formation of metallic Na and $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$ phase, respectively.

**EXPERIMENTAL DETAILS:** NaBH$_4$ and MgH$_2$ commercial powders were purchased from Aldrich (98% purity) and Tego Magnan (95% purity), respectively. In order to obtain a homogeneous mixture, NaBH$_4$ and MgH$_2$ were ball-milled for 20 h in a 2:1 molar ratio by means of a Planetary Fritsch Pulverisette P5 mill. The powders were sealed in 4 stainless steel vials (250 ml capacities each one) in order to prepare a large amount of material. The milling was performed under an argon atmosphere with 7 balls (7 g), a ball to a powder mass ratio of 10:1 and a plate rotation speed of 230 rpm. It should be noted that the powders were always manipulated inside a glove box (MBrain-20-G) in a high-purity argon atmosphere with O$_2$ and H$_2$O levels below 0.1 ppm.

The as-milled powders were annealed at different temperatures in the range of 350-450 °C (with no holding time) and at 450 °C for diverse times of isothermal holding (15 min, 1, 2, 3, 4, 5, 10 and 15 h). In particular, 200 mg of milled powders were put inside an alumina crucible and thermally treated under Ar in a furnace placed inside the glove box. The heating and cooling rates were chosen to be 2 and 10 °C min$^{-1}$, respectively.

The compositional and structural properties were investigated by XRPD using a BrukerD5005 diffractometer with Cu Kα$_1$ radiation ($\lambda = 0.15406$ nm). The powders were placed in a suitable sample holder (Bruker A100B36) to avoid oxidation during the analysis. In this device, the powders were dispersed, under Ar atmosphere in the glove- box, on a 20 mm diameter silicon wafer with high-index surface orientation. The Si slice is fixed on a low background plastic disk, which is sealed to a low background domelike plastic cap by means of a polymeric O-ring. The microstructural parameters were evaluated by fitting the full XRPD patterns using MAUD (Materials Analysis Using Diffraction), a Rietveld refinement program.$^{26}$
Solid state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker Avance 400 MHz spectrometer with a wide bore 9.4 T magnet and by employing a boron-free Bruker 4 mm CPMAS probe. The spectral frequencies were 128.33 MHz for the $^{11}$B nucleus and 105.85 for the $^{23}$Na nucleus. The NMR chemical shifts were reported in parts per million (ppm) externally referenced to BF$_3$ O(CH$_2$CH$_3$)$_2$ and NaCl, respectively. The powder materials were packed into 4 mm ZrO$_2$ rotors in an argon-filled glove box and were sealed with tight fitting Kel-F caps. Sample spinning was acted using dry nitrogen gas. MAS experiments were performed at room temperature at sample rotation frequencies varying between 9 and 12 kHz. The one dimensional (1D) $^{11}$B MAS-NMR spectra were acquired after a 2.7 $\mu$s single $\pi/2$ pulse (corresponding to a radiofield strength of 92.6 KHz) and with the application of a strong $^1$H signal decoupling by using the two-pulse phase modulation (TPPM) scheme $^{27}$. The recovery delay was set to 10 seconds. Spectra were acquired at 20 ºC, with the temperature controlled by a Bruker BCU unit.

For the preparation of Na$_2$[B$_{12}$H$_{12}$], acid/base and cation exchange resins were utilized. Neutralization of [Et$_3$NH]$_2$[B$_{12}$H$_{12}$] with NaOH yielded the Na$_2$[B$_{12}$H$_{12}$] salts. The chemicals used, namely hydroxides and chloride salts, were received from Sigma Aldrich and used as purchased. Details of the synthesis route are reported in a previous work $^{28}$. 


RESULTS AND DISCUSSION:

Heat treatments of the 2NaBH₄ + MgH₂ mixture: ex-situ X-ray powder diffraction characterization

We showed in previous papers¹²-¹⁵ that dehydrogenation of 2 NaBH₄ + MgH₂ mixture takes place in two steps, according to the reaction scheme:

\[
2\text{NaBH}_4 (s) + \text{MgH}_2 (s) \rightarrow \text{Mg} (s) + \text{H}_2 (g) + 2 \text{NaBH}_4 (s) \quad \text{eq.1}
\]

\[
2\text{NaBH}_4 (s) + \text{Mg} (s) \rightarrow 2\text{Na} (s) + \text{MgB}_2 (s) + 4\text{H}_2 (g) \quad \text{eq.2}
\]

with the first step starting at around 330 °C, with the release of 1.8 wt % H₂, and the second one taking place at a minimum temperature of 440 °C, with release of about 7.9 wt % H₂. Starting from these results, we chose 350 °C and 450 °C as the temperature values for thermal treatments suitable to study the desorption pathway of the system.

As it can be seen from XRPD patterns A in Figure 1a, annealing the 2NaBH₄ + MgH₂ mixture at 350 °C leads to the almost complete vanishing of the MgH₂ reflections, contrasted with formation of the Mg peaks, while NaBH₄ is still unreacted. In pattern B, corresponding to the sample treated at 450 °C, the peaks of NaBH₄, Mg and MgB₂ (2θ angle of 42.5°) are present, confirming that MgH₂ is completely decomposed, and that dehydrogenation of NaBH₄ just started at this temperature. In pattern C, corresponding to the sample kept at 450 °C for 15 min, the main peak of the Na phase appears at the 2θ angle of 29.5° (see also Fig. 1b). In addition, the intensity related to the reflections of the NaBH₄ and Mg phases decrease.
Figure 1. (a) Experimental (magenta circles) and fitted (blue lines) XRPD patterns for the 2:1 mixtures recorded at different temperatures and isothermal annealing: 350 °C (A), 450 °C (B), 450 °C + 15 min (C), 450 °C + 3 h (D), 450 °C + 10 h (E). Symbols: □ NaBH₄ (ICSD #74-1891), ⬆ Na (ICSD # 01-0832), □ MgO (ICSD # 38-1369), ◆ Mg (ICSD # 35-0821), ● MgB₂ (ICSD # 38-1369), ◆ MgH₂ (ICSD # 74-0934). (b) An enlargement of Figure a in the 25°-35° angular range.

Pattern D (450 °C, 3 h) confirmed this trend. Finally, for the mixture heat treated at 450 °C for 10h the peaks of the Na and MgB₂ phases were detected. Rietveld refinement of the experimental patterns proved that the crystallite size of MgB₂ was quite small, i.e. 70 ±5Å, in the mixture just heated at 450 °C and increased with the isothermal treatment prolonging up to the value of 393 ±5Å.

Remarkably, the formation of the Na phase was proven, confirming the full desorption of NaBH₄ and suggesting that Na cannot be seen during in situ XRPD measurements due to the fact it is in liquid state (melting T = 98 °C). At the end of the cooling step, the crystallization of the aforementioned phase is achieved and therefore easily detectable by XRPD measurements. It is important to remark that the formation of reactive Na during the dehydrogenation process could explain the fast re-absorption kinetics obtained for this system, as discussed in a previous work.

Table 1 reports the weight % fraction of the different phases detected in the patterns of Figure 1. As evident, desorption of MgH₂ and NaBH₄ starts at 350 °C and 450 °C, respectively, in agreement with
the results from the volumetric analysis. At 350 ºC (sample B), the dehydrogenation of MgH₂ to Mg is almost completed and only 4 wt. % of the hydride phase is still present at this step. A decrease in the Mg amount starts at 450 ºC until it disappears completely in the sample annealed for 10 hours.

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Table 1. Weight % fraction of the phases present in the XRPD patterns plotted in Figure 1. MgO⁺ amount detected is less than 1 wt. % for each mixture. To serve as reference, the weight % fraction of the as-prepared mixture is presented.

The formation of Na is closely related to the desorption of NaBH₄ and 3 wt. % of the metallic phase is detected in the mixture just heated at 450 ºC. Na amount increases up to 8 wt. % after 15 min of isothermal annealing at 450 ºC and, interestingly, drastically increases in the mixture that was heat treated for 3 h (sample D). The amount of NaBH₄ detected goes from 59 to 27 wt. % in the sample C and D, respectively, confirming that the maximum conversion rate of NaBH₄ to Na is achieved between sample C and D. In addition, a large amount of MgB₂ is detected for sample B. This trend can be explained considering that nanocrystalline MgB₂ is formed at a temperature below 450 ºC when free Mg is able to react with NaBH₄.
Solid-state $^{11}$B and $^{23}$Na MAS NMR study on the desorption process of the 2NaBH$_4$ + MgH$_2$ mixture

Solid-state MAS NMR technique was employed to identify the amorphous intermediates and final products formed during the decomposition reactions of the 2NaBH$_4$ + MgH$_2$ mixture. In Figure 2, $^{11}$B$^1$H$^1$ ($I = 3/2$) (a) and $^{23}$Na$^1$H$^1$ ($I = 3/2$) (b) NMR spectra of the starting 2NaBH$_4$ + MgH$_2$ mixture are displayed. Both $^{11}$B$^1$H$^1$ and $^{23}$Na$^1$H$^1$ have a single unique site in the asymmetric unite of cubic NaBH$_4$. A sharp line, indicated by the full width at half-maximum (FWHM) value, of 81 Hz at -42.04 ppm (Figure 2 a) is assigned to the boron nucleus in the tetrahedral [BH$_4^-$] units in NaBH$_4$. The peak for the $^{23}$Na spectrum (Figure 2 b) is located at -15.5 ppm with a half line width of about 165 Hz.

Figure 2. $^{11}$B$^1$H$^1$ (a) and $^{23}$Na$^1$H$^1$ (b) MAS (12 kHz) single pulse NMR spectra of the as prepared 2NaBH$_4$ + MgH$_2$ mixture. Spinning side bands are marked with *.

In Figure 3 the $^{11}$B$^1$H$^1$ (a) and $^{23}$Na$^1$H$^1$ (b) spectra of the 2NaBH$_4$ + MgH$_2$ mixture heated up to 350 °C (A), 450 °C (B) and 450 °C for 1h (C) are shown. Regarding $^{11}$B$^1$H$^1$ measurements, for spectra A, B and C, sharp peaks were assigned to [BH$_4^-$] units of NaBH$_4$. The chemical shift values observed...
are summarized in Table 2. In sample A, a chemical shift of -42.03 ppm was detected, in accordance with the typical chemical shift of pure NaBH₄ and the value obtained for the as-prepared mixture. In sample B and C, shifts of the central bands are imperceptible, being the chemical shifts of -42.04 and -41.96 ppm, respectively.

Figure 3. $^{11}\text{B}^{\{1\text{H}\}}$ (a) and $^{23}\text{Na}^{\{1\text{H}\}}$ (b) MAS (12 kHz) single pulse NMR spectra of the 2NaBH₄ + MgH₂ mixture: annealed at 350 °C (A), 450 °C (B) and 450 °C for 1 h (C). Spinning side bands are marked with *.

Apart from irrelevant deviations in chemical shift values, differences in line widths were detected. In general, there are several effects that result in a broadening of the central transition of a quadrupolar nucleus under magic angle spinning. Amongst them, a larger disorder in a material caused for example by small variations in bond lengths and angles can lead to distributions of chemical shift values and quadrupolar interaction parameters resulting in a broadening of the resonance. After annealing at 350 °C, 450 °C and 450 °C for 1 h, the $^{11}\text{B}^{\{1\text{H}\}}$ resonances of NaBH₄ present in the mixture were broadened compared to the as-prepared material. The FWHM values for the central transitions of the $^{11}\text{B}$ are shown in Table 2. It should be noticed that the constant increase of the central bands line
width in spectra A, B and C is most likely caused by the increase of disorder in the NaBH₄ phase during the desorption process.

Figure 3b displays the experimental $^{23}\text{Na} \{^1\text{H}\}$ spectra of the 2NaBH₄ + MgH₂ mixture collected at room temperature after annealing at 350 ºC, 450 ºC and 450 ºC for 1h. In spectrum A, the maxima $^{23}\text{Na} \{^1\text{H}\}$, -15.48 ppm, shows a similar chemical shift compared to the starting mixture reported in Figure 2b. As shown in Table 2, because the chemical shift values were still approximately the same for spectra B and C, we could suppose that the local structure of NaBH₄ is preserved. Moreover, as in the $^{11}\text{B} \{^1\text{H}\}$ profiles, the line width of $^{23}\text{Na} \{^1\text{H}\}$ spectra increased with the desorption evolution, confirming an enhancement in disorder in the material. Note that the absence of a peak at -11.09 ppm indicated that the formation of NaH at any stage of the sample processing is highly unlikely. This conclusion is also supported by careful examination of XRPD data, as discussed above.
Table 2. $^{11}$B{$^1$H} and $^{23}$Na{$^1$H} NMR parameters obtained by fit of the experimental spectra using a Lorentzian/Gaussian function. Observed isotropic chemical shift, $\delta_{iso}$ (±0.1 ppm), asymmetric parameter, L/G, and the full width at half-maximum, FWHM (±5 Hz), and corresponding assignments are reported.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>$^{23}$Na NMR parameters</th>
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<td>L/G</td>
<td>FWHM (Hz)</td>
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In Figure 3 $a$, spectra B and C, the appearance of broad peaks at -98.97 (FWHM = 1983 Hz) and -98.26 ppm (FWHM = 1929 Hz), respectively, was reported. These broad peaks can be assigned to solid MgB$_2$ by direct comparison with the starting material, confirming its formation when the 2NaBH$_4$ + MgH$_2$ mixture is heat treated at temperatures close to 450 ºC. Note that the broadening of the
centerband line width of MgB$_2$ in B and C suggests that the size of the MgB$_2$ crystals is very small, in agreement with prior XRPD studies. Regarding the line width, a small increase in the FWHM values was observed in spectra B and C. On the contrary, a significant decrease in line width of the MgB$_2$ resonance was detected in the spectrum of the mixture heated at 450 °C for 2h (Figure 4, spectrum A). In this case, the MgB$_2$ peak is located at 97.55 ppm and presented a line width of 1768 Hz. Note that this value is almost similar to the data reported for the mixture annealed at 450 °C for 3, 4, 5 and 15h (see Table 2).

**Figure 4.** $^{11}$B{$^{1}$H} (12 kHz) single pulse NMR spectra of the 2NaBH$_4$ + MgH$_2$ mixture: annealed at 450 °C for 2 h (A), 450 °C for 3 h (B) and 450 °C for 15 h (C).

In Figure 4 the experimental $^{11}$B{$^{1}$H} MAS spectra of the mixture heat treated at 450 °C for 3 and 15 h (spectrum B and C, respectively) are also shown. If we focus on this picture, it is possible to establish that the intensity of the MgB$_2$ peak increases from A to C, whereas the NaBH$_4$ peak also appears, although with at a low intensity, in the chemical shift range of – 42.14 ±0.1 ppm. In spectrum B, the
peak corresponding to the [BH₄]⁻ unit has almost disappeared, suggesting that the complete desorption of NaBH₄ was already been achieved after only two hours of heat treatment at 450 ºC. Unfortunately, the low quality of the spectrum did not allow us to quantify the relative amount of the singular phase present in all spectra. However, it is not plausible that the dehydrogenation is almost completed for this mixture. In fact, from the volumetric measurements, the sample heated at 450 ºC for 3 hours contains 20 wt. % H₂ compared to the as-prepared mixture. Therefore, one reason could be the high broadening of the NaBH₄ peak that could be then confused with the background of the spectrum.

A second reason could be ascribed to the nature of the MgB₂ peak. It is know that MgB₂ crystallizes in the fairly simple AlB₂-type structure, consisting of alternating hexagonal layers of Mg atoms and graphite-like honeycomb layers of B atoms. As for the graphite, the layer of boron in MgB₂ conduces to high delocalization of the electrons and introduces the anisotropic bulk magnetic susceptibility that cannot be completely removed by MAS. In a MAS spectrum, the line broadening effect attributed to the anisotropic magnetic susceptibility is influenced by the layered structure size. Indeed, larger layered structure corresponds with strong line broadening effect. Thus, the spectra resolution of MgB₂ would improve when the material is diluted with another phase, such as Na, that does not contain layered structure.

At temperatures above 350 ºC, an interface reaction between NaBH₄ and Mg takes place. In this step, the formation of a small amount of MgB₂, less than 10 wt. %, is achieved. Therefore, the dehydrogenation of the NaBH₄ phase starts at a temperature that is slightly lower than 450 ºC, (440 ºC is the value resulting from the volumetric measurements). The release of hydrogen from the [BH₄]⁻ groups lead to boron atoms being reorganized in a structure like graphite with the magnesium atoms located between the boron layers. It is plausible to suppose that, during this process, a significant number of magnesium sites could be exchanged with atoms of sodium influencing the electronic structure of the MgB₂ phase. As reported in our recent work, the magnetic properties of the magnesium diboride were also affected by the incorporation of Na in its structure. This event could be the key
reason for the observed narrowing of the MgB$_2$ peaks described above, in accordance with the similar
effect observed by J-Z. Hu et al. $^{34}$.

Figure 5 $a$ shows the experimental spectra for the mixture heated at $450 \, ^\circ C$ for 2 h collected at 12 kHz
with proton Composite-Pulse Decoupling (magenta circles) and without proton Composite-Pulse
Decoupling (blue line).

**Figure 5.** ($a$) $^{11}$B{$^1$H} (magenta circles) and $^{11}$B (blue line) MAS (12 kHz) single pulse NMR spectra of
the 2NaBH$_4$ + MgH$_2$ mixture annealed at $450 \, ^\circ C$ for 2 h. ($b$) $^{11}$B{$^1$H} (magenta circles) and $^{11}$B (blue
line) MAS (9 kHz) single pulse NMR spectra of the 2NaBH$_4$ + MgH$_2$ mixture annealed at $450 \, ^\circ C$ for
2h. The abbreviation $^{11}$B, instead of $^{11}$B{$^1$H}, indicates a typical boron NMR experiment conducted
without a Composite-Pulse Decoupling (CPD) signal. Spinning side bands are marked with *.

High-resolution NMR spectroscopy of $^{11}$B in the solid state is normally rendered difficult due to the
strong heteronuclear $^1$H–$^{11}$B dipolar couplings. Even under very high-speed magic-angle spinning
(MAS), these couplings are not completely removed. The undesirable result is a decreasing in the
intensity signal. Composite-Pulse Decoupling (CPD) allows us to obtain high-resolution NMR spectra
and, particularly in this work, it was very useful to distinguish between species that contain boron atoms bonded with H-atoms.

In the spectrum acquired without decoupling the proton (blue line), a decrease of the signal relative to the \([\text{BH}_4]^+\) unit at -42.14 ppm was observed. For the MgB\(_2\) signal located at 97.55 ppm, it is possible to evaluate that its intensity is not influenced by proton CPD. This behaviour is due to the fact that these species contain B-atoms that are not bonded with hydrogen. However, it can be clearly observed that the signal for one of the MgB\(_2\) sidebands (*), located at 1.1 ppm, decreases when the experiment is conducted without proton CPD. Moreover, the shape of this sideband is very anomalous, which is also the case if compared with the other one. In order to clarify this point, a further NMR experiment on the same powders was acquired at 9 kHz (Figure 5b). In this spectrum, an unidentified phase, characterized by a broad featureless line, was detected in the chemical shift range 0 to -25 ppm. Note that the signal of the broad peak increased in the proton decoupling experiment (blue line), suggesting that B-H species are present in this phase. Furthermore, in earlier work, this signal has been attributed to \([\text{B}_n\text{H}_m]\) species which were observed during the decomposition process of LiBH\(_4\) or similar materials M(BH\(_4\))\(_n\)\(^{21,35-37}\).

In Figure 6a, the experimental spectra for the mixture heated at 450 °C for 15 h collected at 9 kHz with proton CPD (magenta circles) and without proton CPD (blue line), are displayed. The measurements proved that the broad signal assigned to the \([\text{B}_n\text{H}_m]\) species can also be observed at the end of the desorption process. Moreover, a very small signal of NaBH\(_4\) was still present.
Figure 6. (a) $^{11}$B\textit{\{H\}} (magenta circles) and $^{11}$B (blue line) MAS (9 kHz) single pulse NMR spectra of the 2NaBH$_4$ + MgH$_2$ mixture annealed at 450 °C for 15 h. (b) Zoom inset of the spectrum in Figure a. The Na$_2$[B$_{12}$H$_{12}$] spectrum is reported as a reference. Spinning side bands are marked with *.

In our recent study, the pure Na$_2$[B$_{12}$H$_{12}$] compound was synthesized by wet chemistry and characterized by TPD and $^{11}$B\textit{\{H\}} MAS NMR, to be reinforced 38. A sharp line (FWHM) 158 Hz at -15.36 ppm (Figure 6 b, red line) was assigned to the boron nucleus in the dodecahedral [B$_{12}$H$_{12}$]$^{2-}$ units in Na$_2$[B$_{12}$H$_{12}$]. As shown in Figure 6 b, the chemical shift of Na$_2$[B$_{12}$H$_{12}$] can be associated to the broad signal detected in this range. Starting from this point, we can confirm that amorphous Na$_2$[B$_{12}$H$_{12}$] is formed during the hydrogen desorption reaction of the 2NaBH$_4$ + MgH$_2$ mixture. Moreover, CP (Cross Polarization) experiment conducted on the desorbed powders, only gives rise to signals of $^{11}$B with $^1$H linked. The CP-dynamic, Fig. 7, is analog to that found for [B$_{12}$H$_{12}$]$^{2-}$ in K$_2$[B$_{12}$H$_{12}$] by Hwang et al. 21 and for that reason we assign this signal to Na$_2$[B$_{12}$H$_{12}$].
Figure 7. Relative intensities of the $^{11}$B CP/MAS signal for the $2\text{NaBH}_4 + \text{MgH}_2$ powders after desorption step, as a function of the mixing time.

Note that $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$ could not be easily detected by XRPD analysis due its amorphous nature and the relative low amount in the desorbed sample. Furthermore, it should be noticed that, even though the amorphous $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$ phase is formed in an intermediate step of the desorption pathway (after 2 h at 450 ºC), it cannot be considered an intermediate, but instead a side product, in fact it was still present at the end of the reaction. This result is in agreement with a recent work by R. Caputo et. al., where the calculated enthalpy of formation of $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$ in the monoclinic structure, at $T = 0$ K, is -1086.196 kJ mol$^{-1}$, confirming that this is a very stable compound$^{38}$. As this by-product could hamper the reversibility of the system, it is now under a more detailed study.
CONCLUSIONS: In this work we reported new findings on the desorption reaction of the 2NaBH₄ + MgH₂ reactive hydride composite system. *Ex-situ* XRPD and solid state $^{11}$B and $^{23}$Na MAS NMR experiments were performed to study the dehydrogenation pathways and characterize the decomposition products.

As evinced by *ex-situ* XRPD and MAS NMR, the desorption of the 2:1 mixture follows a multi-step reaction. After full decomposition of MgH$_2$ to Mg, the NaBH$_4$ phase is able to react with free Mg to produce MgB$_2$ and Na phases, with a strong release of hydrogen. Interestingly, the formation of elemental Na was experimentally observed at temperature higher than 450°C and it started together with the dehydrogenation of NaBH$_4$.

The NMR measurements, in agreement with the XRPD data, proved the formation of nanocrystalline MgB$_2$. $^{11}$B{$\textsuperscript{1}$H} NMR experiments revealed that during the formation of MgB$_2$ a significant number of magnesium sites are exchanged with atoms of sodium, thereby influencing its electronic structure and supporting the presence of an intermediate specie. Moreover, the $^{23}$Na{$\textsuperscript{1}$H} NMR measurements evidence that the local structure of the NaBH$_4$ is still preserved up to 450°C. Finally, the amorphous Na$_2$[B$_{12}$H$_{12}$] phase was detected in the partially decomposed sample (2 h at 450°C) as well as in the final products of the dehydrogenation reaction. By our knowledge, this study resulted in the first direct observation of the M[B$_{12}$H$_{12}$] specie in the dehydrogenation of a multi-component system. Indeed, NMR experiments conducted by coupling and decoupling the proton have been proven useful to distinguish species that contain boron atoms bonded with H-atoms. The presented results bring new contributes to the study of the reaction mechanism of reactive hydride composite systems. In particular, Na$_2$[B$_{12}$H$_{12}$] may play a crucial role for the partial reversibility observed in the 2NaBH$_4$ + MgH$_2$ system.
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FIGURE CAPTIONS:

Figure 1. (a) Experimental (magenta circles) and fitted (blue lines) XRPD patterns for the 2:1 mixtures recorded at different temperatures and isothermal annealing: 350 °C (A), 450 °C (B), 450 °C + 15 min (C), 450 °C + 3 h (D), 450 °C + 10 h (E). Symbols: □ NaBH₄ (ICSD #74-1891), ◼ Na (ICSD # 01-0832), □ MgO (ICSD # 38-1369), ◼ Mg (ICSD # 35-0821), • MgB₂ (ICSD # 38-1369), ◼ MgH₂ (ICSD # 74-0934). (b) An enlargement of Figure a in the 25°-35° angular range.

Figure 2. 

Figure 3.  

Figure 4. 

Figure 5. (a) 11B{1H} (magenta circles) and 11B (blue line) MAS (12 kHz) single pulse NMR spectra of the 2NaBH₄ + MgH₂ mixture annealed at 450 °C for 2 h (A), 450 °C for 3 h (B) and 450 °C for 15 h (C). The abbreviation 11B, instead of 11B{1H}, indicates a typical boron NMR experiment conducted without a Composite-Pulse Decoupling (CPD) signal. Spinning side bands are marked with *.

Figure 6. (a) 11B{1H} (magenta circles) and 11B (blue line) MAS (9 kHz) single pulse NMR spectra of the 2NaBH₄ + MgH₂ mixture annealed at 450 °C for 15 h. (b) Zoom inset of the spectrum in Figure a. The Na₂[B₁₂H₁₂] spectrum is reported as a reference. Spinning side bands are marked with *.

Figure 7. Relative intensities of the 11B CP/MAS signal for the 2NaBH₄ + MgH₂ powders after
desorption step, as a function of the mixing time.

TABLES:

Table 1. Weight % fraction of the phases present in the XRPD patterns plotted in Figure 1. MgO* amount detected is less than 1 wt. % for each mixture. To serve as reference, the weight % fraction of the as-prepared mixture is presented.

Table 2. $^{11}$B($^1$H) and $^{23}$Na($^1$H) NMR parameters obtained by fit of the experimental spectra using a Lorentzian/Gaussian function. Observed isotropic chemical shift, $\delta_{iso}$ (±0.1 ppm), asymmetric parameter, L/G, and the full width at half-maximum, FWHM (±5 Hz), and corresponding assignments are reported.
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