Supporting Information for

Warming up for mechanosynthesis - Temperature development in ball mills during synthesis

Hannes Kulla, Manuel Wilke, Franziska Fischer, Mathias Röllig, Christiane Maierhofer, and Franziska Emmerling

Experimental set-up for in situ Raman spectroscopy

Raman measurements were conducted on a Raman RXN1™ analyser (Kaiser Optical systems, France), equipped with a CCD detector (1024x256 pixels) and a non-contact probe head (working distance: 6 cm, spot size: 1 mm). The excitation wavelength was 785 nm. A measurement was performed every 30 s, consisting of five accumulated spectra with a radiation time of 5 s.

Experimental set-up for thermography

For recording the temperature at the surface of the milling jar, an infrared (IR) camera with a mercury cadmium telluride (MCT) focal plane array (FPA) detector was used being sensitive in the spectral range from 8 to 9 µm. The specified temperature resolution is at least 35 mK at 30 °C with an absolute accuracy of ± 1% or 1 K within the selected temperature measuring range from 10 °C to 100 °C. This corresponds to an integration time of 140 µs. The FPA consists of 640 x 512 detectors, but only a quarter frame of 160 x 128 pixels was used for recording long sequences with a frame rate of 50 or 60 Hz consisting of up to 5 x 10^4 thermograms. The lens has a field of view of (23, 1 x 18, 6) °. The IR camera was mounted at a distance of 0.7 m to the jar as shown in Figure S1. Thus a spatial resolution of 0.43 mm/pixel was obtained.

In the spectral range of the IR camera, the material of the jar (PMMA) is opaque [1] enabling a direct measurement of its surface temperature. The emissivity of the material was determined according to VDI/VDE 3511 Part 4 [2] using a calibrated thermal contact sensor. This resulted in a value of $\varepsilon = 0.84 \pm 0.09$.

Data analysis for Thermography

First, the thermogram recorded before the start of the experiment was subtracted from the whole sequence, thus temperature differences to the conditions at the beginning of the experiment were analyzed. A region of interest (ROI) with a width of 12 pixels and a height of 3 pixels was selected at a position located in the middle of the jar. The temperature of this ROI was averaged and displayed as a function of time. Due to the movement of the jar, a temperature fluctuation of up to 1 K is observed, which is considerably higher than the usual thermal noise between 35 and 50 mK. The measured temperatures are related to the surface of the grinding jar, thus the temperature of the reaction mixture in the jar might be higher.

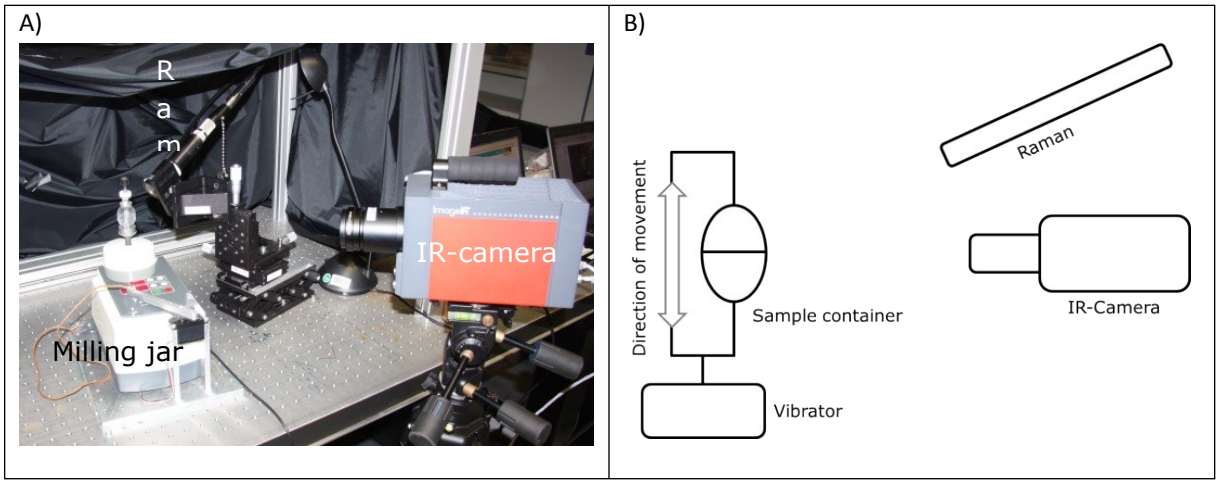

Figure S1. A) Photo and B) sketch of the experimental set-up showing the milling jar, the IR camera and the laser for Raman spectroscopy.

[1] IRCON Application Note AN108, Plastic film measurement. IRCON, 05/2006. http://support.fluke.com/ircon-sales/Download/Asset/3310192_6127_ENG_C_W.PDF

[2] VDI/VDE 3511 Part 4 Temperature measurement in industry, Radiation thermometry, Verein Deutscher Ingenieure e. V., Düsseldorf, 2011.

Chemicals

The following chemicals were used without further purification: Theobromine (99%, Acros Organics, Belgium), oxalic acid dihydrate (≥99+%, Acros Organics, Belgium), pyrazinamide (for synthesis, Merck,

Germany), anhydrous oxalic acid (98%, Acros Organics, Belgium), cadmium acetate dihydrate (purum, p.a., Fluka, Switzerland) and phenylphosphonic acid (98%, Acros Organics, USA).

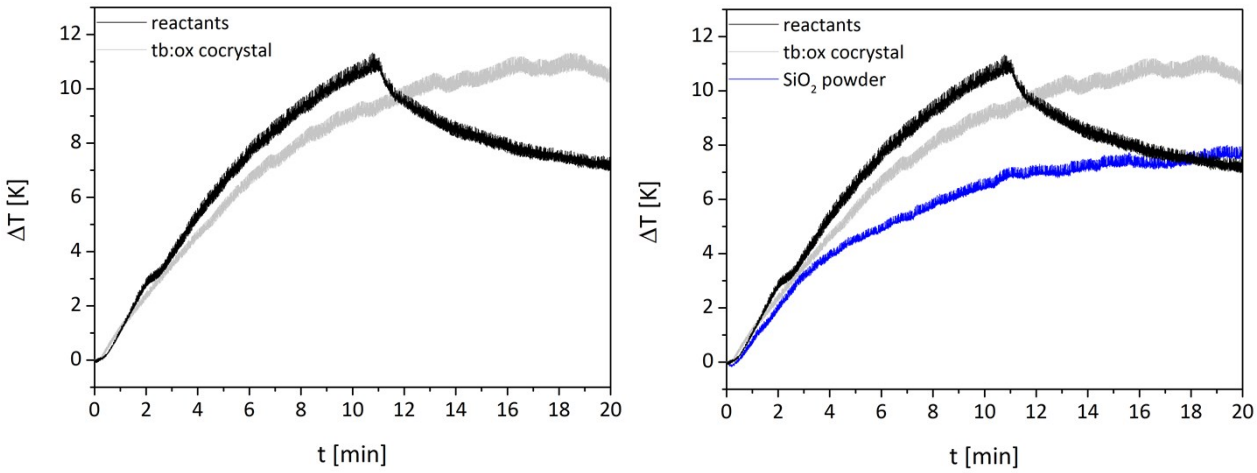

Figure S2. Left: Temperature development in the milling jar during the cocrystallisation of tb and ox-dh as a function of time (black line) compared to milling the freshly prepared and dried tb:ox cocrystal powder under the same conditions (grey line). Right: Temperature development in comparison to milling SiO_2 powder under the same conditions.

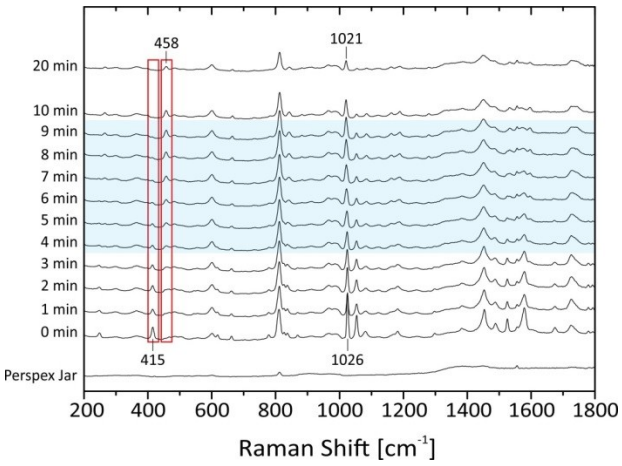

Figure S3. Simultaneously recorded in situ Raman spectra obtained during the formation of the cocrystal pza:ox, starting materials: pza and ox anhydrous. The reaction progress can be followed by the decreasing intensity of the Raman band of pza at 415 cm^{-1} and the rise of the signal at 458 cm^{-1} which belongs to the pza:ox cocrystal (highlighted in red).Blue area: reaction period.

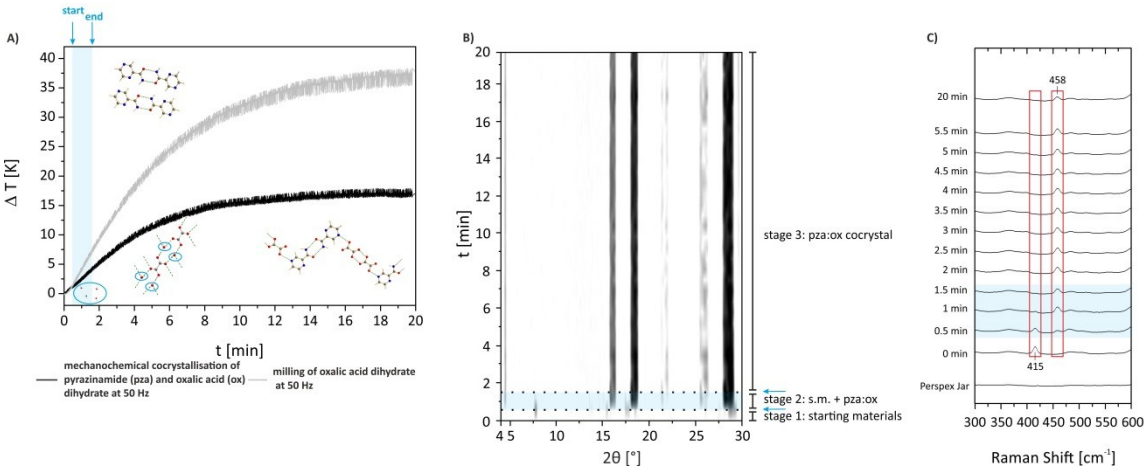

Figure S4. A) Temperature development in the milling jar during the cocrystallization of pza and ox dihydrate at 50 Hz as a function of time (black line) compared to milling ox-dh under the same conditions (grey line). Shaded blue area: start and end of the cocrystallization. The hydrogen bonding system in the crystal structures of the reactants and the cocrystal are shown as insets. B) In situ XRD data of the formation of the pza:ox cocrystal investigated under the same reaction conditions. Blue area: reaction period. C) Simultaneously recorded in situ Raman spectra. The reaction progress can be followed by the decreasing intensity of the Raman band of pza at 415 cm^{-1} and the rise of the signal at 458 cm^{-1} which belongs to the pza:ox cocrystal (highlighted in red). Blue area: reaction period.

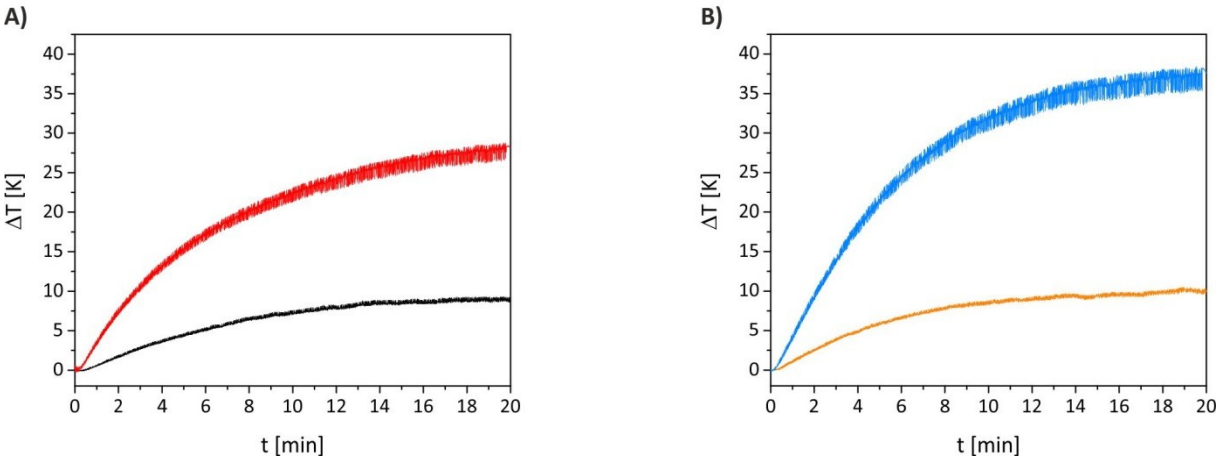

Figure S5. Thermographic profiles for milling 1 g of pure A) oxalic acid anhydrous at 30 Hz (black line) and 50 Hz (red line) and B) oxalic acid dihydrate at 30 Hz (orange line) and 50 Hz (blue line). Higher temperatures are observed for milling at 50 Hz in comparison to 30 Hz. As no reaction takes place in these cases the higher temperature can be related to an increased friction caused by the greater mechanical impact at 50 Hz.