Poster

The scientific case for in-situ diffraction investigations of mechanochemical processes: recent developments and state of the art.

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Mechanochemical technologies are transforming how we think about chemical reactivity, whilst offering new, sustainable routes for industrial manufacture. However, mechanochemistry's true potential is limited by our lack in understanding of how these processes work. Mechanochemical reactions are preceded by an induction period, during which time no reaction is observed. We showed recently[1] that such induction period involves the evolution of crystal microstructure that destabilizes solid reagents to enhance their reactivity.[2] Ball milling generates materials in metastable states, characterised by small crystal size (generally < 100 nm) and large (micro)strain. As crystals become smaller and the strain increases, the stability of polymorphic materials can theoretically become different from the bulk stability. Correspondingly, ball milling can in principle generate otherwise inaccessible polymorphic phases. Indeed, our team showed that the solid form (polymorph) of a mechanochemical product also depends on how microstructure develops under mechanochemical conditions.[3] There is evidence from in-situ X-ray diffraction monitoring that milling reactions reach a final plateau and that the microstructural features of the products do not change as long as the mechanical treatment is not interrupted or modified. Our ability to control the structure and microstructure of the products and the reaction rates of these environmentally benign reactions depends on our understanding of how the microstructure evolves under mechanochemical conditions and the nature of the reaction final steady states. Our recent results also showed that crystal microstructure relaxes quickly (within minutes) once milling has stopped; data obtained from ex situ diffraction thus cannot give accurate insight into the true microstructure of mechanochemically reacting solids. Understanding how mechanochemical conditions affect material microstructure, and its relation to the rate and outcome of a given mechanochemical reaction, can only be obtained by collecting diffraction data in situ while the reaction is happening.

Using a small commercial mixer mill, we have produced a flexible miniaturized milling setup which: optimizes the diffraction geometry; is easy to carry around; is suitable for most powder diffraction beamlines; is easy to use and compatible with liquid assisted grinding, where tiny amounts of solvent are added to the reactants. It allows for monitoring with: X-ray diffraction at soft energies (~12.4 keV or less) to improve the instrumental resolution function (IRF) and investigate peak profile evolution in detail over the milling transformation; neutron diffraction to deconvolute the crystal size and microstrain contributions to peak broadening at the milling steady state. We have defined specific functions to describe the triplet peak profile and correction for the parallax effect with flat detectors.[4] We provide data collection strategies to maximize the signal to background ratio and practical methods to collect a diffraction standard. With in-situ X-ray diffraction, the miniaturized setup, in combination with the data collection and data analysis strategies proposed, allows for experiments with very small quantity of sample (10 mg or less) which is essential for materials that are toxic and/or scarce.

We here present the application of such in-situ diffraction monitoring on a few case studies that we have been investigating over the last few years: the metathesis reaction KI + CsCl = KCl + CsI (Fig.1); the cocrystallization of glycine with glutaric acid; the nature of ZIF-8, a zinc imidazolate metalorganic framework, under milling conditions.

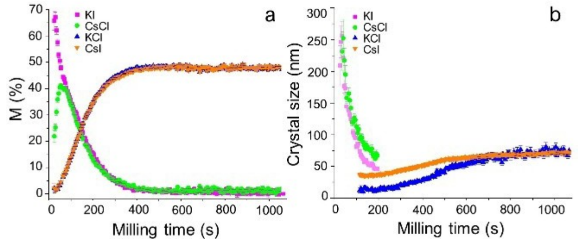

Fig. 1. Phase abundances (a) and crystal size (b) evolution under ball mill grinding conditions of the reaction KI + CsCl = KCl + CsI. Estimated standard deviations are shown as error bars. Crystal size is shown for phases more abundant than 20 M%. [1]

[1] Lampronti, G.I., Michalchuk, A.A., Mazzeo, P.P., Belenguer, A.M., Sanders, J.K., Bacchi, A., Emmerling, F. (2021). *Nat. Commun.*, **12(1)**, 6134.

[2] Linberg, K., Röder, B., Al-Sabbagh, D., Emmerling, F. Michalchuk, A.A., 2023. *Faraday Discuss*, **241**, 178.

[3] Belenguer, A. M., Lampronti, G I., Cruz-Cabeza, A. J., Hunter, C. A., Sanders, J. K.M. (2016). *Chem. Sci.* **7(11)**, 6617.

[4] Mazzeo, P.P., Lampronti, G.I., Michalchuk, A.A., Belenguer, A.M., Bacchi, A., Emmerling, F. (2023). *Faraday Discuss*, **241**, 289.