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Mechanochemical synthesis of NaBH₄ starting from NaH-MgB₂ reactive hydride composite system

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Abstract

The present investigation focuses on a new synthesis route of NaBH₄ starting from the 2NaH þ MgB₂ system subjected to mechanochemical activation under reactive hydrogen atmosphere. The milling process was carried out under two different hydrogen pressures (1 and 120 bar) with two different rotation speeds (300 and 550 rpm). The reaction products were characterized by ex-situ solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR), ex-situ X-ray powder diffraction (XRPD) and Infrared Spectroscopy (IR). From the results of these analyses, it can be concluded that milling in all the considered conditions led to the formation of NaBH₄ (cubic-Fm-3m). In particular, a reaction yield of 5 and 14 wt% is obtained after 20 h of milling at 120 bar of H₂ for the tests performed at 300 rpm and 550 rpm, respectively. The presence of MgH₂ is also detected among the final products on the as milled powders. The influence of the milling conditions and the evaluation of the parameters related the mechanochemical process are here discussed.

1. Introduction

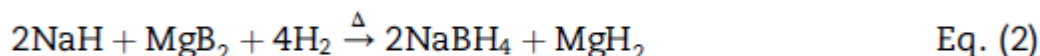
In the field of the hydrogen storage materials, sodium boro-hydride (NaBH₄) has attracted considerable attention due to its theoretically high gravimetric hydrogen capacity (10.8 wt %) and high volumetric hydrogen density (115 kg H₂/m³) combined with a relative stability under air, which appears ideal for on-board applications [1,2]. NaBH₄ can release pure hydrogen via hydrolysis if assisted by a suitable catalyst. However, the formation of highly stable NaBO₂·H₂O does not allow to reversibly return to the original sodium boro-hydride. An alternative method may occur by using the thermal dehydrogenation. In fact, at 773 K NaBH₄ starts to decompose under thermal activation with the formation of sodium, boron and hydrogen, as reported in the following reaction:



Unfortunately, the too high dehydrogenation temperature (773 K) represents a limiting factor to the use of sodium borohydride as hydrogen storage carrier for on-board systems integrated with fuel cells technology. Recently, many efforts have been devoted to decrease the hydrogen desorption temperature of NaBH₄. Several opportunities of tuning the thermodynamic and kinetic properties were reported as, for example, combining it with a second hydride phase [3e7] or confining it in a nanoporous carbon or SBA-15 matrix [8,9].

A further aspect that needs to be taken into account is the lack of reversibility of the Reaction (1). In fact, despite a favorable enthalpy of reaction (88 kJ mol⁻¹ H₂), the formation of NaBH₄ from its elements requires harsh conditions in terms of temperatures and pressures [10]. This can be ascribed to the high kinetic barrier played by boron during (re) hydrogenation: boron is known to be an extremely inert material and, therefore, reluctant to react [11]. In order to overcome these kinetic constraints, Barkhordarian et al. [12] and Vajo et al. [13] proposed independently a novel synthetic approach based on the replacement of elemental boron with MgB₂, that was envisaged in the field of Reactive Hydride Composites (RHC). This approach leads to a considerable reduction of

the kinetic barrier, due to an unexpected kinetic effect of MgB_2 in the reaction, leading to the borohydride formation [e.g., NaBH_4 , LiBH_4 and $\text{Ca}(\text{BH}_4)_2$]. In case of NaBH_4 , the reaction can be summarized as it follows:



62 $\text{kJ mol}^{-1} \text{H}_2$, about 26.2 $\text{kJ mol}^{-1} \text{H}_2$ less than the decomposition enthalpy of single NaBH_4 [6]. The Reaction (2), that occurs by thermal activation, was extensively investigated by both Pistidda et al. [14] and Nwakwuo et al. [15] as a function of the applied hydrogen pressure. The authors demonstrated that direct formation of NaBH_4 was possible only at 5 bar of hydrogen, with no intermediate formation of NaMgH_3 (side product), any unknown hydride phase, nor an unidentified B-containing phase, which were instead observed at pressures higher than 20 bar H_2 [14]. However, both the high temperatures and the slow kinetics achieved for the formation of NaBH_4 make this process not desirable.

Mechanochemistry is a well-known powerful tool to promote chemical transformations between gas-solid interface [16] and it represents a valid and well-recognized method in the preparation of hydrogen storage materials [17e22]. For instance, LiBH_4 was synthesized from a mixture of LiH and B milled under hydrogen pressure for the first time by Agresti and Khadelwal [19]. In addition, the borohydride phase was obtained in an amorphous state with a yield up to 27 wt% [19]. Since boron evidences kinetic constraints, milling the hydride with the respective metal boride following Reaction (2) can represent a valid strategy. For example, $\text{Ca}(\text{BH}_4)_2$ was synthesized by reactive ball milling starting from a mixture of CaB_6 and CaH_2 with a reaction yield of 19 wt%. After the powder was doped with a Ti-based additive, a 60 wt% yield was achieved after re-hydrogenation [21], without thermal activation. These encouraging results set the basis for the preparation of NaBH_4 , that requires, as mentioned above, high temperatures under static condition.

In this work, we present the solvent-free synthesis of NaBH_4 at room temperature performed by reactive ball milling of the $2\text{NaH} \text{ } \text{MgB}_2$ powders mixture. Mechanical synthesis of the desorbed materials is conducted under two different hydrogen pressures, 1 and 120 bar, and at two different milling speeds, i.e. 300 and 500 rpm. X-ray powder diffraction (XRPD), infrared (IR) and solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy were employed in order to characterize the reactants and the final products. The crosslink of the results obtained employing these different experimental techniques and computational thermodynamics evaluation (CALPHAD) is expected to give a tangible evidence of the formation of the NaBH_4 phase. Moreover, an estimation of the energies involved during the milling process of the $2\text{NaH} \text{ } \text{MgB}_2$ system is presented.

2. Experimental details

NaH and MgB_2 commercial powders were purchased from Aldrich (95% purity) and Alfa Aesar (96% purity), respectively. NaH and MgB_2 were ball-milled for 20 h in a 2:1 molar ratio by means of a Planetary Fritsch Pulverisette P6 mill. The powders were sealed in a stainless steel vial (Evico Magnetics) that allows continuous in-situ monitoring of the reaction temperature and pressure. The milling was performed under hydrogen atmosphere, 1 and 120 bar H_2 respectively, with 37 balls (10 mm diameter), a ball to powder mass ratio of 30:1 and two different rotational speeds (300 and 550 rpm). Experiments were performed at 1 bar of hydrogen in order to guarantee a high resolution. A maximum pressure of 120 bar was selected for safety reasons. The powders were always handled inside an MBraun-20-G glove box in a high-purity argon atmosphere with O_2 and H_2O levels below 0.1 ppm.

X-ray diffraction analysis was carried out using a Philips XPERT diffractometer (Bragge-Brentano configuration) with XCelerator RTMS detector, using $\text{Co K}\alpha$ radiation (1/4 0.178901 nm). The powders were spread onto a silicon single crystal and sealed in the glove box with an airtight hood of Kapton foil. The microstructural parameters were evaluated by fitting the full XRPD patterns using MAUD (Materials Analysis Using Diffraction), a very versatile Rietveld refinement software [23].

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. The NMR chemical shifts are reported in parts per million (ppm) externally referenced to $\text{BF}_3\text{O}(\text{CH}_2\text{CH}_3)_2$. 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 of 12 kHz. The one dimensional (1D) ^{11}B MAS-NMR spectra were acquired after a 2.7 ms single p/2 pulse (corresponding to a radiofield strength of 92.6 kHz) and with the application of a strong ^1H signal decoupling by using the two-pulse phase modulation (TPPM) scheme [24]. The recovery delay was set to 10 s. Spectra were acquired at 293 K, and the temperature controlled by a BRUKER BCU unit.

IR spectra were collected with 2 cm^{-1} resolution and 64 scans per spectrum using an Attenuated Total Reflection (ATR) cell instrument (Bruker Alpha) with a diamond crystal. The ATR-IR instrument was placed inside an Ar filled glove box.

3. Results and discussion

The first milling run of the $2\text{NaH} \text{ } \text{MgB}_2$ powders mixture was conducted under moderate conditions: 1 bar of H_2 pressure and a rotational speed of 300 rpm for 20 h. No variation in the absolute hydrogen pressure was recorded by the Evico vial sensor. The XRPD pattern (not presented here) collected at the end of the milling process does not evidence any peak ascribable to NaBH_4 and/or MgH_2 . The as processed powders were subsequently analyzed by solid state MAS-NMR: Fig. 1(a) shows the $^{11}\text{B}\{^1\text{H}\}$ NMR

spectrum of the $2\text{NaH} \cdot \text{MgB}_2$ mixture, both manually mixed (A) and ball milled under 1 bar of H_2 (B). Concerning spectrum B, the strong peak at 99.50 ppm can be assigned to MgB_2 by direct comparison with the starting reference material (A). Furthermore, in sample B, another weaker signal at 42.45 ppm is visible. This signal corresponds to the NaBH_4 chemical shift, as also evidenced by profile C, that belongs to the pure NaBH_4 , reported as a reference. In Fig. 1(b), an enlargement of the spectra is reported, highlighting that the $[\text{BH}_4]$ units are clearly present in the materials characterized by spectrum B. However, the amount of NaBH_4 produced by milling of the initial $2\text{NaH} \cdot \text{MgB}_2$ powders mixture under reactive H_2 atmosphere is very small (less than 2 wt%). On the other hand, the process, conducted by mechanochemical treatment confirms that, even though far from the equilibrium, the reaction seems to follow the path indicated by the Eq. (2). This is surprising, considering that NaBH_4 is formed at only 1 bar H_2 pressure. With the aim of obtaining a higher yield of the reaction product (NaBH_4), the driving force was tentatively increased by performing the milling under 120 bar of H_2 and at different rotational speed.

The temperature profile and the variation in the moles of hydrogen during the mechanical treatment of the $2\text{NaH} \cdot \text{MgB}_2$ mixture, performed at the two different rotational speeds, are reported in Fig. 2 as a function of time t . In both cases, after 2.5 h of milling a rapid increase of the temperature up to 328 K and 325 K for the experiments conducted at 300 rpm (Fig. 2a, dark line) and 550 rpm (Fig. 2b, dark line), respectively, was observed. Thus, the reaction does not take place at room temperature, owing to the fact that during each impact a certain amount of heat is transferred by the balls to the walls of the vial, leading to a global increase of temperature inside the reactor. Nevertheless, the temperatures involved in the milling process are definitely lower than those required for the reaction just thermally activated. After 20 h of reactive milling, the temperature reaches a maximum of 328 K for the milling performed at 300 rpm and 331 K for the milling performed at 550 rpm. The increase of the temperature can also be correlated to the exothermic reaction with hydrogen by the $2\text{NaH} \cdot \text{MgB}_2$ mixture. This is confirmed by the decrease of the hydrogen pressure charged in the vial during the milling, as shown both in Fig. 2a and b by blue squares. The number of moles of hydrogen absorbed during the milling (H_2 moles) is calculated from the pressure and temperature values measured using the gas equation of state. The reacting amount of hydrogen was calculated to be 0.04 and 0.05 mol for the experiments reported in Fig. 2a and b, respectively.

In order to confirm this point, XRPD investigations were carried out on the powders at the end of the milling processes. The XRPD pattern shown in Fig. 3 evidences the formation of NaBH_4 . As reported in Fig. 3A, the mechanical treatment of the $2\text{NaH} \cdot \text{MgB}_2$ mixture conducted at 300 rpm leads to the formation of the NaBH_4 cubic phase. The reflections of the NaBH_4 phase in the XRPD profile appear broad and clearly indicate the occurrence of a fine microstructure in the hydride phase. Rietveld refinement of the XRPD pattern indicates average crystallite size of 50.95 nm for the NaBH_4 phase, and its relative fraction corresponding to 5.2 wt% in the mixture. The peaks of the unreacted NaH and MgB_2 phases are still present, confirming that the full transformation is not achieved under the abovementioned mechanochemical

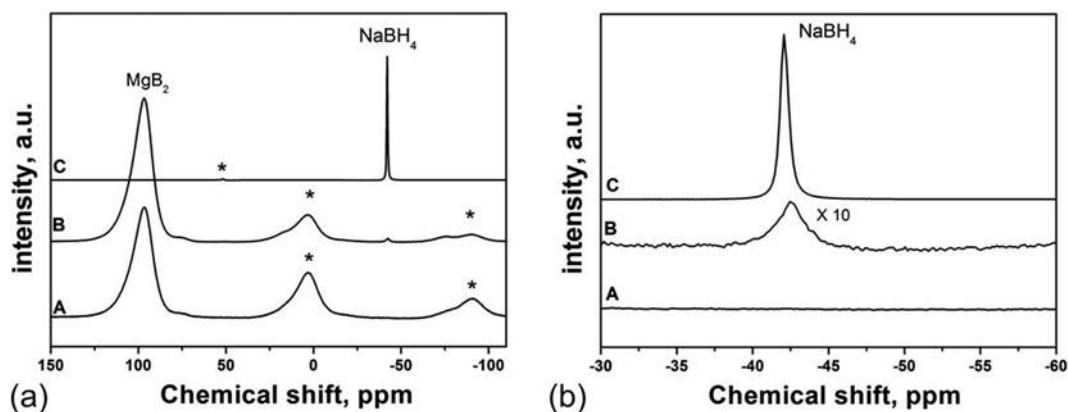


Fig. 1 (a) $^{11}\text{B}\{^1\text{H}\}$ MAS (12 kHz) single pulse NMR spectra of the $2\text{NaH} \cdot \text{MgB}_2$ manual mixed mixture (A), the mixture ball milled for 20 h under 1 bar of H_2 (B), and pure NaBH_4 as a reference (C). (b) Zoom inset of the spectrum in (a). Spinning side bands are marked with *

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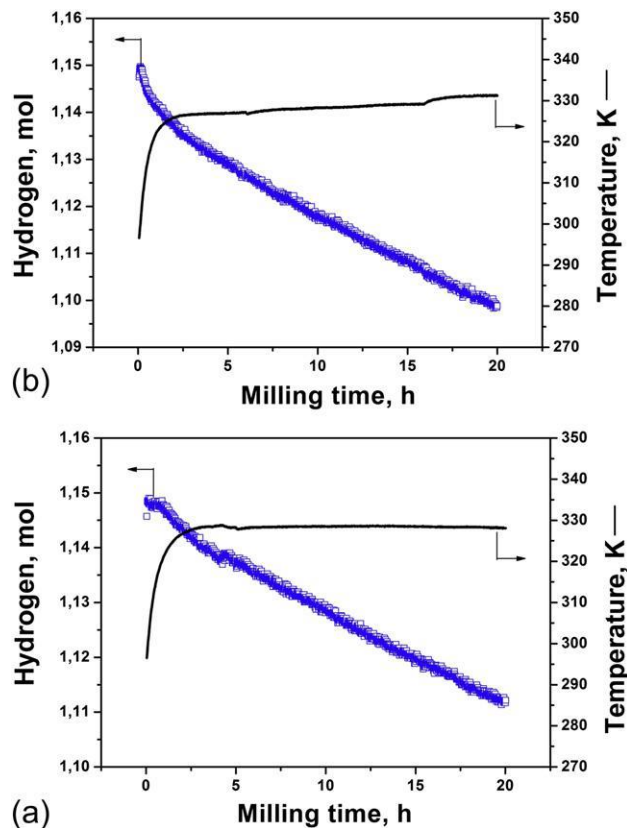


Fig. 2 e Evolution of the hydrogen amount (squares) and temperature (solid line) as a function of the milling time for the 2NaH D MgB₂ system milled under 120 bar of H₂ at 300 and 550 rpm of rotational speed.

conditions. Reflections of both Fe and NaOH are also visible. Presence of iron is ascribable to the friction/corrosion of the balls occurred during the mechanical treatment and despite the strong intensity of its main peak at the 2 θ angle of 52.4 , its

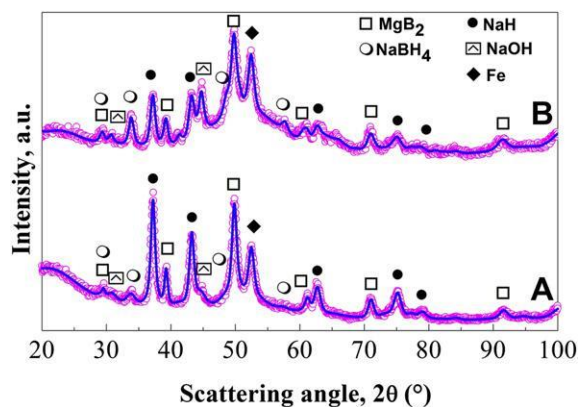


Fig. 3 e XRPD patterns of the 2NaH D MgB₂ powders after 20 h of mechanical treatment under 120 bar of H₂ conducted at 300 (A) and 550 (B) rpm. The continuous line (blue) corresponds to the Rietveld fit profile. Co K α 1 radiation [0.15406 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

relative amount in the mixture turns out to be lower than 4 wt %. On the contrary, the consistent amount of the NaOH phase detected in the powder is due to the oxidation of NaH during the XRPD measurements. In pattern b, corresponding to the powder milled at 550 rpm for 20 h, the main NaBH₄ peak appears at the 2 θ angle of 33.8 and a significant amount of it (14 wt%) was detected, confirming that the conversion increases as a function of ball milling intensity (Fig. 2b). In addition, the average crystallite size determined for the NaBH₄ phase corresponds to 20.5 nm. This value is 2.5 times lower than that reported for the same phase formed in the previous experiment (300 rpm) and it demonstrates that an effective milling process leads to nanostructured NaBH₄. It should be mentioned that pristine NaBH₄ is extremely resistant even for long-term milling time to be refined up to the nanocrystalline range [25,26]. Finally, as in pattern a, impurity of Fe and NaOH are observed together with the starting reagents, NaH and MgB₂. The MgH₂ phase is not detected in both patterns despite its formation is predicted by the Eq. (2). Nevertheless, traces of MgH₂ could not be excluded because, due to its small amount, its reflections could be emerged with the background of the XRPD pattern or within the tails of nearby peaks from other phases. In fact, considering Eq. (2), the maximum amount of NaBH₄ expected corresponds to 78 wt%, therefore not more than 22 wt% can exist as MgH₂. In our synthesis, as the best, we obtain 14 wt% of NaBH₄, therefore the quantity of MgH₂ could not be higher than 4 wt%, i.e. close to its detectable limit. Apart from the established small volume fraction, it should be taken into account that the detection of MgH₂ can be made further difficult due to its small crystallite size associated with an increase of the broadening of its XRPD peaks.

In order to verify the presence of residual side-products not detected by XRPD, IR spectroscopy was used as additional technique due to its specific sensitivity. The infrared spectrum for the pure NaBH₄ (Fig. 4A) was mainly composed by the bands due to the stretching and bending modes of [BH₄] anion in the 2000-2500 cm⁻¹ and 900-1300 cm⁻¹ range, respectively. MgH₂ exhibited a large broad signal in the 700-1400 cm⁻¹ range [27]. The IR spectrum of MgH₂ presents an additional shoulder in the 500-800 cm⁻¹ range, that was

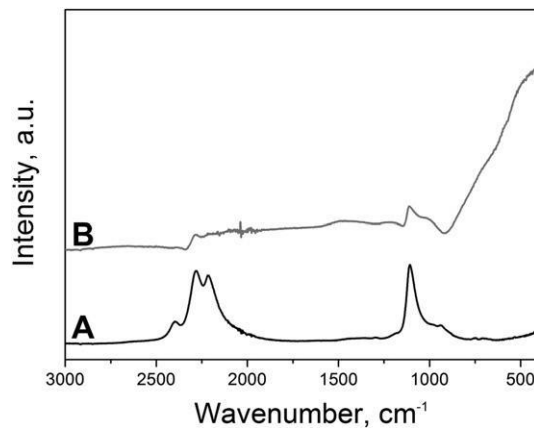


Fig. 4 e IR spectra for the reference NaBH₄ (A) and for the 2NaH + MgB₂ milled for 20 h under 120 bar of H₂ at 550 rpm.

also observed for the NaH phase [27]. In the powders milled at 550 rpm for 20 h (Fig. 4B) two groups of IR signals were observed: one between 900 and 1300 cm⁻¹ and another, less intense, between 2000 and 2500 cm⁻¹, belonging to NaBH₄. Furthermore, two broad peaks in the 900-1600 cm⁻¹ (related to MgH₂) and 500-800 cm⁻¹ (associated to NaH) range were also detected. The IR spectrum of the milled sample confirms the formation of NaBH₄ according to the XRPD measurement (Fig. 3) and supports the expected presence of MgH₂ in the final mixture. Finally, no trace of the vibration line of the NaMgH₃ perovskite-type phase (1200-1300 cm⁻¹ [27]) is observed in the IR spectrum shown in Fig. 4B, evidencing that the hydrogenation process of the 2NaH + MgB₂ system follows Reaction (2).

The different yield of Reaction (2) as a function of milling conditions can be explained in terms of thermodynamic arguments. On the basis of a consistent thermodynamic database for hydrogen storage systems, developed by the CALPHAD approach [28], the driving force for nucleation of NaBH₄ from the 2NaH + MgB₂ mixture has been calculated. According to experimental results, the occurrence of the NaMgH₃ was neglected, so this phase was suspended from calculations.

The results are shown in Fig. 5, where the free energy change for the synthesis reaction (Eq. (2)) is reported as a function of temperature for the H₂ pressures used in the experiments. It is clear that the increase of the driving force for nucleation of the product phases is related to the increase of the H₂ pressure according to:

$$G_{\text{H}_2}^{\text{gas}}(T, P) = G_{\text{H}_2}^{0, \text{gas}}(T) + RT \ln(P/P_0) \quad \text{Eq. (3)}$$

where $G_{\text{H}_2}^{0, \text{gas}}$ is the standard Gibbs energy for hydrogen in the gas state and P_0 is the standard pressure of 101,325 Pa.

In terms of classical nucleation theory [29], the free energy necessary to form a critical radius of a new phase from a parent phase is given by:

$$\Delta G^* = \frac{16\pi \sigma^3}{3 \Delta G_v^2} \quad \text{Eq. (4)}$$

where σ is the interfacial energy and ΔG_v is the free energy difference per unit volume. Even if the reaction mechanism is

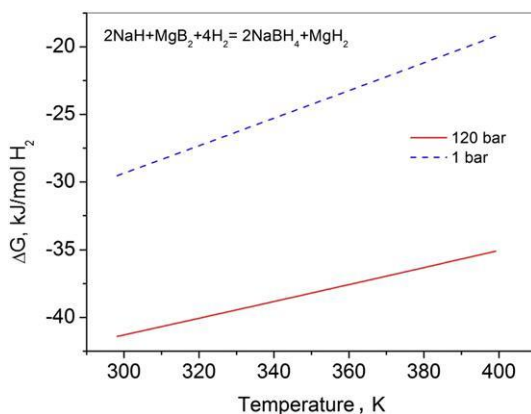


Fig. 5 e Free energy difference for Reaction (2) as a function of temperature for different H₂ pressures.

not known in details, from the results shown in Fig. 5, a halving of ΔG^* can be estimated at 300 K passing from 1 bar to 120 bar, if other parameters remains constant. Increasing the temperature, an increase of the ratio between the two values would be expected, reaching 2.5 at 350 K. These simple considerations can explain, together with kinetic arguments, the effect of H₂ pressure in the vial in promoting the reaction, which becomes more important for increasing temperatures, as actually observed during ball milling.

By the experiments reported above, it is possible to understand that the rotational speed of the milling process plays a fundamental role on the amount of NaBH₄ produced. In order to clarify this point, the energy (E) transferred to the powder during the milling process was calculated for both experiments using the expression developed in the work of Magini et al. [30]. The so-obtained values are reported in Table 1. For a mechanochemistry reaction, the net dependence of the amount of gas absorbed with the milling frequency could be better represented by the energy dose of the mechanical treatment. This parameter, D, allows to estimate the total energy absorbed by the powder during a given milling time and it can be defined as it follows:

$$D = I \cdot t \quad \text{Eq. (5)}$$

where t is the milling time and I is the milling intensity that is related to the frequency of collision, f , and the energy transferred to the powders, E , by the following expression:

$$I = E \cdot f \quad \text{Eq. (6)}$$

The parameter f depends on the type of milling device and its quantification requires complex and accurate experimental and modeling procedures [31e33]. For the P6 apparatus it can be assumed that the vibrational frequency of the mill is proportional to the rotational speed and D parameter can be simply calculated from Eq. (5). The D values calculated for both experiments are reported in Table 1, together with the specific dose indicated by the symbol D_m , that represents the mechanical work performed on the system per mass unit.

The specific dose values (D_m) reported in Table 1 seem to be connected to the yield of the NaBH₄ formed. The conversion of the starting materials (2NaH + MgB₂) to the final product NaBH₄ was easily promoted when the powder was subjected to higher mechanical work (14 wt % and 0.475 kJ/g). However, if we indicate the ratio between the reaction yield of the final product (NaBH₄) and the specific dose, D_m , as the mechano-chemistry yield mean of the reaction, it is interesting to observe that this value decreases in case of the experiment conducted at higher energy milling (76.9 g/kJ and 29.5 g/kJ for 300 rpm and 550 rpm, respectively). The energy impact was, in fact, partly dissipated in heat as a consequence of the impact

Table 1 e Milling parameters relevant to mechanical treatment of the 2NaH D MgB₂ system.

v (rpm)	m _b (g)	m _p (g)	E (J)	f _b (Hz)	I (W)	D (kJ)	D _m (kJ/g)
300	4	5	1.99*10 ³	2.24	4.5*10 ³	0.324	0.065
550	4	5	7.99*10 ³	4.11	3.3*10 ²	2.376	0.475

of the balls to the vial walls as also previously indicated by the temperature increase in Fig. 2. This effect is even more pronounced for the powders milled at 550 rpm (Fig. 2b). As a consequence, not all specific energy dose supplied to the powders during each collision is involved to activate the hydrogenation process. Along this way, we can consider our approach as a tentative to rationalize a synthesis of chemical hydride by mechanical activation in order to extend this method on large scale. Anyway, further efforts are needed to estimate in more details the mechanisms of the milling process for this reaction and in particular the minimum energetic value suitable to activate the NaBH₄ formation as well as the mechanism behind it.

4. Conclusions

In this work, NaBH₄ was synthesized by mechanochemical process starting from the 2NaH þ MgB₂ reactive hydride composite mixture. The milling process was performed under a reactive atmosphere of 1 and 120 bar of hydrogen gas, and at two different rotational speeds of 300 and 550 rpm, respectively. As evinced by ex-situ MAS NMR, the formation of NaBH₄ was experimentally observed already under moderate milling condition of 1 bar of H₂ and 300 rpm. The nucleation of NaBH₄ from the 2NaH þ MgB₂ mixture, calculated by CALPHAD approach, was found to be promoted by H₂ pressure in the vial. The effect of the pressure on the nucleation becomes more important for increasing temperatures. For the experiments performed at higher pressure (120 bar), XRPD reveals NaBH₄ formation at the end of the mechanical process and the reaction yield turns out to be 5 and 14 wt% for the experiment conducted at 300 rpm and 550 rpm, respectively. The sodium borohydride phase was identified in nanostructured conditions for both experiments. Interestingly, presence of MgH₂ in the final mixture was ascertained by IR spectroscopy as indicated by the theoretical reaction. Moreover, it emerged that the powders subjected to more intensive mechanical work presented a higher content of NaBH₄ at the end of the milling: 5 wt% of NaBH₄ for 4.5*10³ W (300 rpm) and 14 wt% of NaBH₄ for 3.3*10² W (550 rpm). This effect coexists with a better NaBH₄ crystallite size refinement obtained at higher mechanical work. Finally, the mechanically-induced yield of NaBH₄ has been investigated as a function of the milling intensity. It was found that the conversion degree is basically decreased at 550 rpm with respect to 300 rpm, due to the fact that the energy transferred at each impact is partly dissipated as heat to the wall of the reactor.

Acknowledgments

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