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Mechanochemical synthesis of $NaBH_4$ starting from NaH-MgB_2 reactive hydride composite system

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Abstract

The present investigation focuses on a new synthesis route of $NaBH_4$ starting from the 2NaH þ MgB_2 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 $NaBH_4$ (cubic-Fm-3m). In particular, a reaction yield of 5 and 14 wt% is obtained after 20 h of milling at 120 bar of H_2 for the tests performed at 300 rpm and 550 rpm, respectively. The presence of MgH_2 is also detected among the final products on the as milled powders. The influence of the milling conditions and the eval-uation of the parameters related the mechanochemical process are here discussed.

1. Introduction

In the field of the hydrogen storage materials, sodium boro-hydride ($NaBH_4$) has attracted considerable attention due to its theoretically high gravimetric hydrogen capacity (10.8 wt %) and high volumetric hydrogen density (115 kg H_2/m^3) combined with a relative stability under air, which appears ideal for on-board applications [1,2]. $NaBH_4$ can release pure hydrogen via hydrolysis if assisted by a suitable catalyst. However, the formation of highly stable $NaBO_2\$H_2O$ 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 $NaBH_4$ starts to decompose under thermal activation with the formation of sodium, boron and hydrogen, as reported in the following reaction:

$$NaBH_4 \xrightarrow{\Delta} Na + B + 2H_2 \qquad \text{Eq. (1)}$$

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 $NaBH_4$. Several opportunities of tuning the thermodynamic and kinetic properties were re-ported 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] H_2), the formation of $NaBH_4$ from its elements requires harsh condi-tions 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 MgB_2, that was envisaged in the field of Reactive Hydride Composites (RHC). This approach leads to a consid-erable reduction of the kinetic barrier, due to an unexpected kinetic effect of MgB_2 in the reaction, leading to the borohy-dride formation [e.g., $NaBH_4$, $LiBH_4$ and $Ca(BH_4)_2$]. In case of $NaBH_4$, the reaction can be summarized as it follows:

$$2NaH + MgB_2 + 4H_2 \xrightarrow{\Delta} 2NaBH_4 + MgH_2 \qquad \text{Eq. (2)}$$

62 kJ mol 1 H_2, about 26.2 kJ mol 1 H_2 less than the decom-position 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 tempera-tures 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 gasesolid inter-face [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 constrains, milling the hydride with the respective metal boride following Reaction (2) can represent a valid strategy. For example, $Ca(BH_4)_2$ 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 addictive, 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 2NaH þ 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 2NaH þ 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 temper-ature 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). Experi-ments were performed at 1 bar of hydrogen in order to guar-antee 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 (BraggeBrentano configuration) with XCelerator RTMS detector, using Co Ka radiation (l ¼ 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 evalu-ated by fitting the full XRPD patterns using MAUD (Materials Analysis Using Diffraction), a very versatile Rietveld refine-ment 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 BF_3\$$O(CH_2CH_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 ^{1}H 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 2NaH þ 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 $^{11}B\{^{1}H\}$ NMR spectrum of the 2NaH þ 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 corre-sponds to the $NaBH_4$ chemical shift, as also evidenced by profile C, that belongs to the pure $NaBH_4$, reported as a refer-ence. In Fig. 1(b), an enlargement of the spectra is reported, highlighting that the $[BH_4]$ units is clearly present in the materials characterized by spectrum B. However, the amount of $NaBH_4$ produced by milling of the initial 2NaH þ 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 2NaH þ MgB_2 mixture, performed at the two different rota-tional 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 con-ducted 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 tempera-tures 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 tempera-ture can also be correlated to the exothermic reaction with hydrogen by the 2NaH þ 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 of the 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 2NaH þ 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 50.9 5 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

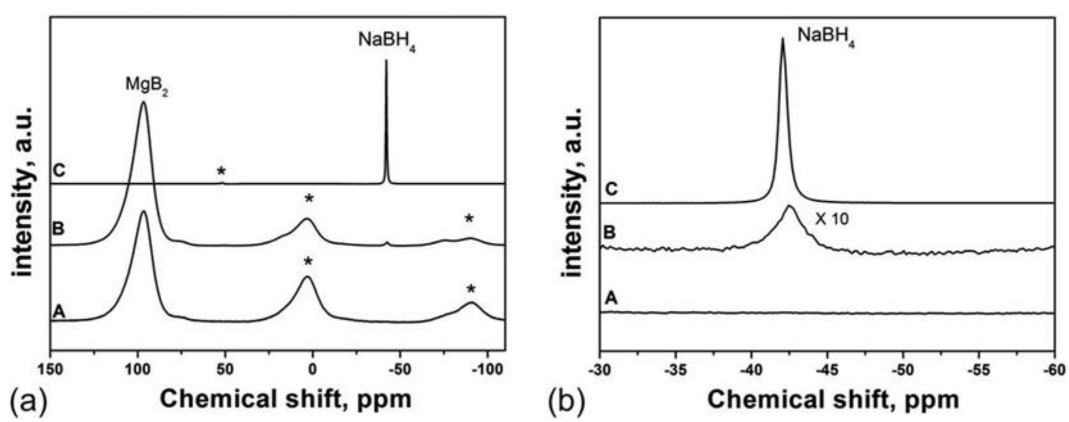

Fig. 1 e (a) $^{11}B\{^1H\}$ MAS (12 kHz) single pulse NMR spectra of the 2NaH D MgB_2 manual mixed mixture (A), the mixture ball milled for 20 h under 1 bar of H_2 (B), and pure $NaBH_4$ as a reference (C). (b) Zoom inset of the spectrum in (a). Spinning side bands are marked with

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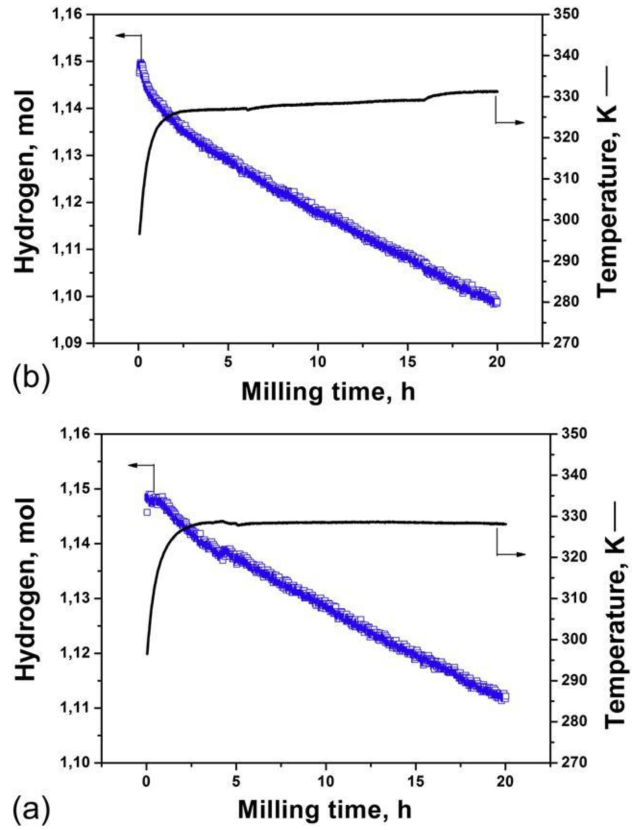

Fig. 2 e Evolution of the hydrogen amount (squares) and temperature (solid line) as a function of the milling time for the 2NaH D MgB_2 system milled under 120 bar of H_2 at 300 and 550 rpm of rotational speed.

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 2q angle of 52.4 , its

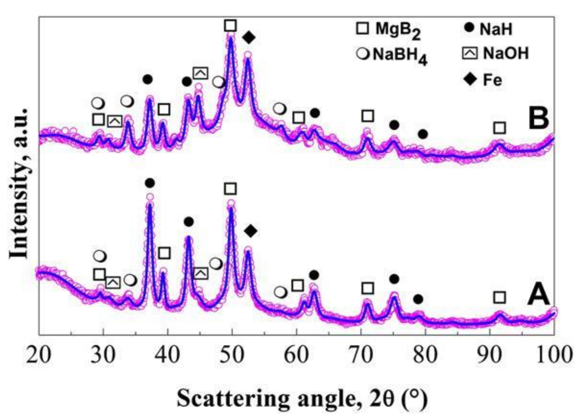

Fig. 3 e XRPD patterns of the 2NaH D MgB_2 powders after 20 h of mechanical treatment under 120 bar of H_2 conducted at 300 (A) and 550 (B) rpm. The continuous line (blue) corresponds to the Rietveld fit profile. Co Ka1 radiation [0.15406 nm. (For interpretation of the references to color in this figure 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 $NaBH_4$ peak appears at the 2q 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 $NaBH_4$ 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 $NaBH_4$. It should be mentioned that pristine $NaBH_4$ 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 MgB_2. The MgH_2 phase is not detected in both patterns despite its formation is predicted by the Eq. (2). Nevertheless, traces of MgH_2 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 $NaBH_4$ expected corresponds to 78 wt%, therefore not more than 22 wt% can exist as MgH_2. In our synthesis, as the best, we obtain 14 wt% of $NaBH_4$, therefore the quantity of MgH_2 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 MgH_2 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 $NaBH_4$ (Fig. 4A) was mainly composed by the bands due to the stretching and bending modes of $[BH_4]$ anion in the 2000e2500 cm ^{1} and 900e1300 cm ^{1} range, respectively. MgH_2 exhibited a large broad signal in the 790e1400 cm ^{1} range [27]. The IR spectrum of MgH_2 presents an additional shoulder in the 500e800 cm ^{1} range, that was

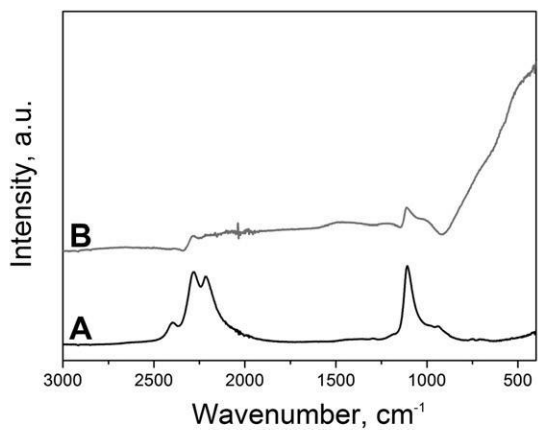

Fig. 4 e IR spectra for the reference $NaBH_4$ (A) and for the 2NaH D MgB_2 milled for 20 h under 120 bar of H_2 at

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 $NaBH_4$. Furthermore, two broad peaks in the 900e1600 cm ^{1} (related to MgH_2) and 500e800 cm ^{1} (associated to NaH) range were also detected. The IR spectrum of the milled sample confirms the formation of $NaBH_4$ according to the XRPD measurement (Fig. 3) and supports the expected presence of MgH_2 in the final mixture. Finally, no trace of the vibration line of the $NaMgH_3$ perovskite-type phase (1200e1300 cm ^{1} [27]) is observed in the IR spectrum shown in Fig. 4B, evidencing that the hydrogenation process of the 2NaH þ MgB_2 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 $NaBH_4$ from the 2NaH þ MgB_2 mixture has been calculated. According to experimental results, the occurrence of the $NaMgH_3$ 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 H_2 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 H_2 pressure according to:

$$G_{H_2}^{gas}(T,P) = G_{H_2}^{0,gas}(T) + RT\ln(P/P_0) \qquad \text{Eq. (3)}$$

where $G^0H^{;gas}$ 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:

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

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

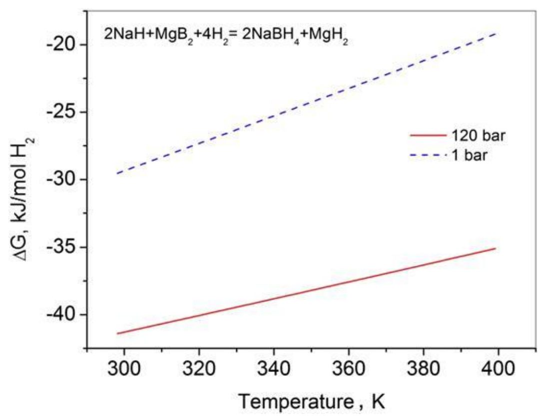

Fig. 5 e Free energy difference for Reaction (2) as a function of temperature for different H_2 pressures.

not known in details, from the results shown in Fig. 5, a halving of DG* 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 H_2 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 $NaBH_4$ 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 depen-dence 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 esti-mate the total energy absorbed by the powder during a given milling time and it can be defined as it follows:

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

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

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

The parameter f depends on the type of milling device and its quantification requires complex and accurate experi-mental and modeling procedures [31e33]. For the P6 appa-ratus 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 $NaBH_4$ formed. The conversion of the starting materials (2NaH þ MgB_2) to the final product $NaBH_4$ 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 ($NaBH_4$) 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 MgB_2 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 considerer 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 $NaBH_4$ formation as well as the mechanism behind it.

4. Conclusions

In this work, $NaBH_4$ was synthesized by mechanochemical process starting from the 2NaH þ MgB_2 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 $NaBH_4$ was experimentally observed already under moderate milling condition of 1 bar of H_2 and 300 rpm. The nucleation of $NaBH_4$ from the 2NaH þ MgB_2 mixture, calculated by CALPHAD approach, was found to be promoted by H_2 pressure in the vial. The effect of the pressure on the nucleation becomes more important for increasing temper-atures. For the experiments performed at higher pressure (120 bar), XRPD reveals $NaBH_4$ 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 experi-ments. Interestingly, presence of MgH_2 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 $NaBH_4$ at the end of the milling: 5 wt% of $NaBH_4$ for $4.5\$10^{3}$ W (300 rpm) and 14 wt% of $NaBH_4$ for $3.3\$10^{2}$ W (550 rpm). This effect coexists with a better $NaBH_4$ crystallite size refinement obtained at higher mechanical work. Finally, the mechanically-induced yield of $NaBH_4$ 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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