Substituting steel for a polymer in a jar for ball milling does matter

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Organic reactions [12]. The results obtained with a plastic jar in a model device used in synchrotron experiments may not be therefore directly indicative of the same process conducted in a metal jar in the laboratory. This makes it difficult to compare correctly the results of ex situ and in situ mechanochemical experiments, as well as of the in situ experiments performed by different groups.

The aim of this work was to compare the results of mechanical treatment of a sample from the same batch in the same mill and following exactly the same protocol with the only difference being the jar material: steel or different polymers (polylactic acid PLA, Polyethylene terephthalate glycol PETG, and acrylonitrile butadiene styrene ABS). For a case study we took a sample of the β-polymorph of glycine (\(\text{NH}_3\text{-CH}_2\text{-COO}\)) prepared as fine powder.

β-Glycine was prepared by freeze-drying from a 5% solution in a mixed THF-water solvent containing 19.6 mass % of THF [13]. The light porous sample had density of \(\sim 50\,\text{mg/cm}^3\), with a narrow particle size distribution, with particles < 1 μm diameter. Between the experiments, samples of β-glycine were stored in closed containers in a desicator over annealed silica gel (relative humidity about 20%) to exclude any interaction with the moisture from the air. Before and after each experiment the samples were characterised by X-ray powder diffraction at a laboratory diffractometer (STOE STADI MP, CuK\(\alpha\), \(\lambda = 1.54060\) Å”, 40 kV/40 mA, bent Ge (111) monochromator, Dectris MYTHEN 1K linear detector). The results were analysed using WinXPOW 3.05 software [Stoe & Cie (2009)], WinXPOW Version 3.05. Stoe & Cie, Darmstadt, Germany). The samples were mechanically treated in a vibrational mill VIBRATOR DDR-GM9458 NARVA (50 Hz, a single steel ball with 9.5 mm diameter and 9.5 mm diameter...
mass 3.5 g). The treatment was continuous during 20 minutes. A standard sample mass was 15 mg. Polymer (PLA, PETG and ABS) inserts into the steel jar were 3D-printed using a Wanhao GR2 printer with a brass nozzle (0.4 mm diameter) (Fig. 1). A glass mirror (210 x 250 x 4 mm) was used as a support. No significant heating of the milling jars was observed to result from treatment.

On storage or on heating, β-glycine has been reported to transform into the pure α-polymorph, pure γ-polymorph, or a mixture of the two [14]. We have found that the mechanical treatment of β-glycine results in its polymorphic transformation into the pure α-form. Remarkably, this is not the thermodynamically stable polymorph under ambient conditions. In the course of experiments, we have observed that the polymorphic transformation of the β-polymorph into α-form was significantly faster if the ball was taken by the fingers before placing it into the jar. The powder sample stuck to the ball in this case, and this made mechanical action on it more efficient when a ball hit the jar wall (Fig. 2). We have then carried out two series of experiments: 1. Experiments without control of the purity of the surfaces of the ball and the jar; 2. Experiments in which the surfaces of the ball and the jar were carefully cleaned from even traces of grease from the fingers using soap foam with subsequent multiple rinsing by distilled water and drying in a special drying box. The surface of the ball was treated by ethanol and dried, and subsequently handled using a specially treated instrument.

Independent of the preliminary treatment of the ball and the jar, the α-polymorph accumulated faster on mechanical treatment of the β-polymorph in a steel jar, as compared to the treatment when the polymer inserts were used (Fig. 3). This is contrary to the effect of polymers when added as powder and can be supposed to account for different rheology and not to chemical interactions between glycine and the polymers. For different types of polymer the transformation rate was similar for the jars made of PLA and PETG. No transformation into the α-polymorph could be observed in the jars made of ABS (at least during the equivalent time).

For the jar made from the same material the degree of transformation of the β-polymorph into the α-form was higher if the surface was not cleaned specially from fingers tracers and/or the ball was put into the jar by fingers (for the same treatment time). In the steel jars the transformation of the β-
Thus, our case study has shown that a substitution of the steel jar for a polymer can reduce drastically the rate of the mechanochemical transformation in a vibrational ball mill. Also the choice of the polymer matters. This must be taken into account when planning in situ synchrotron radiation diffraction experiments. The transformation rate both in metal and in plastic jars may be increased, if the milling ball is preliminary touched by fingers and in this way greased, to improve the contact between the sample and the milling bodies.

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Notes and references

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