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A kinetic study of mechanically activated atom exchange: the effect of milling frequency and ball mass†

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This study investigates the mechanochemical reaction of hydrogen isotope exchange between solid benzoic acid and liquid heavy water. The systematic change of milling conditions revealed that the reaction rate scales with the milling frequency and the mass of the milling balls. The ball size being always the same, faster reactions stem from the use of higher milling frequencies and heavier balls. The kinetic curves are described by a kinetic model that accounts for the statistical, deformational and chemical factors involved in mechanochemical transformations. The results indicate that the reaction is driven by the generation of a new interface area caused by the deformation of the solid reactants.

1. Introduction

Starting from the end of the 1960s, mechanochemistry has reiteratively gone through periods of expansion.[1–3] After first changing the face of metallurgy, and then of materials science, it is presently innovating the synthetic strategies of inorganic and organic chemistry within the framework of green chemistry.[1–3] And yet, the proper identification and understanding of the kinetic and mechanistic features of mechanochemical reactions has remained an open issue despite its particular significance for fundamental science and practical exploitation.

The challenging nature of kinetic studies in mechanochemistry is well known.[4] Mechanochemical transformations have multifaceted character and their inherent complexity emerges regardless of the system investigated and the method of mechanical processing utilized. In any case, the physical and

chemical changes occur simultaneously across a broad range of length and time scales. This is especially evident for mechanochemical transformations activated by ball milling (BM).[5]

The BM of powders is based on the occurrence of impacts between milling tools. During individual impacts, a few cubic millimetres of powder are compressed within a few hundred microseconds at the most.[6] The consequent dynamic compaction takes place at high strain rates[7] and results in the uneven distribution of local mechanical stresses.[8] Intense forces build up at the contact points between powder particles, determining comminution and deformation on the micrometre scale over time intervals of microseconds.[8] Local shearing allows the generation of interfaces where dislocation activity can affect the surroundings of individual atoms and molecules at rates of nanometres per nanosecond.[9] Eventually, molecules may react with each other as long as local temperatures, which can decrease at rates of about tens of Kelvin degrees per nanosecond,[10] ensure the necessary energy and mobility.

Consequently, mechanochemical reactions are a concoction of factors related to mechanical energy deposited during the impacts, mutual exposure of fresh surfaces of reactant phases and intrinsic chemical behaviour of reactant molecules as they come in contact.[11,12] Separating each of these contributions to the overall mechanochemical transformation has proved to be demanding. We have recently been able to study in macroscopic[13] and microscopic[14] detail a purely mechanically activated reaction that does not depend on mixing, but solely on the absorption of mechanical energy during impacts. First, we have demonstrated a linear relationship between the reaction rate and the kinetic energy that the reacting system absorbed from the milling ball.[13] Second, we have realised that the overall reaction rate observed on the bulk stems from minute transformations occurring upon each individual impact.[14]

Here, we study the mechanochemical process in the other extreme, where we expect the reaction to be dominated by interface generation and mixing. For this purpose, we investigate the hydrogen isotope exchange (HIE) between solid benzoic acid and liquid heavy water (D_2O) (Scheme 1). We expect

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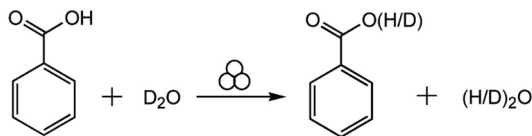
Scheme 1 The mechanochemical reaction of hydrogen isotope exchange between solid benzoic acid and liquid heavy water.

the statistical distribution of deuterium atoms to be established resulting with 1/3 benzoic acid molecules with protium and 2/3 deuterated benzoic acid. There will also be 4/9 water molecules as HOD or DOH, 4/9 as DOD and 1/9 as HOH.

The primary objective of the study is to verify the occurrence of the HIE reaction under BM conditions and to examine its kinetics. To this aim, we monitored the reaction *in situ* by Raman spectroscopy and estimated the relative amounts of the hydrogenated and deuterated species. We systematically changed the milling frequency as well as the mass of the two milling balls used in experiments. We had the foresight to use milling balls made of different materials with the aim of using balls with the same volume. In this way, we avoid undesired kinetic effects related to the different ball volume and, possibly, the different amount of powder effectively compressed during individual impacts. We show that HIE occurs without difficulties according to a sigmoidal kinetics. The reaction rate changes with both the milling frequency and the ball mass.

2. The system

Benzoic acid is a white crystalline solid poorly soluble in water at room temperature, only about 3.5 g of benzoic acid can be dissolved in 1.0 L of water.[15] In aqueous solution, it is a weak acid with a dissociation constant approximately equal to 6.4×10^{-5} mol L^{-1}.[16] In the presence of D_2O, the acidic hydrogen of the carboxylic group exchanges with deuterium forming, on the bulk, a partially deuterated sample of benzoic acid. The poor solubility of benzoic acid does not allow rapid H/D exchange and, in the absence of external factors, no significant progression of the deuteration process can be expected in the solid benzoic acid in short observation times. Indeed, HIE can only affect the small amount of benzoic acid dissolved in D_2O and the molecules lying at the liquid–solid interface. Therefore, the area of the liquid–solid interface represents an intrinsic limiting factor of the deuteration process. Under these conditions, mechanical processing by BM can be very effective in speeding up the deuteration through the continuous generation of fresh interface area that can then participate in the HIE reaction.

3. Mechanically activated deuteration

BM was performed utilizing an InSolido Technologies IST500 ball mill that makes a cylindrical jar undergo a pendulum-like oscillation in the horizontal plane. 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. In each reaction, 2 mmol of benzoic acid was weighed in one half of the jar and 2 mmol of D_2O was added using a micropipette in the 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, but not the ball size. In this way, at least to a first approximation, the changes in the rate of HIE cannot be ascribed to a change in the ball size and possible changes in the geometry of ball impacts.

Deuteration was monitored by *in situ* Raman spectroscopy as described elsewhere in detail.[17] As previously shown, benzoic acid remains a pure solid phase without a change of its polymorphic form, and it also remains in the form of a free flowing powder.[18] In the course of BM, only the carboxylic H atom becomes partially replaced by D, together with the formation of HOD and H_2O from D_2O. Exchange with D at benzoic acid is observable in the Raman spectrum of the reaction mixture as an increase of intensity of the band at 765 cm^{-1} and a corresponding decrease in intensity of the band at 793 cm^{-1}. Reaction profiles were obtained by fitting the changes in the intensity of the Raman band at 765 cm^{-1} belonging to deuterated benzoic acid, as described before.[18] Prior to fitting, the spectral range between 560 cm^{-1} and 870 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. Full details on the experimental methods can be found in the ESI.†

The change of the obtained peak intensities with the BM time constitutes the reaction profile for each reaction. The reaction profiles at different frequencies for the different pairs of milling balls are shown in Fig. 1. It can be seen that the kinetic curves have the same shape. At first glance, the curves seem to have merely an exponential character. However, a closer look at the initial stages of the kinetics suggests that the curves are slightly sigmoidal, with a very short induction period. In all the different cases, the effect of the milling frequency is evident. The rate of deuteration increases as the milling frequency increases. Nevertheless, a change in the milling frequency does not change the shape of the kinetic curve. Therefore, we can say that the transformation is isokinetic with the milling frequency, which involves the different curves being made to overlap with one another if their abscissae are scaled by a suitable factor (see ESI† for details).

4. Kinetic modelling

The phenomenological relationships so far can find a more formal description within the framework of a kinetic model able to take into account the inherent features of the mechanical processing by BM. The model has been fully described
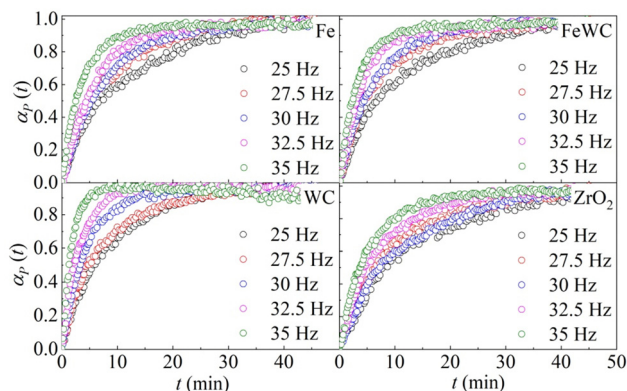
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PCCP

Fig. 1 The molar fraction of deuterated benzoic acid, $\alpha_P(t)$, as a function of time, t. Data refer to the BM experiments performed using balls made of different materials.

elsewhere,[11] but details can be also found in the ESI.† The model takes into account the statistical nature of the mechanical processing by BM and relates the mechanochemical transformation to individual impacts. To this aim, it is assumed that the volume of powder compressed during individual impacts experiences heterogeneous mechanical loading conditions. Accordingly, the mechanochemical transformation occurs only in the set of small sub-volumes $v^{\star}$ where the intensity of mechanical loading exceeds a certain threshold, thus enforcing critical loading conditions (CLCs). It is also assumed that the volumes $v^{\star}$ are stochastically involved in CLCs and that the total volume affected by CLCs, v, does not change during the mechanical processing. Under these circumstances, the sub-volumes $v^{\star}$ are affected by CLCs at a rate k corresponding to the product between the frequency of impacts and the ratio between v and the total volume of powder, V, inside the jar. The volume fraction of powder, $\chi_i(t)$, that has undergone CLCs i times after a time interval t can be expressed as

$$\chi_i(t) = [(kt)^i/i!]\exp(-kt). \tag{1}$$

Concerning the chemical changes induced by CLCs in sub-volumes $v^{\star}$, it is reasonable to associate to volume fractions $\chi_i(t)$ specific values $\alpha_{P,i}$ of the transformation degree in sub-volumes $v^{\star}$ after i CLCs. Therefore, the total transformation degree, $\alpha_P(t)$, can be written as the weighted average of the transformation degrees $\alpha_{P,i}$ over the volume fractions $\chi_i(t)$

$$\alpha_P(t) = \sum_{i=1}^{\infty} \chi_i(t)\alpha_{P,i} \tag{2}$$

While $\alpha_P(t)$ refers to the global kinetics, $\alpha_{P,i}$ concerns the local kinetics. In this respect, we assume that the transformation rate is proportional to the interface area attained in sub-volumes $v^{\star}$ after i CLCs, which increases from the initial value, S_0, to the final one, S_{fin}, at a rate r. Under the further assumption that the reaction occurs with probability Π between reactant molecules that are in contact at the interface, the molar fraction of product $\alpha_{P,i}$ in sub-volumes $v^{\star}$ can be expressed as

$$S_i = S_0 S_{fin}/[S_0 + (S_{fin} - S_0)\exp(-ri)] \tag{3}$$

$$\alpha_{P,i} = 1 - \{[S_0\exp(ri) + (S_{fin} - S_0)]/S_{fin}\}^{-2\Pi S_{fin}/[rS_{AB}(N_{A,0} + N_{B,0})]}, \tag{4}$$

where S_{AB} is the contact area between two neighbouring reactant molecules and $N_{A,0} + N_{B,0}$ is the total number of reactant molecules.

Eqn 2 combines three main factors, namely the statistics of mechanical processing through eqn 1, the mechanical deformation, or rheology, of reactant phases through the increase of the interface area described by eqn 3 and the chemical behaviour of molecular species at the interface based on the reaction probability is taken into account in eqn 4. The statistical, deformational and chemical factors cover, in principle, the main processes involved in the kinetics of mechanochemical reactions. Therefore, eqn 2 can provide a key to interpret the experimental evidence.

In the case of deuteration studied here, we have two reactant phases with very different properties. At room temperature, the benzoic acid is a solid with the melting point at around 120 °C, while D_2O is a liquid. Given the relatively low melting point of benzoic acid, the sudden compression of the solid at impacts can be expected to induce significant deformation. Combined with the mobility and permeability of the liquid phase, such deformation can generate relatively large interface areas between the reactants. The fact that the chemical reaction can occur only once the reactants are in contact at the interface makes the kinetic curve intrinsically sigmoidal, in principle. The slope of the sigmoidal curve depends on both the rates of interface area generation and chemical reaction at the interface. In our case, both these rates can be expected to be relatively high, which means that the sigmoidal shape cannot be very pronounced. Indeed, this is what we actually observe.

We used eqn 2 to best fit the experimental kinetic curves and the results are shown in Fig. 2. The model curves almost overlap the experimental data. In all the different cases, the model quantities related to the deformational and chemical factors do not differ significantly from case to case. This suggests that individual impacts induce an extensive deformation of the solid phase and that, accordingly, interface area is generated effectively. Under such circumstances, the reaction rate is limited by the amount of powder that undergoes CLCs during individual impacts, which is measured by the volume fraction of powder that undergoes CLCs in the unit time, k. In fact, we observe a linear change of k with the third power of the milling frequency, f, as shown in Fig. 3a.

Such dependence finds further evidence in the linear plot of $\ln k$ versus $\ln f$ shown in Fig. 3b. Indeed, the slopes for the different datasets are quite similar to each other and compatible with a value of 3, namely 2.68 ± 0.23 for WC balls, 2.72 ± 0.44 for ZrO_2 balls, 2.82 ± 0.28 for Fe balls and 2.99 ± 0.01 for mixed Fe and WC balls. This is not unexpected. A similar dependence has been already observed in several cases already reported in the literature, mostly regarding the formation of nanostructured metals and amorphous alloys by mechanical alloying.[13,19] In all these cases, at least to a first approximation, the dependence of the apparent rate constant k on the third
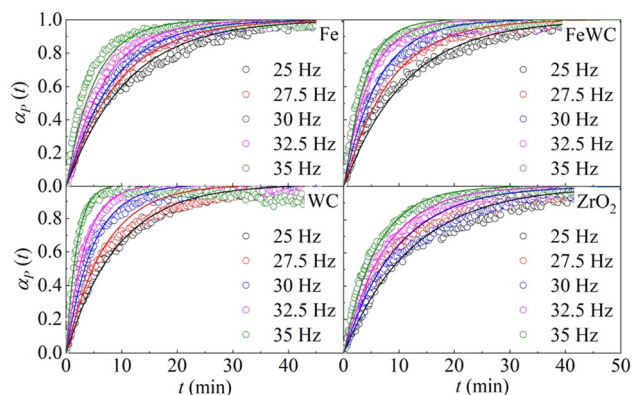
Fig. 2 The molar fraction of deuterated benzoic acid, $\alpha_P(t)$, as a function of time, t. Data refer to the BM experiments performed using balls made of different materials. Best-fitted curves are shown.
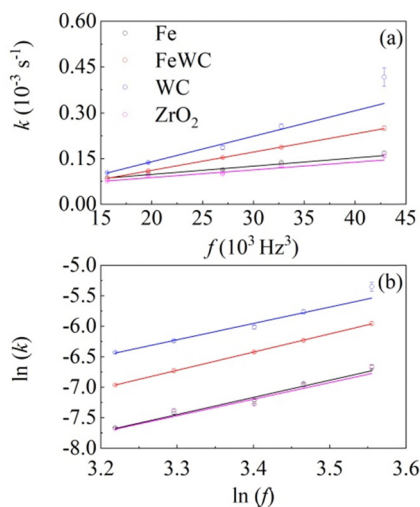

Fig. 3 (a) The volume fraction of powder that undergoes CLCs in the unit time, k, as a function of the third power of the milling frequency, f. Data refer to the BM experiments performed using balls made of different materials. Best-fitted lines are also shown. (b) The logarithmic plot of k as a function of f. Best-fitted lines have a similar slope of about 3.

power of the milling frequency f can be related to the linear dependence of the impact frequency and impact velocity on f. Observing an exponent equal to 3 and a dependence on the ball mass strongly suggests that the local kinetics is governed by the kinetic energy that the ball transfers to powder compressed during the impact.[13,19]

It is worth noting that other scenarios can be, in principle, observed.[20] Discriminating between such scenarios necessarily requires reducing the experimental uncertainties in the kinetic data. The problem does not concern exclusively the dependence of reaction rates on the milling frequency, but, more generally, the proper analysis of kinetic data. For instance, the uncertainties affecting our experimental kinetic curves do not allow the dependence of the interface area generation rate on the milling frequency to be reliably pointed out. Data are scattered and any

attempt to finely tune the S_0, S_{fin}, and r values appears as forcing. This is also true for the reaction probability between reactant molecules at the interface, Π. In this latter case, however, it is quite reasonable to use the same value for all the different cases investigated. Indeed, we do not expect that BM conditions affect the inherent chemical behaviour of the reactant species, at least to a first approximation.

5. Conclusions

The mechanical processing of benzoic acid and heavy water by BM results in the exchange of the acidic hydrogen of the benzoic acid with the deuterium made available from heavy water. The kinetic curves at different milling frequencies exhibit the same shape and a suitable scaling of the experimental reaction times can make the curves overlap. The scaling coefficients are proportional to the third power of the milling frequency, which can be interpreted as a signature of the isokinetic character of the mechanically induced deuteration process with the reaction extent being dependent on the total dose of mechanical energy transferred to the processed mixture. Further supporting evidence is that the scaling coefficients are also proportional to the mass of the milling balls.

The experimental kinetic curves can be satisfactorily best fitted by the equations derived from a kinetic model that accounts for the statistical, deformational and chemical factors involved in mechanochemical transformations. The kinetic model suggests that the rate of the deuteration process is dominated by the amount of reactants effectively involved in mechanical loading processes during individual impacts. The rate constants we obtain exhibit a linear dependence on the third power of the milling frequency, which confirms the considerations made on a strictly phenomenological basis regarding the shape and overlapping of experimental kinetic curves. Furthermore, the kinetic model also suggests that the benzoic acid is deformed during impacts, resulting in the generation of the interface area between the two reactants.

The results of our kinetic study highlight the need for quality kinetic data to disentangle the different factors involved in mechanochemical reactions and gain deeper insight into the mechanistic features. It seems that the chemical factor is the most interesting quantity to study and only its accurate estimation can unveil truly mechanochemical effects and throw light on how mechanical forces ultimately affect molecular solids on the scale of individual molecules.

Conflicts of interest

There are no conflicts to declare.

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