Mechanochemical Synthesis

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Mechanically activated metathesis reaction in NaNH$_2$–MgH$_2$ powder mixtures

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ABSTRACT

The present work addresses the kinetics of chemical transformations activated by the mechanical processing of powder by ball milling. In particular, attention focuses on the reaction between NaNH$_2$ and MgH$_2$, specific case studies suitably chosen to throw light on the kinetic features emerging in connection with the exchange of anionic ligands induced by mechanical activation. Experimental findings indicate that the mechanical treatment of NaNH$_2$–MgH$_2$ powder mixtures induces a simple metathetic reaction with formation of NaH and Mg(NH$_2$)$_2$ phases. Chemical conversion data obtained by X-ray diffraction analysis have been interpreted using a kinetic model incorporating the statistical character of the mechanical processing by ball milling. The apparent rate constant measuring the reaction rate is related to the volume of powder effectively processed during individual collisions, and tentatively connected with the transfer of mechanical energy across the network formed by the points of contact between the powder particles trapped during collisions.

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Introduction

Mechanical processing of powders by ball milling (BM) is based on the transfer of mechanical energy from milling tools to solid reactants [1–3]. At any given collision induced by the movement of the reactor, or of part of it, a small amount of powder is trapped between two impacting balls, or between one ball and the reactor walls, and undergoes mechanical loading [4, 5]. Nature, rate and severity of loading conditions at local level exhibit considerable variability due to the irregular distribution of non-hydrostatic mechanical stresses across the disordered network of contacts between the powder particles within the compressed volume [5]. The physical and chemical processes that can take place are correspondingly affected.

On the macroscopic scale, frictional heating and plastic deformation can activate the cold-welding, fracturing and work hardening of powder particles [1–4, 6, 7]. On the microscopic scale, physical and chemical transformations take place consequent to the forced mixing of chemical species, mediated by mass transport processes involving the athermal displacement of both individual atoms and relatively large atomic clusters [8–18].

In principle, the combination of thermal and athermal components makes mechanochemistry richer than thermochemistry in terms of possible mechanistic scenarios. In practice, no parallel between the two chemistries can be really drawn. Indeed, in contrast to thermochemical processes, which have been characterized in their deepest details, the elementary events governing mechanical activation lack rigorous investigation so far. This can be mostly ascribed to the not yet surmounted difficulties arising in connection with the in situ investigation of mechanochemical transformations on the time and length scales spanned by local processes during individual collisions.

Luckily, the unfeasibility of a direct study does not prevent the investigation of local processes occurring during individual collisions by indirect approaches. In this regard, some progress has been made analyzing the macroscopic kinetics of mechanochemical transformations in the light of the statistical nature of the mechanical processing by BM [19–21]. In particular, relating the kinetic analysis to the statistics underlying ball milling allowed gaining insight into the role of individual collisions in activating transformations [19–23]. The results obtained further emphasize the crucial need of moving from global to local study of mechanochemical transformations [24].

The statistical description of transformation kinetics was originally applied to the case of mechanical alloying of elemental metals, by far the most intensely studied transformation promoted by BM [22]. It is a gradual mechanochemical transformation involving the intimate mixing of two, or more, metallic species consequent to the mechanical activation of the powder mixture [19, 22]. Typically, the process requires tens of hours, which correspond to millions of collisions [1–3, 25–27].

The statistical interpretation of the mechanical alloying kinetics suggests that such huge number of collisions simply stems from the extremely small fraction of powder charge effectively worked during each collision [2]. The forced mixing of metallic species and the consequent loss of crystalline order only take place in small sub-volumes of the powder trapped at collision [28, 29]. Similar results have been obtained in the case of mechanically activated self-propagating reactions in binary mixtures [23].

The present work aims at extending the above-mentioned conceptual framework to the case of inorganic chemical systems different from metal-based ones. In particular, experiments addressed here the mechanical activation of $NaNH_2$–MgH_2 binary mixtures with 2:1 stoichiometry.

This choice stems from the interest attracted by amide–hydride mixtures in the field of hydrogen storage. Within such context, the reaction between $NaNH_2$ and MgH_2 exhibits a peculiarity that makes it particularly suitable for investigating the effects of mechanical activation on the kinetics of transformation processes involving inorganic phase. Indeed, the reactants give rise to an apparently simple metathesis that results in the formation of NaH and $Mg(NH_2)_2$ phases [30, 31].

The present investigation provides detailed information about the macroscopic kinetics of the metathetic transformation and allows deepening the insight into the microscopic processes governing it. In particular, it is shown that the metathesis takes place at any given collision, including the very first one, involving a very small volume of the total powder charge.

Experimental methods are described in the following.

Experimental methods

Experiments were performed using commercial NaNH₂ (hydrogen storage grade) and MgH₂ (98% purity) powders purchased from Sigma-Aldrich and Alfa Aesar, respectively. NaNH₂ and MgH₂ powders were suitably mixed to prepare homogeneous mixtures with 2:1 chemical composition. In each experimental run, 8 g of powder of the 2:1 powder mixture was sealed in a stainless steel reactor with 3 stainless steel balls of 3.8 g each, and subjected to mechanical processing using a SPEX Mixer/Mill 8000 working at the standard 875 rpm rotation speed. The mechanical treatment was interrupted at selected times, and powders sampled, to monitor the on-going transformation. Handling and sampling were invariably carried out inside a MBraun-20-G glove-box under a high-purity Ar atmosphere with O_2 and H_2O levels below 0.1 ppm.

The metathetic reaction was monitored by X-ray diffraction (XRD) using a Stoe Stadi P equipped with a Mo Kα $\lambda = 0.71093$ Å tube radiation in a Debye–Scherrer geometry. Specimens were sealed in a capillary chamber specifically used to keep moisture and oxygen sensitive materials uncontaminated. The angular range was accurately selected to include all the relevant XRD reflections of the involved phases, thus enabling a reliable quantitative analysis of the resulting XRD patterns. Structural and microstructural information was obtained by interpolating the XRD patterns using Materials Analysis Using Diffraction (MAUD) software, which allows the quantitative Rietveld analysis [32].

Results

The XRD patterns of the NaNH₂–MgH₂ powder mixtures subjected to mechanical processing for different and selected times are shown in Fig. 1. The initial powder mixture consists of the crystalline NaNH₂ and MgH₂ phases. Deriving from MgH₂ starting powders, Mg trace impurities below 4.2 wt% are also observed.

After 4-h mechanical activation, the crystalline reflections in the XRD pattern exhibit reduced intensity and broadening ascribable to both reduction in average grain size and accumulation of lattice disorder consequent to milling. The Rietveld analysis suggests for the grain size a decrease from the
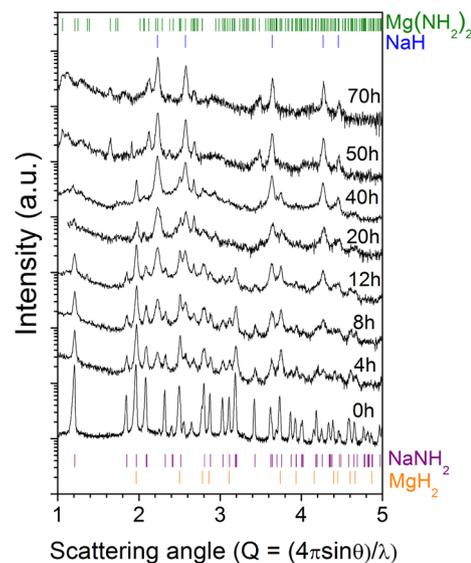

Figure 1 XRD patterns of the NaNH₂–MgH₂ mixtures mechanically processed for the time intervals indicated.

1000 ± 100 Å value estimated at 0 h to 680 ± 60 Å for NaNH₂, and from 980 ± 100 to 700 ± 70 Å for MgH₂. Angular XRD peak positions do not point out any significant variation in the lattice parameters of the NaNH₂ and MgH₂ phases. The XRD pattern does not allow detecting phases different from reactant ones, although a small signal around $Q = 2.2$ can be associated, in principle, to NaH.

Product phases appear in XRD patterns pertaining to powder mixtures subjected to mechanical activation for time intervals longer than 4 h. After 8 h of mechanical processing, the crystalline reflections pertaining to NaNH₂ and MgH₂ reactants start decreasing. In particular, the intensity of the NaNH₂ (111) peak reduces significantly. In parallel, the intensity of the peaks associated with NaH starts to increase. Clear evidence of the formation of a nanostructured Mg(NH₂)₂ phase becomes available only after 40 h of mechanical processing. Finally, only the peaks pertaining to the product Mg(NH₂)₂ and NaH phases are detected in the XRD pattern of powder mixtures mechanically activated for 70 h.

Overall, in agreement with part of available literature [29, 30], the experimental evidence suggests the occurrence of the purely metathetic transformation described by the chemical equation

$$2NaNH_2 + MgH_2 \rightarrow 2NaH + Mg(NH_2)_2. \quad (1)$$

The chemical behavior schematically summarized in Eq. (1) is quite interesting, particularly in the light

of the more complicated reaction paths emerging in the literature with reference to the combination of amides and hydrides under both thermochemical and mechanochemical conditions [30, 31].

In this regard, it is worth noting that the reaction of $NaNH_2$ and MgH_2 mixtures with stoichiometry different from 2:1 results in a multi-step conversion mechanism involving $MgNH$ and Mg_3N_2 as intermediate and product phases, respectively [30]. Gaseous H_2 also forms throughout the mechanical processing [30]. The mechanistic interpretation of such experimental evidence significantly emphasizes the role of mixed interactions between amide and hydride groups, with the formation and subsequent release of gaseous H_2.

Quite interestingly, no such intermediates and products are observed in the case of 2:1 $NaNH_2$–MgH_2 mixtures [30, 31]. In addition, no release of gaseous H_2 was observed. A further element of interest arises in connection with the kinetics of the thermochemical transformation of 2:1 $NaNH_2$–MgH_2 mixtures [31, 33, 34]. Different from mechanical activation, thermal activation results, indeed, in the formation of the Na-based tetra-amide phase $Na_2Mg(NH_2)_4$ and the consequent release of gaseous H_2 [31]. It follows that the metathesis observed in 2:1 $NaNH_2$–MgH_2 mixtures is a mechanochemical transformation with no thermochemical counterpart. Therefore, it represents one of those rare case studies particularly suited for highlighting the effects of mechanical activation in contrast to those emerging under thermal input.

The quantitative Rietveld analysis of XRD patterns allowed reconstructing the kinetic curves describing the chemical conversion processes taking place in 2:1 $NaNH_2$–MgH_2 mixtures subjected to mechanical activation. Relevant data are shown in Fig. 2, where the mass fractions of reactant, $NaNH_2$ and MgH_2, and product, NaH and $Mg(NH_2)_2$, phases are plotted as a function of time, t.

It can be seen that the relative amount of reactant phases decreases monotonically from the initial value to zero, whereas a corresponding increase takes place for products. For prolonged milling times, the relative amounts of reactants and products reach monotonically the final values. The kinetic curves describing reactant consumption and product formation are homologous, i.e., exhibit the same shape. In addition, the experimental data demonstrate that the transformation of reactants into products takes
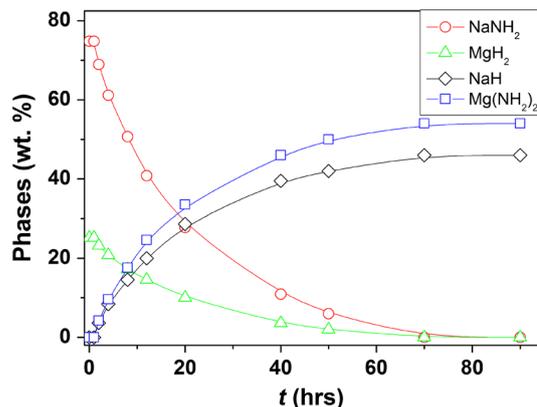

Figure 2 The mass fraction of $NaNH_2$ (*red circle*), MgH_2 (*green triangle*), NaH (*black rhombus*) and $Mg(NH_2)_2$ (*blue square*), as a function of milling time, t (h).

place with perfect synchronicity and full respect of stoichiometry. This can be easily deduced from the experimental points shown in Fig. 3, where the ratio between the relative amounts of reactants, $NaNH_2 + MgH_2$, and products, $NaH + Mg(NH_2)_2$, is shown as a function of time, t. The values, indeed, keep approximately constant over the whole time interval spanned by the metathetic reaction.

Reactant consumption and product formation exhibit a simple dependence on time. Specifically, the semi-logarithmic plot of the relative amounts of $NaNH_2$ and MgH_2 as a function of time, t, shown in Fig. 4, gives rise to definitely linear arrangements, thus revealing an exponential functional dependence.

Accordingly, the mass fraction of the two reactants can be satisfactorily described by the expression
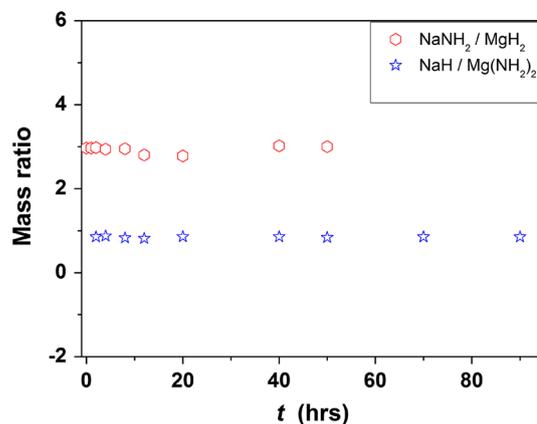

Figure 3 The mass ratio of reactants, $NaNH_2$–MgH_2 (*red hexagon*) and products MgH_2 (*blue star*) is plotted as a function of the increasing milling time, t (h).
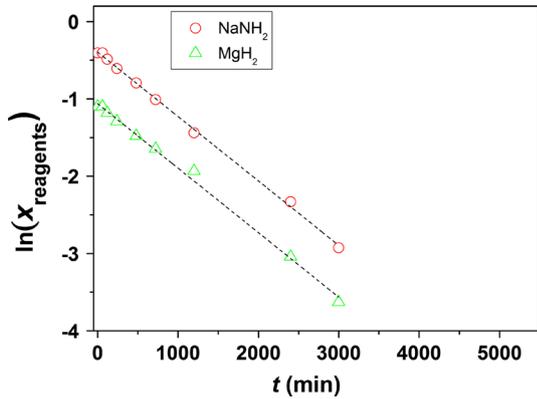
Figure 4 The Napierian logarithm of molar fraction, X, of reagents, $NaNH_2$ (*red circle*) and MgH_2 (*green triangle*) as a function of milling time, t (min). The best-fit lines (*dark dash*) are also shown.

$$\chi_0(t) = \chi_0\, e^{-Kt}, \tag{2}$$

where χ_0 represents the initial mass fraction of each reactant and K is the apparent rate constant of the reactant consumption. It follows that

$$\ln \chi_0(t) = \ln \chi_0 - Kt. \tag{3}$$

Thus, K corresponds to the slope of the linear plots. The best-fitted lines allow estimating the K values for $NaNH_2$ and MgH_2 consumption processes, which are both equal to about 8.3×10^{-4} min^{-1}. The coincidence of K values confirms that the reactants consume exactly at the same rate. Products develop complementarily at the same rate.

Deeper insight into the conceptual framework emerging from the above-mentioned experimental evidence can be gained using a kinetic model capable of taking into due account the statistical nature of the mechanical processing by BM. Developed and discussed in detail in previous work [22, 34], the model is summarized below and applied to the case study investigated here.

Kinetic modeling

Describing the kinetics of transformations activated by BM necessarily requires accounting for its characteristic features [2, 29, 35, 36]. In this regard, it is worth noting that only a small amount of powder is involved in each collision and that the trapping of powder between the surfaces of colliding milling tools is approximately stochastic. In addition, the amount of a component involved in a given collision can be expected to be proportional to the relative amount of such component in the powder mixture, and that the chemical composition of the powder charge remains approximately uniform during the entire mechanical treatment. Furthermore, each collision can be expected to result in critical loading conditions (CLCs), i.e., to generate mechanical stresses of the intensity needed to activate a given transformation process, only in a sub-volume V^* of the trapped powder. Thus, V^* represents the volume of powder effectively processed, which can vary, together with CLCs, from process to process. For a given transformation, V^* can be assumed to keep constant during the mechanical processing.

The volume fraction of powder subjected to CLCs is $k = V^*/V$, where V is the total volume of the powder charge inside the reactor. To a first approximation, any volume element V^* in which the powder charge can be divided has the same probability of being involved in a given collision. If χ_0 is the volume fraction of a given component of a powder mixture, $k\,\chi_0$ is the volume fraction subjected to CLCs during a single collision.

Initially, the powder charge consists of a volume fraction $\chi_0(0) = 1$ of powder never subjected to CLCs and exhibits perfect homogeneity. The occurrence of collisions during the mechanical processing by BM modifies such condition. After one collision, the powder charge includes two volume fractions of powder processed zero and one times, $\chi_0(1)$ and $\chi_1(1)$, respectively. After two collisions, the volume fraction of powder processed two times, $\chi_2(2)$, also appears. After n collisions, the volume fraction $\chi_0(n)$ of powder that has never been subjected to CLCs can be expressed as

$$\chi_0(n + 1) = \chi_0(n) - k\chi_0(n). \tag{4}$$

Accordingly, each collision makes $\chi_0(n)$ decrease by the fraction $k\chi_0(n)$. A similar expression can be written for the fraction $\chi_i(n)$ of powder processed i times after n collisions. As shown below,

$$\chi_i(n) = \chi_i(n-1) - k\chi_i(n-1) + k\chi_{i-1}(n-1). \tag{5}$$

Three terms are present in the right-hand side of Eq. (5). The term $k\chi_i(n-1)$ accounts for the fraction of powder processed i times that, after n collisions, becomes processed for $i+1$ times. Since such fraction contributes to $\chi_{i+1}(n)$, it is subtracted from $\chi_i(n-1)$. In contrast, the term $k\chi_{i-1}(n-1)$ accounts for the

fraction of powder processed $i-1$ times that, during the nth collision, becomes processed i times. Hence, its addition to $\chi_i(n-1)$.

Under the assumption that k is significantly smaller than 1, Eqs. (4) and (5) can be written into the corresponding continuous forms shown below:

$$d\chi_0 = -k\chi_0(n)dn; \qquad (6)$$

$$d\chi_i(n) = -k\chi_i(n)dn + k\chi_{i-1}(n)dn. \qquad (7)$$

Equation (6) is solved by the expression

$$\chi_0(n) = \chi_0 e^{-kn}, \qquad (8)$$

whereas the solution for Eq. (7) is

$$\chi_i(n) = \chi_0 \frac{(kn)^i}{i!} e^{-kn}. \qquad (9)$$

Equations (8) and (9) satisfy the condition $\sum_{i=0}^{\infty} \chi_i(n) = \chi_0$, which states the balance of volume fractions processed i times after n collisions for any given component of a powder mixture.

Equations (8) and (9) provide a basis for describing the kinetics of mechanically activated transformations. In particular, an exponential variation of the volume fraction of reactants with time can be obtained assuming that final products form already when powder is subjected to CLCs one single time. It follows that Eq. (8) describes the reduction in the volume fraction of reactants with the number n of collisions, whereas the volume fraction of products, χ_p, can be expressed as

$$\chi_p(n) = \chi_{p,f}(1 - e^{-kn}), \qquad (10)$$

where $\chi_{p,f}$ corresponds to the final value reached by χ_p once the transformation is complete.

Equations (8) and (10) can be written as a function of time, t, if a direct proportionality exists between t and n. This condition is fulfilled when collisions take place at constant frequency, N. In such case, $n = Nt$. The same condition allows moving, vice versa, from time to collisions. This is quite useful since, as shown in the following, the mechanically activated process investigated in the present work take place at constant frequency.

Discussion

BM experiments were performed using 3 balls of equal mass. The occurrence of collisions inside the reactor was monitored using piezoelectric transducers attached to the external reactor surface, according to the experimental methodology described in detail elsewhere [22, 37–39]. Here, it is simply worth remembering that the piezoelectric sensor generates an electric signal every time a ball collides with either the lateral wall of the cylindrical reactor, or the bases. If the 3 balls undergo a disordered dynamics inside the reactor and collide with its walls independent of each other, the piezoelectric transducer can be expected to give rise to a disordered sequence of signals. In contrast, a regular milling dynamics results in an ordered sequence of signals.

An ordered sequence of signals is exactly what the piezoelectric transducer generates during the mechanical activation of $NaNH_2$–MgH_2 powder mixtures. As shown in Fig. 5, only two signals per cycle of reactor displacement are observed. This suggests that the 3 balls move synchronously between the opposite reactor bases, their dynamics being governed by almost perfectly inelastic collisions. It follows that the overall collision frequency, N, is equal to three times the frequency of the signals generated by the piezoelectric transducer. Based on data shown in Fig. 5, N is, then, equal to about 87 Hz.

The evaluation of the collision frequency N allows referring the apparent rate constant of the metathesis between $NaNH_2$ and MgH_2, K, to individual collisions. Given the condition $kn = Kt$, k is equal to K/N. Thus, k is approximately equal to 1.6×10^{-7}.

The kinetic model described above suggests that such value represents a measure of the volume fraction of powder subjected to CLCs, then susceptible of metathesis, during individual collisions. Since the molar volumes of $NaNH_2$ and MgH_2 are known and equal to 28.07 and 18.15 cm^3 mol^{-1}, respectively, the total volume occupied by the powder charge, V,
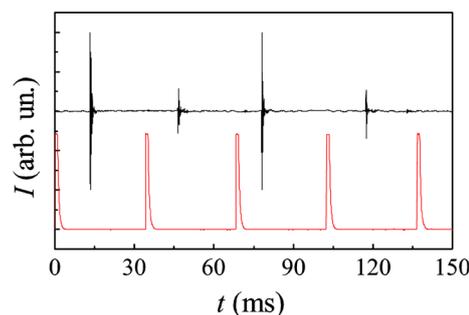

Figure 5 The electric signals generated by the piezoelectric transducer (*black line*, *top*) and marking the inversion points of the reactor displacement (*red line*, *bottom*).

amounts approximately to 5.70 cm^3. Therefore, the volume of NaNH$_2$–MgH$_2$ powder mixture effectively processed during the first collision, V^*, is equal to about 9.1×10^{-7} cm^3.

Such value indicates that the volume of reactant powders affected by CLCs, and then undergoing metathesis, is definitely quite small. It can be expected to result from the contribution of smaller sub-volumes dispersed within the total volume of powder trapped between the milling tools during the collision. In this regard, it is worth noting that independent measurements indicate that the amount of powder trapped during each collision, m^*, by 8 g stainless steel milling balls corresponds roughly to 1 mg [3, 22, 37, 40]. Since the densities of NaNH$_2$ and MgH$_2$ phases are equal to about 1.39 and 1.45 g cm^{-3}, respectively, the volume occupied by 1 mg of 2:1 NaNH$_2$–MgH$_2$ powder mixture is equal to about 0.71 mm^3. Based on a simple linear scaling between ball diameters, a 3.8 g stainless steel ball can be expected to trap about 0.27 mm^3 of the 2:1 NaNH$_2$–MgH$_2$ powder mixture. The comparison between this latter value and the V^* one of about 9.1×10^{-4} mm^3 reveals that only the 0.34% of the powder volume trapped during individual collisions undergoes CLCs.

NaNH$_2$ and MgH$_2$ powders exhibit similar particle size, 44 and 38 μm, respectively. To a first approximation, it can be set equal to about 41 μm for both reactants. Accordingly, each powder particle occupies a spherical volume of about 2.9×10^{-4} mm^3. It follows that approximately 930 powder particles become trapped during the collisions of a 3.8 g stainless steel ball. Stochastically involved in collisions, these powder particles undergo a relatively high-rate mechanical loading, which hardly allows a rearrangement of particle positions within the trapped volume. Thus, the high-rate mechanical loading involves a disordered ensemble of powder particles.

According to the literature [41, 42], a disordered ensemble of spherical particles of the same size exhibits a relative density of 0.8. Under such circumstances, each particle has, on the average, 3.2 points of contact with neighboring particles. Due to the density difference between reactants, a different number of NaNH$_2$ and MgH$_2$ powder particles are trapped during collisions. The relative number of reactant particles is such that metathesis can take place only at the 50% of the points of contact per particle. It follows that metathesis involves about 1.6

points of contact per particle. Since the number of powder particles trapped during collision is equal to about 930, at most the reaction between NaNH$_2$ and MgH$_2$ can involve 1488 points of contact that can be regarded as uniformly dispersed within the trapped volume of the NaNH$_2$–MgH$_2$ powder mixture. Therefore, the volume of powder reacted at each point of contact is equal to about 6.1×10^{-7} mm^3.

The observed reaction can be ascribed to the transfer of mechanical energy from balls to powders during each collision. To a first approximation, the energy transfer can be expected to concentrate at the points of contact between the powder particles, where loading conditions are more severe. The collision energy of about 0.073 J can be expected to distribute uniformly among the 1488 points of contact, which results in about 4.9×10^{-5} J per point of contact. Taking into account that 3.7×10^{-8} mol of reactants transform into products during the first collision, only 2.5×10^{-11} mol are involved at each point of contact. Therefore, the reactants involved in metathesis at each point of contact somehow absorb, to a first approximation, 1.9×10^6 J mol^{-1}, a quite high energy.

These rough calculations indicate that the mass fraction of powder involved in metathesis undergoes extreme processing conditions. During each collision, points of contact first and, then, all the trapped powder are subjected to severe thermal and mechanical stresses. Overall, the emerging scenario is still confused, and further studies are needed. In fact, a sound description of the mechanistic scenario underlying the observed kinetics can only stem from a detailed understanding of the processes taking place on the atomic scale.

Conclusions

This work provides experimental information on the chemical reactivity of 2:1 NaNH$_2$–MgH$_2$ powder mixtures subjected to mechanical processing by BM. Experimental findings deriving from quantitative XRD analyses of mechanically processed powder demonstrate that the mechanical activation induces a metathesis between the NaNH$_2$ and MgH$_2$ reactant phases, which results in the formation of NaH and Mg(NH$_2$)$_2$ products. The metathesis only proceeds under mechanical processing conditions, which represents an element of significant interest. Whereas the

thermally activated reaction exhibits a multi-stage mechanism involving the formation of solid intermediates and the evolution of gaseous H_2, the mechanochemical process is mono-stage, and occurs via the simple exchange of anionic species between cations. Therefore, the reaction between $NaNH_2$ and MgH_2 can be included in the very small number of chemical processes that follow different kinetic paths when subjected to thermal or mechanical activation. This makes the metathesis intriguing as a case study for understanding purely mechanochemical effects.

Concerning the reaction kinetics, a model correlating the volume of powder subjected to CLCs during each collision with the total chemical conversion has been used to interpret the experimental findings. Based on simple considerations involving the number of points of contact between the powder particles trapped during each collision, a rough estimate of the energy deposited at each point of contact has been given.

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Compliance with ethical standards

Conflict of interest   The authors declare that they have no conflict of interest.

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