

**Mechanochemistry**

# Mechanochemical Reactions from Individual Impacts to Global Transformation Kinetics

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**Abstract:** Typically induced by the mechanical processing of powders in ball mills, mechanochemical transformations are considered to result from the application of mechanical force to solid reactants. However, the undeniable deep connection between the dynamic compaction of powders during impacts and the overall transformation degree has yet to be disclosed. In the present work, we show that the square planar *bis*(dibenzoylmethanato)Ni<sup>II</sup> coordination compound undergoes trimerization when its powder experiences even a single ball impact. Based on systematic experiments with individual ball impacts and analysis by Raman spectroscopy, we provide here quantitative mapping of the transformation in the powder compact and deduce bulk reaction kinetics from multiple individual impacts.

equal-channel angular pressing, extrusion and high-pressure torsion have been widely employed in materials science and, now, extrusion particularly, are beginning to be applied to chemical synthesis and formulation.<sup>[19–22]</sup> However, the most common method used to mechanically activate physical and chemical transformations, in the past and presently, is ball milling (BM) of powders.<sup>[23–27]</sup>

BM is based on vigorous stirring of milling balls and powders inside a closed reactor leading to repeated impacts, or sliding contacts, between balls and reactor walls.<sup>[23,24]</sup> Each impact compresses a small amount of the milled powder. As the dynamic compaction progresses, individual particles experience local mechanical stress fields, which evolve into force chains spreading through the contact points. The particles start deforming as local mechanical stresses become higher than yield stresses and they give rise to plastic behaviour or fracture depending on a ductile or brittle response to deformation. The formation of new surfaces and interfaces, and the related processes that take place at the microscopic scale, enhance the chemical reactivity and concur to the initiation and progression of a mechanochemical transformation.<sup>[28–31]</sup>

Within this framework impacts are crucial and yet, despite that their importance was recognized as early as in the 1970s,<sup>[32–34]</sup> the link between individual impacts and the overall transformation kinetics remained elusive.<sup>[35–37]</sup> Consequently, many fundamental questions of mechanochemical transformations remain open. For instance, is the very first impact able to induce a chemical transformation in the powder trapped between colliding surfaces? If so, how is the product distributed in the impacted volume? If one impact is not enough, how many impacts are needed to initiate conversion? How many impacts are required to completely transform the chemical species contained in the trapped volume? More generally, how does the transformation kinetics at the level of individual impacts determine the overall kinetics in the bulk powder, which is the one that is typically evaluated?

These are difficult questions to address due to the very nature of mechanical processing of a powder by BM, which renders a direct experimental investigation of individual impacts out of reach due to moving parts, powder agitation, fluctuations in the powder volume trapped between colliding surfaces and variation of the impact loci.

Although the use of hammer-based devices and suitably manufactured ball mills provided interesting evidence concerning the effects of individual impacts,<sup>[38–44]</sup> the only realistic solution is to study individual impacts, and the

## Introduction

Recent years have witnessed a striking growth of a research subject traditionally lying at the intersection of chemistry and materials science, namely mechanochemistry.<sup>[1–12]</sup> In mechanochemistry, a mechanical force is applied to the reacting system to obtain chemical effects.<sup>[13–18]</sup> Mechanochemical methods differ in the way the mechanical force is applied to the reacting materials. Severe mechanical deformation methods such as alternate roll bonding, cold rolling,

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transformations they possibly induce, outside of the mechanochemical reactor. Of course, this implies an estrangement from real processing conditions, which represents an obvious drawback, but enables the experimental investigation of kinetic features that have remained in the shadow so far. To this aim, ball drop experiments appear, in their simplicity, perfectly suited. A ball is dropped, from a certain height, on a powder layer of a given thickness and the powder is analyzed immediately after the impact. Such a straightforward design of the experiment allows a full control of experimental parameters and variables, such as ball size, impact velocity, impact angle, thickness of powder layer, temperature and atmosphere.

In this work, we use individual ball drops to investigate the mechanochemistry of bis(dibenzoilmethanato)Ni<sup>II</sup>, hereafter denoted as Ni(dbm)<sub>2</sub>, a coordination compound in which Ni<sup>II</sup> is in a square planar coordination by four O atoms from the two chelating dibenzoilmethanate anions (see Supporting Information SI.1 for details).<sup>[45]</sup> Our previous work has shown that the BM of Ni(dbm)<sub>2</sub> powders induces the formation of the trimer, [Ni(dbm)<sub>2</sub>]<sub>3</sub>, where O atoms bridge Ni<sup>II</sup> ions giving rise to an octahedral Ni<sup>II</sup> coordination (see Supporting Information SI.1 for details).<sup>[46]</sup> As a consequence of the change in the coordination around Ni<sup>II</sup>, the Ni<sup>II</sup> singlet spin state changes into triplet and the trimerization is accompanied by a colour change from the brown monomer to the green trimer. The reaction stops immediately if BM is interrupted, thus proving that the process is truly a mechanochemical one. In addition, no intermediate phase was detected,<sup>[46]</sup> which allows a simpler kinetic analysis and facilitates comparing the results obtained from individual ball drops and bulk BM experiments.

## Results and Discussion

To unveil the relationship between the global BM kinetics of the apposite Ni(dbm)<sub>2</sub> trimerization reaction<sup>[46]</sup> and the local transformation taking place as a result of individual ball impacts, we first focused on the results of single ball-drop experiments. Then, we examined the effects of multiple ball drops on the same powder sample. Finally, we connected the local reaction kinetics resulting from individual ball impacts with the global kinetics based on the statistical nature of BM. In the following we will discuss the three points separately. Next to Raman microscopy, we used powder X-ray diffraction (PXRD), infrared (IR) spectroscopy, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and nuclear magnetic resonance (NMR) in sample analysis and characterization (see Supporting Information SI.4–SI.7 for details).

### Single ball drops

Ball-drop experiments consisted in dropping a tungsten carbide (WC) ball about 14.1 g in mass and 12.1 mm in diameter on relatively uniform powder layers approximately

0.5 mm thick from a height of 1 m (see Supporting Information SI.8 for details).

The resulting impact ball velocity was approximately 4.4 ms<sup>-1</sup>, which is well within the range of impact velocities usually occurring in common vibratory ball mills.<sup>[46–49]</sup> The corresponding energy of the ball at impact was 0.14 J. The ball drop induces rapid compression of the powder layer in the impacted region, with the consequent formation of powder compacts with an approximately circular shape, such as the one shown in Figure 1a. Powder compacts look like thin inhomogeneous disks of powder with irregular contours, average diameter around 2 mm and thickness of about 0.18 mm (see Supporting Information SI.8 for details).

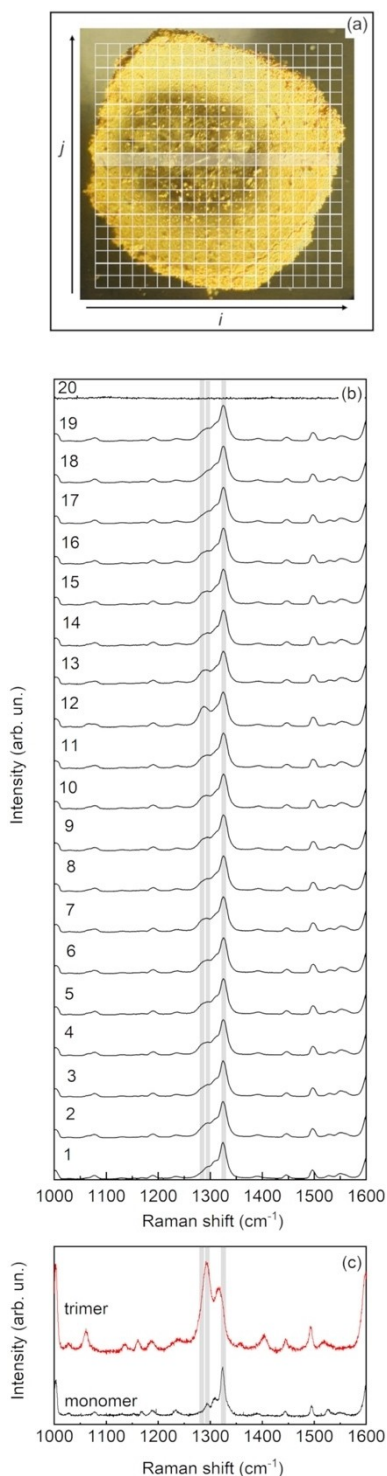
The occurrence of the trimer in the powder compact was examined using Raman spectroscopy (see Supporting Information SI.9 for details). In particular, we divided the image of the powder compact in 20×20 square cells, each cell having sides of 100 μm in length. A focused circular laser beam with a diameter of 70 μm was used to collect the Raman spectra from each cell. The normalized Raman spectra collected from the 20 cells belonging to the (i; 11) row of the square grid are shown in Figure 1b and exhibit differences that indicate sporadic chemical changes in the impacted region, as evident from a shoulder emerging at 1286 cm<sup>-1</sup>. However, this shoulder could not be assigned to the expected [Ni(dbm)<sub>2</sub>]<sub>3</sub> trimer, which has two strong Raman bands at 1296 and 1323 cm<sup>-1</sup> (see Figure 1c).

The impacted sample exhibited a slight colour change from brown to light green indicating the formation of an octahedrally coordinated Ni<sup>II</sup>. In an attempt to identify the unknown product, we ground in air the monomer powder using a mortar and a pestle witnessing a progressive growth of the shoulder at 1286 cm<sup>-1</sup> (see Figure 2 and Supporting Information SI.10 for details).

The light-green phase formed by ball drops and by manual grinding could either be an intermediate on the reaction path from the monomer to the trimer, for instance a dimer, or a side product alternative to the trimer. After failing to find evidence for a dimer intermediate, we have considered the reaction of the monomer with atmospheric moisture. Indeed, the precursor to prepare the monomer was the dihydrate Ni(dbm)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>[45,46]</sup> and its Raman spectrum could readily be matched with the emerging shoulder in the Raman spectra of the ground monomer.

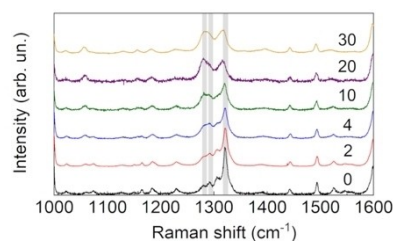
The dihydrate formation was further confirmed by subjecting the light green powder to mild heating at 60 °C for 2 h in air (see Supporting Information SI.11 for details), which is well below 205 °C, the temperature required for the thermal formation of the trimer,<sup>[45]</sup> where we have obtained back the pristine monomer (see Figure 3).

Had the intermediate been a dimer, it would have been more likely for mild heating to further progress the reaction to the trimer. The dihydrate phase was thoroughly characterised based on TG, FTIR, DFT-calculated Raman spectra, and eventually by crystal structure solution from PXRD revealing the *trans* configuration of the two water molecules and hydrogen bonded-chains in its crystal structure. The assignment of Raman bands is further supported by the DFT-calculated Raman spectra of the monomer, the trimer

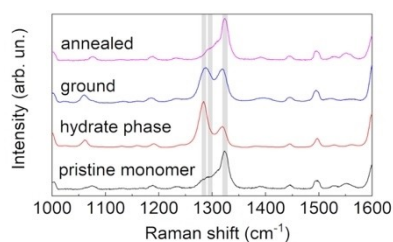


**Figure 1.** (a) A typical powder compact formed by ball drop. A square grid of 400 square cells is superposed to the image obtained by optical microscopy. Each square cell has sides 100  $\mu\text{m}$  long, so that the grid side is 2 mm long. Each cell is univocally identified by the pair of integer numbers ( $i$ ;  $j$ ). (b) Normalized Raman spectra from the 20 cells belonging to the highlighted ( $i$ ; 11) row of the grid. (c) Normalized Raman spectra of monomer and trimer.

and the dihydrate (see Supporting Information SI.12–SI.14 for details).



**Figure 2.** Normalized Raman spectra of monomer ground in the mortar for the reported time intervals (min) and the dehydrate compound.

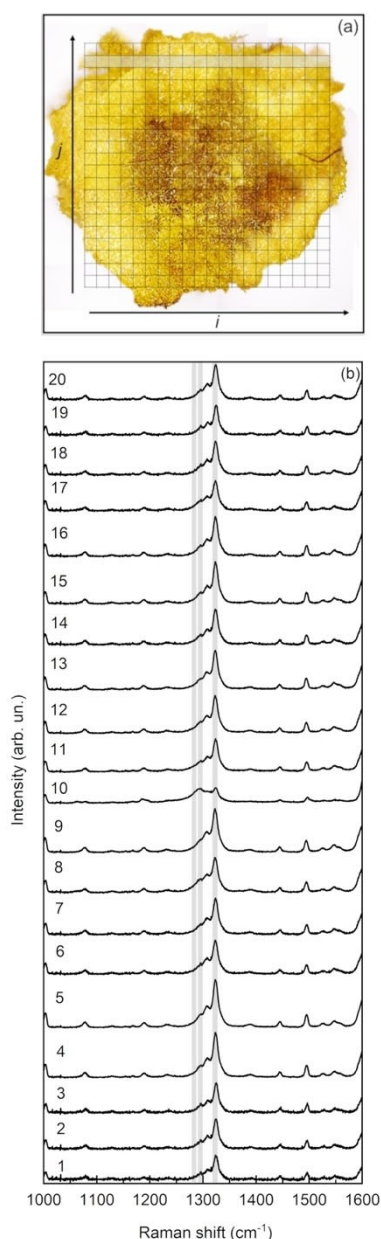


**Figure 3.** Normalized Raman spectra of pristine monomer, powder ground for 40 min in the mortar and powder ground and annealed at 60  $^{\circ}\text{C}$  for 2 h in air.

To avoid the formation of the dihydrate, we have carried out the next set of ball drop experiments inside a glove box under Ar atmosphere with oxygen and humidity contents below 2 ppm (see Supporting Information SI.12 for details). As before, the ball drop induces the formation of powder compacts with approximately circular shape, as the one shown in Figure 4a. The normalized Raman spectra collected from the compact surface exhibit significant differences (see Figure 4b). In particular, we observe a new band emerging at 1296  $\text{cm}^{-1}$ . This band is significantly more intense and its position coincides with the band characteristic of the trimer. Consequently, we conclude that the ball drop in Ar induced the formation of the trimer.

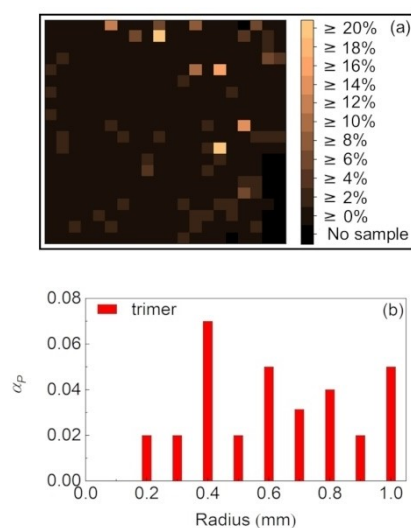
### Phase distribution maps

Analysis of the normalized Raman spectra collected from the powder compacts allowed us to estimate, cell by cell of the square grid, the amounts of the trimer and the dihydrate formed in Ar and in air, respectively. Accordingly, we obtained two-dimensional maps showing the distribution of the different phases in the powder compact after a ball drop (see Supporting Information SI.15 for details). The distribution map obtained from a ball drop in Ar is shown in Figure 5a. The trimer is detected in 13% of cells and its distribution appears to be scattered. In particular, the cells containing the trimer are, in general, relatively far from the centre of the powder compact. As evident from the radial distribution shown in Figure 5b, the probability of finding the trimer is maximum at a radial distance of about 0.4 mm (see Supporting Information SI.15 for details).

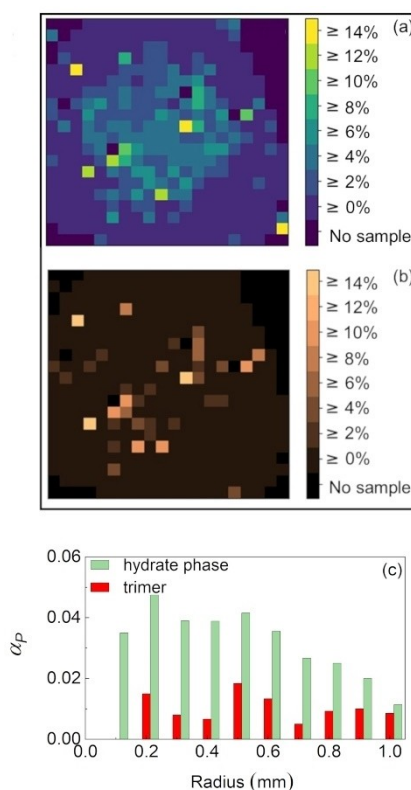


**Figure 4.** (a) A typical powder compact formed by ball drop in Ar atmosphere. A square grid of 400 square cells is superposed to the image obtained by optical microscopy. Each square cell has sides 100  $\mu\text{m}$  long, so that the grid side is 2 mm long. Each cell is univocally identified by the pair of integer numbers  $(i, j)$ . (b) Normalized Raman spectra from the 20 cells belonging to the highlighted  $(i; 19)$  row of the grid.

We have constructed similar maps for powder compacts obtained for ball drop experiments conducted in air. The distribution maps for the hydrate phase and for the trimer are shown in Figures 6a and 6b respectively. The hydrate phase is detected in the 39% of cells, together with a generally smaller amount of the trimer. The cells containing the dihydrate and the trimer are scattered around the centre of the powder compact with a close-to-uniform radial distribution (Figure 6c).



**Figure 5.** (a) Distribution map of trimer after a ball drop in Ar. The colour code indicates the molar fraction of trimer in each cell of the square grid superposed to the image of the powder compact. The map centre approximately coincides with the centre of the powder compact. (b) Radial distribution of cells containing trimer with respect to the centre of the powder compact.



**Figure 6.** Distribution maps of (a) hydrate phase and (b) trimer after a ball drop in air. The colour code indicates the molar fraction of trimer and hydrate phase in each cell of the square grid superposed to the image of the powder compact. The map centre approximately coincides with the centre of the powder compact. (c) Radial distribution of cells containing trimer and hydrate phase with respect to the centre of the powder compact.

### Chemical conversion in single ball drops

The volume of powder irradiated in each cell of the powder compact surface during Raman measurements can be set equal to

$$v_{irr} = \pi r^2 h, \quad (1)$$

where  $r$  is the radius of the laser beam and  $h$  is its penetration depth. In our case,  $r$  and  $h$  are approximately equal to 35  $\mu\text{m}$  and 8  $\mu\text{m}$  respectively. This means that  $v_{irr}$  is equal to  $3.1 \times 10^{-5} \text{ mm}^3$ .

The average molar fraction of a given product in the powder compact can be estimated by the weighted average

$$\kappa = \sum_{i=1}^{N_{irr}} x_i / N_{irr}, \quad (2)$$

where  $N_{irr}$  is the total number of cells in which the surface of the powder compact has been divided and  $x_i$  is the fraction of the product in the  $i$ -th cell. For powder compacts impacted in air, we obtain  $\kappa$  values of about  $1.9 \times 10^{-2}$  for the hydrate phase and  $5.0 \times 10^{-3}$  for the trimer. The  $\kappa$  value for ball drops performed in Ar, determining the formation of the trimer only, is equal to about  $3.5 \times 10^{-3}$ . Therefore, ball drops in air and Ar induce the formation of comparable amounts of trimer.

We can also expect that, to a first approximation, the  $\kappa$  values are representative of the chemical conversion degree across the whole powder compact resulting from the dynamic compression of the powder layer during the ball drop. This means that we can expect to observe the same molar fractions of the dihydrate or the trimer in the total volume of the powder compact,  $V_{compact}$ , and not only in the irradiated portion. It follows that we can express the average molar fraction  $\kappa$  as

$$\kappa = \sum_{i=1}^N x_i v / N v = \sum_{i=1}^N x_i v / V_{compact}, \quad (3)$$

where  $v$  is the volume element from which we have information on  $x_i$  and  $V_{compact}$  is the total volume of the compact, equal to the product between  $v$  and the total number of volume elements in the compact,  $N$ . Given that the average thickness of the compressed layer and the surface area are equal to about 0.18 mm and 3.14 mm<sup>2</sup> respectively, the volume of the powder compact,  $V_{compact}$ , is equal to about 0.56 mm<sup>3</sup>.

### Chemical conversion due to multiple ball drops

To further investigate how the number of ball drops affects the conversion degree, we carried out experiments in which the WC ball was repeatedly dropped in air and in Ar. Although a certain degree of uncertainty in the ball drop is unavoidable, we can safely say that impacts have involved

always the same area of the powder layer. Therefore, we can reasonably relate any change in Raman spectra to the number of ball drops performed.

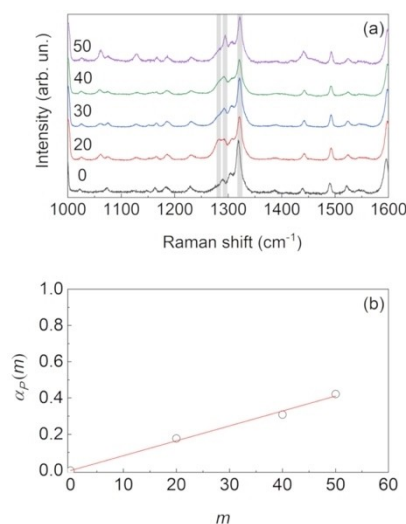
The Raman spectra were collected ex situ from the small areas of powder compressed at impact (see Supporting Information SI.9 for details). In the present case, we were not interested in building a distribution map of the products formed by ball drop, but only to obtain accurate estimates of the average amounts of the monomer, hydrate and trimer phases detected. The Raman spectra shown in Figure 7a indicate that both the hydrate phase and the trimer form when ball drops are performed in air, whereas only the trimer is observed in powders impacted under Ar. Hereafter, we will focus on the latter case.

As evident from Figure 7b, the relative amount of the product increases with the number of ball drops,  $m$ . Data indicate a linear relationship allowing, to a first approximation, to write:

$$\alpha_p(m) \approx \kappa m. \quad (4)$$

The average molar fraction of the monomer transformed per ball drop,  $\kappa$ , can be estimated from the slope of the best-fitted line. We find that individual ball drops in Ar result in a  $\kappa$  value of about  $8.2 \times 10^{-3}$ . This value is in a good agreement with the value of  $3.5 \times 10^{-3}$  that was obtained from single ball-drop experiments.

These findings shed light on the mechanism underlying the mechanically activated transformation of the monomer Ni(dbm)<sub>2</sub> into the trimer [Ni(dbm)<sub>2</sub>]<sub>3</sub>, and confirm the observations reported previously.<sup>[41–44]</sup> The repeated drop of hammers and balls on powder layers can induce physical and chemical changes analogous, in all respects, to those resulting from the BM of powders. In no case, hammer and ball drops have activated a transformation different from



**Figure 7.** (a) Normalized Raman spectra of the impacted area after the number of impacts indicated. Data refer to ball drop experiments performed in Ar. (b) The molar fraction of trimer,  $\alpha_p(m)$ , as a function of the number of ball drops,  $m$ .

the one activated by BM. This is true for organic solids<sup>[41]</sup> as well as for inorganic compounds<sup>[42–44,50]</sup> and materials<sup>[51]</sup>.

What changes is simply the volume of powders involved in the mechanical processing. In the case of hammer and ball drops, the volume of powder subjected to processing is just the volume of powder affected by individual impacts, while during BM impacts affect, time by time, different volumes of powder because the powder is effectively stirred.

This means that, to a first approximation, we can expect different transformation rates because of the different volumes involved in BM and ball drop experiments, but not a different chemistry, particularly when the chemical reaction, as in our case, does not exhibit intermediates and keeps the same kinetics under different BM conditions, which is exactly what we have observed in our previous work on Ni(dbm)<sub>2</sub>.<sup>[46]</sup>

Along this line, we have the opportunity to properly compare the apparent rate constants governing the trimerization under ball drop and BM conditions using the volume of powder involved in processing as a scale factor.

### Comparison of apparent rate constants

According to our previous work,<sup>[46]</sup> the analysis of kinetic curves revealed that bulk BM of Ni(dbm)<sub>2</sub> powders induces the formation of the trimer [Ni(dbm)<sub>2</sub>]<sub>3</sub> described by an exponential kinetic curve:

$$\alpha_p(m) = 1 - \exp(-\kappa m). \quad (5)$$

The rate constant  $\kappa$  in Eq. 5 has the same physical meaning of the molar fraction of powder involved in the chemical transformation in individual ball drops, as defined in Eq. 3. This is why we denote it with the same symbol,  $\kappa$ . The  $\kappa$  values obtained in BM experiments at different milling frequencies using a WC ball of 8 mm in diameter range between  $1.1 \times 10^{-5}$  and  $2.6 \times 10^{-5}$ .<sup>[46]</sup>

In the case of BM experiments, these values were evaluated by averaging over the total amount of powder processed in the vial,  $V_{\text{powder}}$ , which was equal to about 0.135 cm<sup>3</sup>. The reason is that experimental measurements are not restricted to the volume of powder directly involved in individual impacts. Rather, they involve the in situ sampling of the powder inside the moving vial. Therefore, to properly compare the  $\kappa$  values obtained from BM experiments with those obtained from powder compacts, their values must be suitably scaled.

As mentioned before, to a first approximation, the scale factor can be the ratio  $V_{\text{powder}}/V_{\text{compact}}$  between the total volume of powder processed by BM and the volume of the powder compact formed by ball drop. Accordingly, the scaled  $\kappa$  values from BM experiments are approximately equal to  $2.6 \times 10^{-3}$  and  $6.2 \times 10^{-3}$ . These values agree remarkably well with the ones obtained from individual and multiple ball drop experiments (see Table 1).

The observed correspondence between the scaled rate constants, despite their crude estimation, encourages us to believe that the outcomes of ball drop experiments capture

**Table 1:** Comparison of  $\kappa$  estimates.

Single ball drops <sup>[a]</sup>	multiple ball drops <sup>[a]</sup>	BM experiments <sup>[b]</sup>
$3.5 \times 10^{-3}$	$8.2 \times 10^{-3}$	$2.6 \times 10^{-3}$ – $6.2 \times 10^{-3}$

[a] Calculated referring to the volume of the powder compact,  $V_{\text{compact}}$ .  
[b] Calculated using the scale factor,  $V_{\text{powder}}/V_{\text{compact}}$ . The two estimates reported refer, respectively, to the slowest and the fastest trimerization kinetics discussed in Ref. [46].

the essence of the mechanochemical trimerization. In particular, it seems that they suitably represent the result of the whole sequence of local processes involved in the impact loading of powders and the following relaxation. Therefore, the rate constants  $\kappa$  should be regarded as the quantities that phenomenologically condense all the chemical effects resulting from the formidable complexity of the dynamic compaction of powders at high strain rates.

### Solid-state DFT calculations

Despite detailed verification of the rate constants, no mechanistic information can be inferred therefrom so we have conducted simulations of the mechanochemical compression using solid-state DFT (see Supporting Information SI.16 for details). Based on the crystal structure of the monomer which exhibits face-to-face stacking of Ni(dbm)<sub>2</sub> molecules along the *b* axis, we have explored if a compression along *b* could have a tendency for the formation of an octahedral coordination environment around Ni<sup>II</sup>. In effect, the crystal structure of the monomer was squashed along the *b* axis, while it was allowed to relax in the *a* and *c* directions. As compression is increased, coordination number around nickel increases with oxygen atoms becoming bridging between nickel atoms and the spin state of Ni changes from a low-spin to a high-spin state. While such a compression simulation is unrealistic due to the imposed periodic boundary conditions resulting in a polymer instead of a trimer, in essence, it confirms that mechanical compression has the capacity to achieve an octahedral coordination around Ni<sup>II</sup>.

### Discussion

The experimental findings described here directly relate the mechanochemical transformation with ball impacts, which in BM typically occur at a high frequency limiting our studies to overall bulk transformations. We show unequivocally that even a single impact can give rise to chemical changes in the powder trapped between the colliding surfaces. The drop of a 14.1 g WC ball on a 0.5-mm thick Ni(dbm)<sub>2</sub> powder layer induces trimerization in mere few thousandths of a cubic millimetre and only a very small amount of the reactant meets the necessary conditions to transform upon each individual impact.

Mapping of the powder volume effectively compressed during the impact by Raman spectroscopy revealed small

sub-volumes of the product trimer scattered around the impact axis showing that the transformation occurs only in small regions of the powder volume affected by the ball impact. Repeated impacts on the same powder volume increase the transformation degree. In particular, the amount of the product trimer formed increases linearly with the number of ball impacts.

The volume of the powder experiencing the trimerization during a single impact is approximately the same for single and multiple ball drops. This can be justified by the fact that the amount of the monomer involved in trimer formation per impact is very small and we can expect that consecutive ball impacts affect different sub-volumes of the compressed powder without a significant statistical incidence of other previously transformed sub-volumes. Similarly, the fact that the powder compact is compressed several times, with all its consequences in terms of powder particle deformation and compaction, seems to give rise to no, or minor, effect. Therefore, experimental evidence suggests that, to a first approximation, the effects of a given impact are substantially independent of those of the previous impact.

Such considerations allow us to relate, in principle, local effects and global degree of trimerization. According to Eq. 3, the first impact on the monomer powder induces the formation of a volume fraction of trimer  $\kappa$ . In general, the reactant molar fraction after  $m$  impacts can be expressed as

$$\alpha_R(m) = 1 - \sum_{i=1}^m \kappa \alpha_R(m-i), \quad (6)$$

and the product molar fraction as

$$\alpha_P(m) = 1 - \alpha_R(m). \quad (7)$$

Since  $\kappa$  is small, the total number of impacts,  $m$ , required to complete the trimerization is large. Under these circumstances, Eqs. 6 and 7 can be written in the continuous form (see Ref. [36] for details)

$$\alpha_R(m) = \exp(-\kappa m). \quad (8)$$

$$\alpha_P(m) = 1 - \exp(-\kappa m). \quad (9)$$

Eq. 9 is equal to Eq. 5. In other words, we have been able to obtain the kinetic equation for the mechanically induced trimerization process based on the evidence that (i) the maximum molar fraction of monomer by the mechanochemical transformation during a single impact is equal to  $\kappa$  and (ii) there is no intermediate in the reaction mechanism. This means that, in principle, the kinetics of mechanochemical transformation can be predicted from the chemical changes induced in single impacts.

## Conclusion

By studying the effect of individual ball impacts in a purely mechanochemical reaction of trimerisation, we have been

able to determine that the reaction takes place in very small randomly scattered compartments in the impacted sample portion. The reaction occurs even during the very first impact on the pristine monomer and the volume of the monomer that is converted to the trimer in individual impacts is around a few thousandths of  $1 \text{ mm}^3$ . Repeated ball impacts on the same powder compact result in a linear increase of the trimer content showing that the amount of the monomer converted per impact is approximately the same. Such estimates are also close to those obtained from BM experiments. We thus show that mechanochemical reaction kinetics stems from the transformation occurring in individual impacts and highlight their importance in fundamental understanding of bulk mechanochemical transformations.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Impact • Kinetics • Mechanochemistry • Trimerization

- [1] S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steedk, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413–447.
- [2] T. Friščić, *Chem. Soc. Rev.* **2012**, *41*, 3493–3510.
- [3] V. Šepelák, A. Düvel, M. Wilkening, K.-D. Beckerbe, P. Heitjansbc, *Chem. Soc. Rev.* **2013**, *42*, 7507–7520.
- [4] P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutková, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wiczorek-Ciurowam, *Chem. Soc. Rev.* **2013**, *42*, 7571–7637.
- [5] G.-W. Wang, *Chem. Soc. Rev.* **2013**, *42*, 7668–7700.

- [6] L. Takacs, *Chem. Soc. Rev.* **2013**, *42*, 7649–7659.
- [7] D. Tan, F. García, *Chem. Soc. Rev.* **2019**, *48*, 2274–2292.
- [8] J. L. Howard, Q. Cao, D. L. Browne, *Chem. Sci.* **2018**, *9*, 3080–3094.
- [9] A. Porcheddu, E. Colacino, L. De Luca, F. Delogu, *ACS Catal.* **2020**, *10*, 8344–8394.
- [10] A. Krusenbaum, S. Grätz, G. T. Tigineh, L. Borchardt, J. G. Kim, *Chem. Soc. Rev.* **2022**, *51*, 2873–2905.
- [11] S. Pagola, *Crystals* **2023**, *13*, 124.
- [12] E. Boldyreva, *Faraday Discuss.* **2023**, *241*, 9–62.
- [13] A. A. L. Michalchuk, E. V. Boldyreva, A. M. Belenguer, F. Emmerling, V. V. Boldyrev, *Front. Chem.* **2021**, *9*, 685789.
- [14] V. V. Boldyrev, E. G. Avvakumov, *Russ. Chem. Rev.* **1971**, *40*, 847–859.
- [15] P. Butyagin, *Russ. Chem. Rev.* **1971**, *40*, 901–915.
- [16] G. Heinicke, *Tribochemistry*, Akademie-Verlag, Berlin, **1986**.
- [17] E. M. Gutman, *Mechanochemistry of Materials*, Cambridge International Science Publishing, Cambridge, **1998**.
- [18] G. Kaupp, *CrystEngComm* **2009**, *11*, 388–403.
- [19] D. E. Crawford, C. K. G. Miskimmin, A. B. Albadarin, G. Walker, S. L. James, *Green Chem.* **2017**, *19*, 1507–1518.
- [20] Q. Cao, J. L. Howard, D. E. Crawford, S. L. James, D. L. Browne, *Green Chem.* **2018**, *20*, 4443–4447.
- [21] D. E. Crawford, A. Porcheddu, A. S. McCalmont, F. Delogu, S. L. James, E. Colacino, *ACS Sustainable Chem. Eng.* **2020**, *8*, 12230–12238.
- [22] O. Galant, G. Cerfeda, A. S. McCalmont, S. L. James, A. Porcheddu, F. Delogu, D. E. Crawford, E. Colacino, S. Spataro, *ACS Sustainable Chem. Eng.* **2022**, *10*, 1430–1439.
- [23] C. Suryanarayana, *Prog. Mater. Sci.* **2001**, *46*, 1–184.
- [24] C. Suryanarayana, *Research* **2019**, *2019*, 4219812.
- [25] E. Boldyreva, *Chem. Soc. Rev.* **2013**, *42*, 7719–7738.
- [26] *Ball Milling Towards Green Synthesis: Applications, Projects, Challenges* (Eds.: B. Ranu, A. Stolle), RSC Green Chemistry Series, No. 31, Royal Society of Chemistry, Cambridge, **2015**.
- [27] J.-L. Do, T. Friscic, *ACS Cent. Sci.* **2017**, *3*, 13–19.
- [28] F. K. Urakaev, V. V. Boldyrev, *Powder Technol.* **2000**, *107*, 93–107.
- [29] F. K. Urakaev, V. V. Boldyrev, *Powder Technol.* **2000**, *107*, 197–206.
- [30] O. V. Lapshin, E. V. Boldyreva, V. V. Boldyrev, *Russ. J. Inorg. Chem.* **2021**, *66*, 433–453.
- [31] A. A. Michalchuk, I. A. Tumanov, V. A. Drebuschak, E. V. Boldyreva, *Faraday Discuss.* **2014**, *170*, 311–335.
- [32] V. V. Boldyrev, *Kinet. Katal.* **1972**, *13*, 1411–1421.
- [33] W. W. Boldyrev, *Z. Phys. Chem.* **1975**, *256*, 342–348.
- [34] F. Delogu, *J. Mater. Synth. Proc.* **2000**, *8*, 271–277.
- [35] F. Delogu, *Acta Mater.* **2008**, *56*, 905–912.
- [36] F. Delogu, L. Takacs, *J. Mater. Sci.* **2018**, *53*, 13331–13342.
- [37] M. Carta, E. Colacino, A. Porcheddu, F. Delogu, *Phys. Chem. Chem. Phys.* **2020**, *22*, 14489–14502.
- [38] F. K. Urakaev, V. V. Boldyrev, O. F. Pozdnyakov, V. R. Regel, *Kinet. Katal. (USSR)* **1977**, *18*, 350–358.
- [39] F. K. Urakaev, *Phys. Chem. Miner.* **2007**, *34*, 351–361.
- [40] F. K. Urakaev, *Phys. Chem. Miner.* **2008**, *35*, 231–239.
- [41] I. A. Tumanov, A. F. Achkasov, E. V. Boldyreva, V. V. Boldyrev, *CrystEngComm* **2011**, *13*, 2213–2216.
- [42] F. Delogu, *Langmuir* **2012**, *28*, 10898–10904.
- [43] G. Ligios, A. Manuello, F. Delogu, *J. Alloys Compd.* **2013**, *554*, 426–431.
- [44] F. Delogu, *Acta Mater.* **2014**, *66*, 388–395.
- [45] D. V. Soldatov, A. T. Henegouwen, G. D. Enright, G. I. Ratcliffe, J. A. Ripmeester, *Inorg. Chem.* **2001**, *40*, 1626–1636.
- [46] L. Vugrin, M. Carta, S. Lukin, E. Meštrović, F. Delogu, I. Halasz, *Faraday Discuss.* **2023**, *241*, 217–229.
- [47] C. Caravati, F. Delogu, G. Cocco, M. Rustici, *Chaos* **1999**, *9*, 219–226.
- [48] G. Cocco, F. Delogu, L. Schiffrini, *J. Mater. Synth. Proc.* **2000**, *8*, 167–180.
- [49] A. Polo, M. Carta, F. Delogu, M. Rustici, M. Budroni, *Front. Chem.* **2022**, *10*, 915217.
- [50] F. Delogu, *Metall. Mater. Trans. B* **2013**, *44*, 166–174.
- [51] S. A. Humphry-Baker, S. Garroni, F. Delogu, C. A. Schuh, *Nat. Mater.* **2016**, *15*, 1280–1287.

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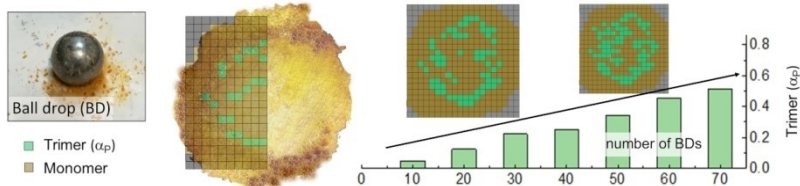


## Research Articles

## Mechanochemistry

M. Carta, L. Vugrin, G. Miletić,  
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Mechanochemical Reactions from Individual Impacts to Global Transformation Kinetics



A single ball drop on a thin layer of loose *bis*(dibenzoylmethanato)Ni<sup>II</sup> powders induces a partial trimerization reaction as a result of the severe mechanical deformation accompanying the formation of

the powder compact. Repeated ball drops on the same powder compact result in an approximately linear increase of the trimer amount.