Electronic Supplementary Material (ESI) for Chemical Communications


# Better understanding of mechanochemical reactions: Raman monitoring reveals surprisingly simple 'pseudo-fluid' model for a ball milling reaction

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Supplementary information

## Contents

**Experimental procedure for obtaining spectra and intensity data**

Ball milling was interrupted and the reaction was sampled at various grinding times (20s, 40s, 60s, 80s, 100s, 120s, 140s, 160s, 180s, 200s, 240s, 360s, 480s, 600s, 720s, 840s, 960s, 1080s, 1200s, 1500s, 1800s, 2100s, 2400s, 2700s, 3000s, 3600s, 5400s). The composition of the reaction mixture was calculated by the calibration method given below. Reactions were repeated under each set of conditions three times, to reduce errors (Figure S3), and the averaged data were used in the calculation of mole fractions. The ambient temperature remained between 18.4°C and 21.4°C and the ambient relative humidity remained between 31% and 59%.

The heights of peaks A and B were measured using GRAMS/AI software (version 7.02). Peaks were magnified and the base line was taken as the start of the peak (green circle in Figure S4). This method provides greater uniformity in measuring multiple spectra than would be the case if an arbitrary baseline were used, and reduces the effects of baseline noise.

**Calibration method**

The intensity of the 1322 $cm^{-1}$ peak which was used to track the starting material had a contribution from the product, which also shows a small band at this position. Therefore the 1322 $cm^{-1}$ intensities were corrected by subtracting off the product contribution, which could be calculated using the intensity of the 970 $cm^{-1}$ band. To convert the spectral intensities measured from the reaction samples into mole fractions of the Him reactant and the $Zn(im)_2$ product, the relative intensities of the absolute signals from both samples were required. These were obtained by recording spectra obtained from 'model' materials representing 0, 50 and 100% of the extent of reaction (specifically a mixture of unreacted starting materials, a 1:1 mixture of the product and the starting materials and from the pure product respectively). Since, for the region of spectrum used, the spectrum at the start of the reaction is mainly due to Him rather than ZnO and Him and ZnO are always at a molar ratio of 2:1 throughout the reaction, the reaction process can be simplified as **A**→**B**, where peak A represents reactant **A** (2 mol equivalent Him) and peak B represents product **B.** Spectra of the calibration samples are compared in Figure S2 with peaks A (1322 $cm^{-1}$) and B (970 $cm^{-1}$), whose intensities were used for monitoring reaction progress, highlighted. For each sample, spectra were obtained from three different regions and averaged peak height data used in subsequent calculation. The heights of peak A and peak B are given as $H_A$ and $H_B$ respectively in Table S1 in arbitrary units.

By definition, the mole ratio of reactant ***A*** in the mid-point sample is 0.5 and the contribution to $H_A$ from reactant ***A*** is therefore 10355.8 ($\frac{1}{2}|H_A|$), while the other half of the mid-point sample gave rise to the height of peak B**,** 18445.5 ($\frac{1}{2}|H_B|$) (see Table 2). Supposing the total

amount of the sample at the mid-point is X mg, the height $\frac{1}{2}|H_A|$ of peak A is caused by $\frac{1}{2}$X mg reactant ***A*** while the height $\frac{1}{2}|H_B|$ of peak B is caused by $\frac{1}{2}$X mg product ***B***. Therefore X mg of reactant ***A*** would contribute height $|H_A|$ to peak A and X mg product ***B*** would contribute height $|H_B|$ to peak B, where the ratio of reactant ***A*** to product ***B***, calculated by $\left(\frac{H_A - H_B \times R}{|H_A|}\right) \Big/ \frac{H_B}{|H_B|}$, must be 1.0. The values $|H_A|$ and $|H_B|$ can now be considered as the absolute standard heights of peak A due to reactant A and peak B.

Hence, applying the above calibration to any spectrum obtained during a given run, the height of peak A due to reactant ***A*** is given by $\{H_A-(H_B\times R)\}$. The amount of reactant ***A*** in any sample is $\left(\frac{H_A - H_B \times R}{|H_A|}\right)$X mg and the amount of product B is $\frac{H_B}{|H_B|}$X mg. Based on this, the composition of any sample can be calculated by the solution $\left(\frac{H_A - H_B \times R}{|H_A|}\right) \Big/ \frac{H_B}{|H_B|}$ which is specifically the mole ratio of reactant ***A*** to product ***B*** remaining in the sample. Therefore the mole fraction of reactant ***A*** in the reaction mixture can be obtained as $\left(\frac{H_A - H_B \times R}{|H_A|}\right) \Big/ \frac{H_B}{|H_B|} + \left(\frac{H_A - H_B \times R}{|H_A|}\right)$.

**Table S1** Heights of selected peaks and their height ratios in the start and end-point calibration samples

| | Sample number | $H_A$(1322cm$^{-1}$) | $H_B$ (970cm$^{-1}$) | $H_A$ /$H_B$ |
|---|---|---|---|---|
| Start-point (mixture of reactants, 0% reaction) | 1 | **19462.45** | **0** | **-** |
| | 2 | **28187.65** | **0** | **-** |
| | 3 | **16963.15** | **0** | **-** |
| End-point (after 60 minutes grinding, 100% reaction) | 1 | **5171.547** | **15819.24** | **0.326915** |
| | 2 | **6798.541** | **17613.16** | **0.385992** |
| | 3 | **9454.697** | **22496.81** | **0.420268** |
| Average (R) | - | **-** | **-** | **0.377725** |

**Table S2** Heights of selected peaks in mid-point calibration sample and their height ratios.

| | Sample No. | $H_A$ (1322cm$^{-1}$) | $H_B$ (970cm$^{-1}$) | $H_A-(H_B\times R)$ (relative contribution to peak height make by reactant ***A***) | $H_B$ (relative contribution to peak height make by product ***B***) | $\frac{H_A-(H_B\times R)}{H_B}$ Ratio of amount of reactant ***A*** to product ***B*** |
|---|---|---|---|---|---|---|
| Mediate Sample | **1** | **21422.78** | **21534.97** | **13288.5** | **21535.0** | **-** |
| | **2** | **14871.23** | **14458.63** | **9409.8** | **14458.6** | **-** |
| | **3** | **13409.03** | **13342.98** | **8369.1** | **13343.0** | **-** |
| Average (calculation) | | **-** | **-** | **10355.8** $(\frac{1}{2}\lvert H_A\rvert)$ | **16445.5** $(\frac{1}{2}\lvert H_B\rvert)$ | **-** |
| Average (Standard) | | **-** | **-** | **20711.6** $(\lvert H_A\rvert)$ | **32891.1** $(\lvert H_B\rvert)$ | **1.0** |

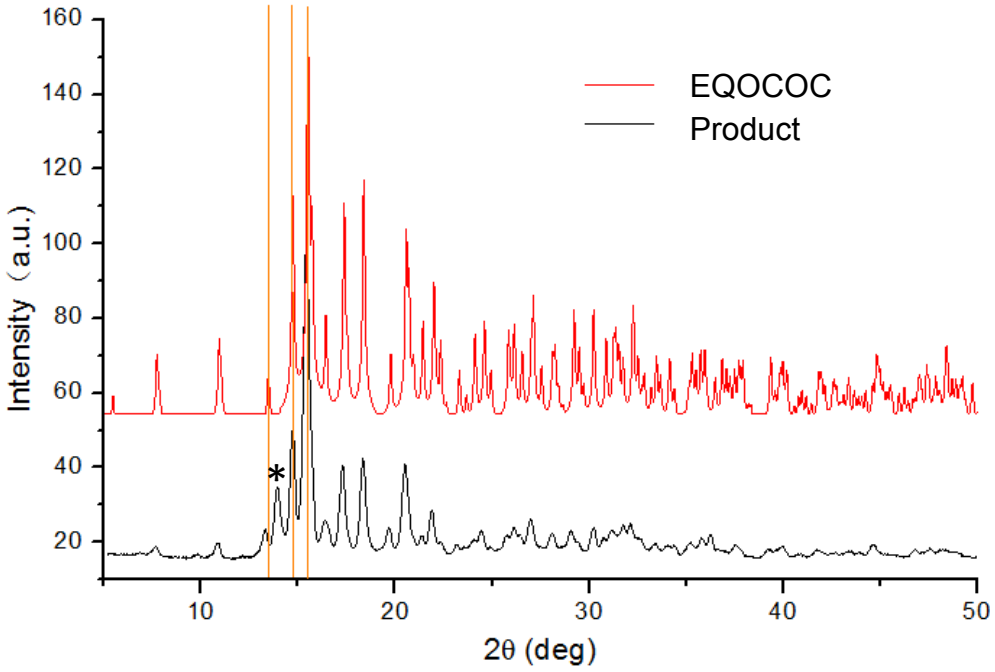



**Figure S1** Comparison of PXRD patterns for the product of the mechanochemical reaction and the pattern simulated for the tetragonal form of $Zn(im)_2.xH_2O$ (also known as ZIF-6) from single crystal crystal data obtained from the Cambridge Structural Database (CSD code EQOCOC). The peaked marked * is assigned as due to an impurity.

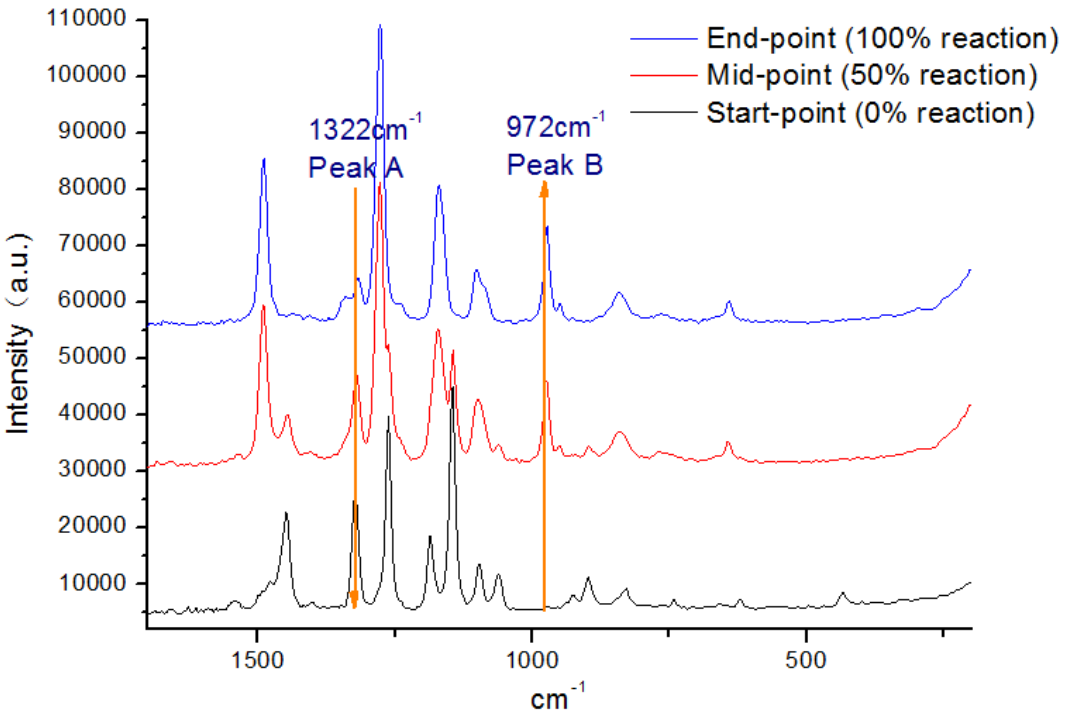



**Figure S2** Comparison of calibration Raman spectra representing reaction start-point (after 0 seconds grinding, bottom), end-point (after 60 minutes grinding, top) and mid-point (mixing equal amount of the starting mixture and the product, middle).

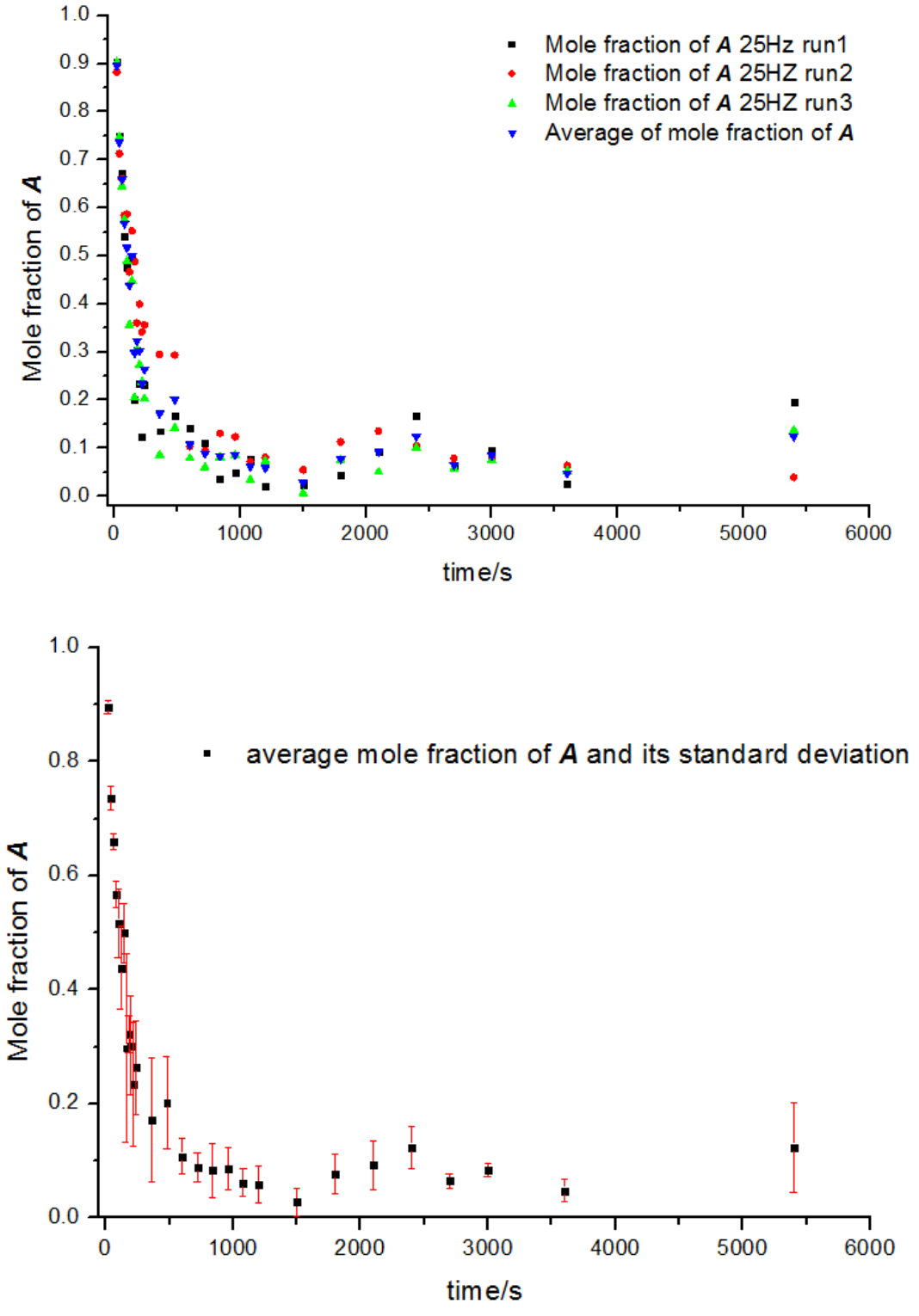
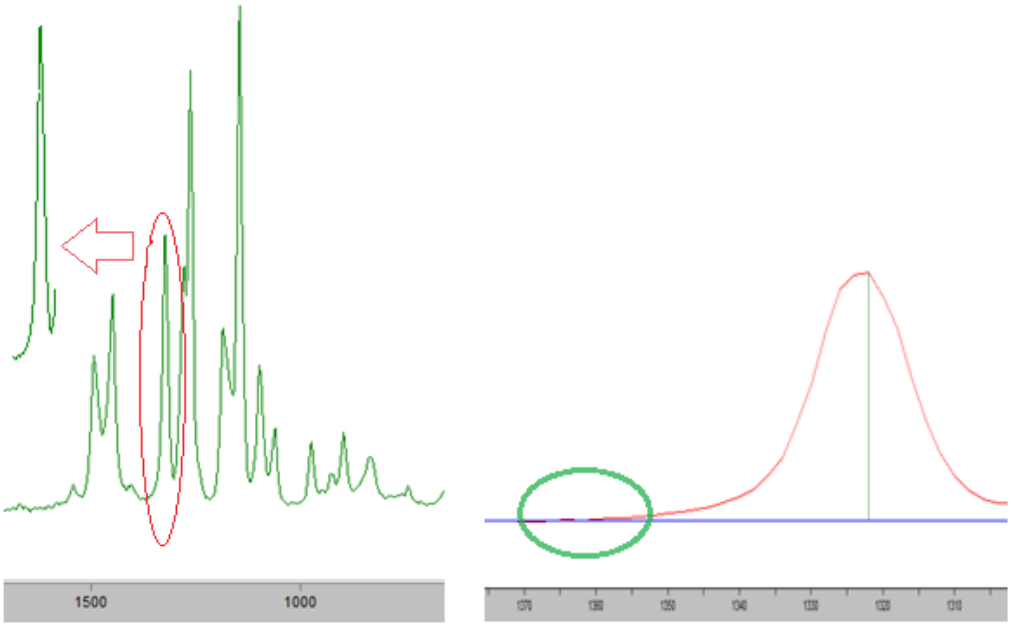



**Figure S3** Example data obtained for three reaction runs (above) and the resulting averaged data (obtained at 25Hz grinding frequency).




| Statistic | Value |
|---|---|
| Left Edge | 1384 |
| Right Edge | 1300 |
| Data Points | 43 |
| Area | 751358.214 |
| Height | 41871.436 |
| Maximum Y | 41180.6958 |
| X of Maximum Y | 1322 |
| X of True Maximum | 1322.92112 |
| Center of Mass | 1323.4086 |
| Full Width at Half Height | 18.2450309 |
| Mean | 8751.06971 |
| Median | 2857.72857 |
| Standard Deviation | 12956.0674 |

**Figure S4** Example of how the heights of peak A and peak B were measured. Raman spectra from 700cm$^{-1}$ to 1700cm$^{-1}$ were viewed with GRAMS/AI software (version 7.02) and the target peak is highlighted in red, upper left. The peak was magnified, and the baseline defined as shown (upper right). The data output is also shown.

**Table S3**. Rate constants $k$ /$s^{-1}$ at various grinding frequencies.

| Grinding Frequency /Hz | Rate constant $k$ /$s^{-1}$ ± standard error |
|---|---|
| 10 | $(0.64 \pm 0.01) \times 10^{-3}$ |
| 15 | $(1.29 \pm 0.02) \times 10^{-3}$ |
| 20 | $(3.47 \pm 0.16) \times 10^{-3}$ |
| 25 | $(12.70 \pm 0.66) \times 10^{-3}$ |

**Dependence of rate on the total amount of material present (including Figure S5)**

To examine the effect of the total amount of material present has on the rate of the reaction, experiments were conducted at both half the scale and double the scale as used in the other experiments. Conversion curves are plotted in Figure S5.

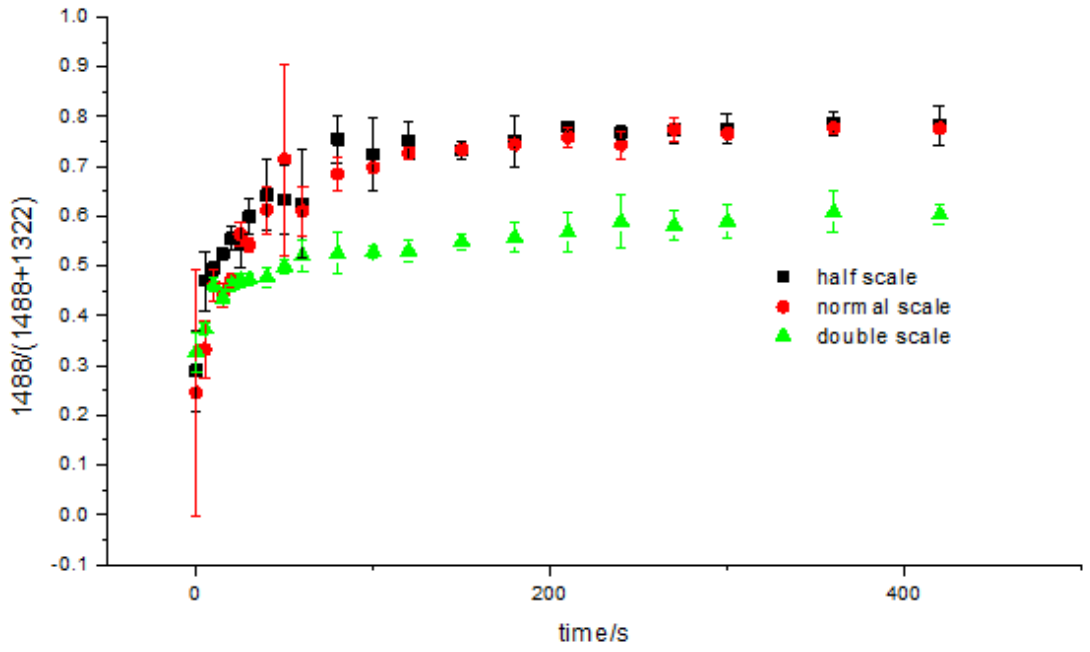



**Figure S5** Comparison of the conversion curves for reactions of half-scale, normal-scale and double-scale at 25Hz, time ranges from 0 to 400 seconds.

The data show that the rate is very similar when the amount of material is reduced to half that used throughout the rest of the experiments but that it is slower when the quantity of material is doubled. We interpret this as evidence that the rate of the reaction at fixed milling frequency is independent of the quantity of material in the jar, provided the quantity is not so large as to modify the nature of the milling process by interfering with the trajectories or velocities of the balls. In essence, if the amount of material is halved then so also will be the amount that will be induced to react by milling in a given time, meaning the rate of the reaction will not change with the total amount of reactants. However, the assumption that the reactant mixture will experience the same forces irrespective of the total fill will break down if the jar is filled beyond a given point since this could alter the velocities of the balls in the jar and mean that the effective milling forces felt within the reaction mixture would change, which will have a dramatic effect on the reaction rate. This is analogous to the situation for solution phase kinetic measurements where experiments use dilute solutions in order to avoid the complicating effects which arise at high solute concentrations.
One interpretation of the reaction model presented in this paper is that since the rate determine factor is the rate of reactive collisions, then the rate should simply be a function of the milling frequency and hence independent of the total amount of reagents present. This cannot be confirmed experimentally since, in our mill, changing the oscillation frequency changes *both* the frequency of collisions within the jar *and* the energy of each collision

(because changing the frequency also changes the velocity at which the balls travel). This means that even if the system could be adjusted to give, for example, twice as many collisions per second, this would not be expected to give twice the rate unless the energy of the collisions could be adjusted to remain the same.