

A kinetic study of the mechanically activated atom exchange: The effect of milling frequency and balls mass

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Supplementary Information

SI.1. Experimental methods

BM was performed utilizing an InSolido Technologies IST500 ball mill. The ball mill is equipped with an electric motor whose rotational speed can be changed in the range between *** and *** rpm. Simple mechanical gears transform the rotational motion into the horizontal angular oscillation of a mechanical arm. A cylindrical jar is fixed at the end of the mechanical arm and undergoes a pendulum-like oscillation at a frequency that usually ranges from 15 Hz to 35 Hz. The ball mill has a built-in control of the milling frequency that can be set by the user using a knob and the set value is read on the mill display. The mill has a feedback loop while operating that adjusts the rotations of the electromotor that translate to the swinging frequency. The rotations of the electromotor adjust to keep the user-set frequency of milling.

Reactions were conducted in PMMA jars with rounded bases using two 7-mm balls made from either stainless steel (SS, mass of each 1.42 g), zirconia (ZrO_2 , 1.06 g), tungsten carbide (WC, 2.86 g) and one combination that used one SS ball and one WC ball (FeWC, 1.42 g and 2.86 g). The balls of different materials have different mass, but the same size. This choice has been made to avoid that ball size effects could significantly affect the milling dynamics, although minor effects due to the elasticity of impact can be expected. The milling frequency is stable during operation and deviations from the set milling frequency are below 0.1 Hz.

In each reaction, 2 mmol of benzoic acid were weighed in one half of the jar and 2 mmol of D_2O were added using a micropipette in other half. Then, the two halves were snap-closed together carefully to ensure no contact between the solid and the liquid prior to the initiation of milling.

Reactions were conducted in duplicate or triplicate at five different frequencies, namely 25.0, 27.5, 30.0, 32.5, and 35.0 Hz. For any given milling frequency, we changed the ball mass. In this way, at least to a first approximation, the changes in the rate of hydrogen isotopic exchange (HIE) cannot be ascribed to a change in the ball size and possible changes in the geometry of ball impacts.

The isotopic exchange with D of the hydrogen of the benzoic acid is observable in the Raman spectrum of the reaction mixture. The intensity of the band at 765 cm^{-1} increases, while the intensity of the band at 793 cm^{-1} decreases correspondingly. Reaction profiles were obtained by fitting the changes in intensity of the Raman band at the 765 cm^{-1} belonging to deuterated benzoic acid, as described in previous work [18***]. Prior to fitting, the spectral range $560\text{-}870\text{ cm}^{-1}$ was baseline-corrected. The spectra were then internally normalized based on the intensity of the Raman peak at 612 cm^{-1} , which remains unaffected upon HIE.

SI.2. Isokinetic behaviour

The reaction profiles obtained at different milling frequencies, shown in Fig. 1, collapse onto a single reaction profile if the time is suitably scaled by a coefficient ϕ_{exp} . As shown in Fig. SI.1, in all the investigated cases the reaction profiles overlap satisfactorily, within the experimental uncertainties affecting the experimental measurements.

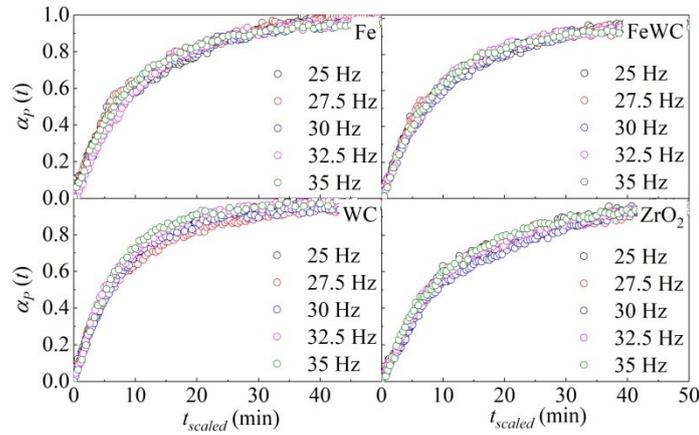


Figure SI.1. The molar fraction of deuterated benzoic acid, $\alpha_p(t)$, as a function of scaled time, t_{scaled} . Data refer to the BM experiments performed using balls made of different material.

In turn, the data plotted in Fig. SI.2 indicate that the scaling coefficients ϕ_{exp} are linear with the milling frequency, f , raised to the third power. With the exception of the ϕ_{exp} value for the experiments performed at 35 Hz with two WC balls, which significantly deviates from the linear behaviour, the points always exhibit a marked linearity. The same linear dependence has already been already observed in previous works [13***], eventually revealing that the progression of the mechanically activated transformation is ultimately related to the total energy dose transferred from milling tools to processed powders, D_{tot} .

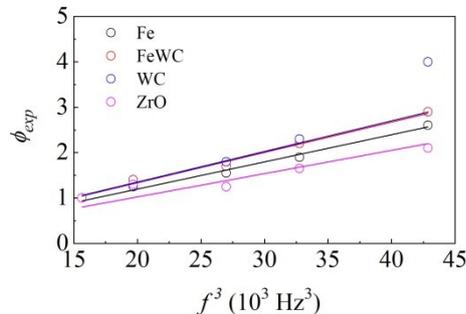


Figure SI.2. The scaling coefficients ϕ_{exp} as a function of the third power of the milling frequency, f . Data refer to the BM experiments performed using balls made of different material. Best-fitted lines are also shown.

This latter quantity can be expressed as the product between the total number of impacts, n , and the average energy of individual impacts, E_{imp} . The number of impacts, n , is simply equal to the product $f_{imp}t$ between impact frequency and time, while the impact energy, E_{imp} , can be calculated as $m_{ball}v_{imp}^2/2$, where m_{ball} is the ball mass and v_{imp} is the average impact velocity. It follows that

$$D_{tot} = f_{imp}m_{ball}v_{imp}^2t/2. \quad (\text{SI.2.1})$$

Eq. SI.1 indicates that, if the transformation is isokinetic with the total energy dose, the time t of transformation scales with $f_{imp}m_{ball}v_{imp}^2/2$. Therefore, this latter quantity represents the theoretical scaling coefficient of the transformation kinetics

$$\phi_{the} = f_{imp}m_{ball}v_{imp}^2/2. \quad (\text{SI.2.2})$$

Now, it is worth noting that, as suggested by previous studies [13***], to a first approximation f_{imp} and v_{imp} change linearly with the milling frequency, f . Along this line, we can expect that the scaling coefficient ϕ_{the} depends on the third power of the milling frequency, f , as is actually observed. Thus, the observed dependence of ϕ_{exp} on f can be regarded as an indirect evidence of the isokinetic character of the deuteration process as a function of the total energy dose, D_{tot} , received by the sample.

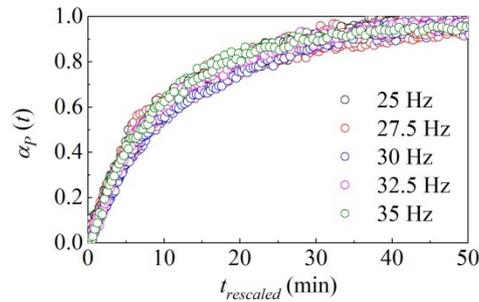


Figure SI.3. The molar fraction of deuterated benzoic acid, $\alpha_p(t)$, as a function of the newly scaled time, $t_{rescaled}$. Data refer to the BM experiments performed using balls made of different material.

We pursue the analysis further: Based on Eq. SI.2.2, the scaling coefficient ϕ_{the} can be expected to depend linearly on the ball mass m_{ball} . As a consequence, if we divide the ϕ_{the} by m_{ball} , we should obtain a normalized scaling coefficient, ϕ_{norm} , that makes all the reaction profiles obtained with balls of different mass collapse onto a single collective profile. This is what we obtain in Fig. SI.3, where the all the reaction profiles, for all frequencies and all variations in milling balls shown in Fig. 1, are replotted, based on the additional ball mass-scaling, as a function of a re-caled time, $t_{rescaled}$. This can be regarded as a further confirmation of the isokinetic character of the deuteration process under

investigation and, thus, of the importance of the total energy dose transferred to the processed mixture.

SI.3. Kinetic modeling

We assume that chemical changes occur on a local scale when the mechanical loading exceeds a certain threshold. We leave deliberately unspecified the threshold and hereafter refer to the loading conditions above the threshold as to the critical loading conditions (CLCs). In particular, CLCs can be expected to involve a set of small volumes v^* that are located in the interior of individual powder particles or at the points of contact between them. For simplicity, we also assume that volumes v^* have all the same size and are distributed randomly in the volume of powder compressed during individual impacts. The total volume of powder affected by CLCs during a single mechanical loading event is equal to v . Furthermore, we assume that the chemical changes that affect the volume v occur on timescales shorter than the characteristic time duration of the mechanical loading events.

Individual volumes v^* can undergo CLCs 1, 2, ..., i , ... times depending on the duration of the mechanical processing. Under the assumption that stirring keeps the powder uniform, any sample volume much larger than v^* is representative of the whole powder charge.

Specifically, the kinetic modelling makes use of the assumptions below:

- 1) mechanical processing can be described as a sequence of discrete mechanical loading events independent of each other;
- 2) chemical changes occur when the intensity of local mechanical stresses exceeds a threshold value that identifies CLCs;
- 3) CLCs affect small volumes v^* located randomly in the volume of material involved in individual impacts;
- 4) during a mechanical loading event, CLCs affect potential volumes v^* with the same probability;
- 5) stirring maintains the powder charge uniform.

The volume fraction of powder that is subjected to CLCs per mechanical loading event, κ , corresponds to the ratio between v and the total volume of powder, V . The volume fraction of powder, $\chi_i(m)$, that has undergone CLCs i times after m impacts is

$$\chi_i(m) = \frac{m!}{[i! (m-i)!]} \kappa^i (1-\kappa)^{m-i} \quad (\text{SI.3.1})$$

The condition

$$\sum_{i=0}^{\infty} \chi_i(m) = 1 \quad (\text{SI.3.2})$$

is always fulfilled.

Since volumes v^* are much smaller than the total volume of processed powder, V , κ is much smaller than 1. Therefore, Eq. SI.3.1 can be approximated as

$$\chi_i(m) = [(\kappa m)^i / i!] \exp(-\kappa m). \quad (\text{SI.3.3})$$

which also fulfils the condition expressed by Eq. SI.3.2.

We note that the number of impacts, m , can be expressed as

$$m = \varphi t, \quad (\text{SI.3.4})$$

where φ is the impact frequency and t is the milling time. Therefore, we can write that

$$\kappa m = \kappa \varphi t = k t, \quad (\text{SI.3.5})$$

where $k = \kappa \varphi$ corresponds to the volume fraction of powder effectively involved in CLCs per unit time. Accordingly, the volume fraction of powder that has undergone CLCs i times during the time interval t , $\chi_i(t)$, can be expressed as

$$\chi_i(t) = [(k t)^i / i!] \exp(-k t). \quad (\text{SI.3.6})$$

We remark that the impact frequency φ is proportional to the milling frequency f [***].

We assume that, in the presence of two molecular species A and B , CLCs induce a gradual mixing in volumes v^* . To a first approximation, mixing can be measured by the interface area. In particular, the interface area reached in volumes v^* after i CLCs, S_i , can be expressed as

$$S_i = S_0 S_{fin} / [S_0 + (S_{fin} - S_0) \exp(-r i)], \quad (\text{SI.3.7})$$

where S_0 , S_{fin} and r represent the initial and final interface areas and the interface area generation rate respectively. The interface allows the direct contact between A and B molecules, which can give rise to a chemical reaction. In particular, we assume that any two A and B molecules that are nearest neighbours can react to form products with a probability Π .

The total number of contacts depends on the total interface area S_i between the A and B solids and can be set equal to

$$N_{m,i} = S_i/s_{AB}, \quad (\text{SI.3.8})$$

where s_{AB} is the contact area between neighbouring molecules. The gradual formation of products reduces the total interface area available to the reaction by the fraction $1 - \alpha_{p,i}$, with $\alpha_{p,i}$ being the molar fraction of product molecules. Therefore, the total number of contacts between A and B molecules is equal to

$$N_{m,i} = S_i(1 - \alpha_{c,i})/s_{AB}. \quad (\text{SI.3.9})$$

The change in the molar fraction of product molecules, $\Delta\alpha_{c,i}$, when the volumes v^* undergo the $(i + 1)$ -th CLCs is

$$\Delta\alpha_{c,i+1} = 2 \Pi S_i(1 - \alpha_{c,i})/[s_{AB}(N_{A,0} + N_{B,0})], \quad (\text{SI.3.10})$$

where $N_{A,0} + N_{B,0}$ is the total number of A and B molecules and the factor 2 stems from the reaction stoichiometry. We can write Eq. 10 in the continuous form and its solution is

$$\alpha_{p,i} = 1 - \left\{ [S_0 \exp(r i) + (S_{fin} - S_0)] / S_{fin} \right\}^{-2 \Pi S_{fin} / [r s_{AB}(N_{A,0} + N_{B,0})]}. \quad (\text{SI.3.11})$$

Eq. SI.3.11 provides an analytical description of the mechanochemical reaction kinetics.