

IN SITU X-RAY DIFFRACTION FOR THE STUDY OF MECHANOCHEMICAL REACTIONS AND THE DISCOVERY OF NEW MATERIALS

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ABSTRACT

The recent introduction of techniques permitting in situ monitoring of milling reactions by synchrotron X-ray powder diffraction and Raman spectroscopy has enabled the first uninterrupted insight into transformations occurring during ball milling reactions. Thus far, these techniques have revealed rapid reactions, multi-step reaction mechanisms, and formation of metastable intermediates that are either impossible or difficult to prepare using conventional synthetic methods. This was recently demonstrated when in situ X-ray diffraction allowed identification and subsequent isolation of the new metastable polymorph of the widely studied zeolitic imidazolate framework ZIF-8 which also possesses a novel topology which was named katsenite (kat). The new phase was discovered during our attempts to improve the environmentally-friendly nature of the mechanochemical process for the formation of ZIF-8. Specifically, we aimed to replace ionic salts and organic liquid additives with diluted aqueous acetic acid. This had expectedly first led to the formation of ZIF-8 which however had unexpectedly undergone amorphisation during prolonged milling. Surprisingly, further milling led to recrystallisation of the amorphous matrix into the katsenite phase which would persist for 10-15 minutes under milling conditions before finally being transformed into the close-packed polymorph of ZIF-8 with diamondoid topology. Besides showing that recrystallisation from amorphous precursors is possible under mechanochemical treatment, these results extend the scope of mechanochemistry for the preparation of new phases even in the systems that were already extensively explored.

Keywords: Mechanochemistry, powder X-ray diffraction, in situ monitoring, zeolitic imidazolate framework, crystal structure

INTRODUCTION

Due to relatively recent raise in awareness of the need to reduce environmental impact of chemical processes, mechanochemical reactions, although known for centuries, have been recognised as an alternative to the traditional chemical processes in that they may offer a new clean, efficient and selective synthetic route [1]. While providing new synthetic pathways to known compounds, mechanochemistry is also known to allow preparation of compounds that are difficult or impossible to obtain from solution by using conventional synthetic methods. In that respect, by controlling the stoichiometry of the initial reaction mixture, mechanochemistry may offer control over the stoichiometry of the product if more than one reaction outcome is possible.

Metal organic frameworks (MOFs) are currently considered as a promising family of materials for a variety of applications [2]. Their synthesis consequently need to be as efficient as possible. However, synthesis of metal-organic frameworks is traditionally performed under solvothermal treatment where heating of reaction mixtures to temperatures above 100 °C for several days is not uncommon rendering such processes energy demanding as well as producing large amounts of waste solvents. On the contrary, mechanochemical synthesis was shown to provide the same materials in a matter of minutes or hours and at room temperature [3]. Among MOFs, zeolitic imidazolate frameworks (ZIFs) are particularly noteworthy for their stability as well as their analogy to known zeolites. Among ZIFs, ZIF-8 [4] can be considered as an archetypal MOF and is also one of only a few commercially available MOFs.

RESULTS AND DISCUSSION

Herein I will focus on our recent results from in situ X-ray diffraction monitoring of mechanochemical transformations in the ZIF-8 system which finally led to the discovery and characterisation of a new polymorph of ZIF-8 possessing also a novel topology [5]. Initial experiments conducted from zinc oxide (ZnO) and 2-methylimidazole (HMeIm) and by using diluted aqueous acetic acid as the liquid additive in the reaction mixture revealed a very fast formation of the target ZIF-8. However, after a couple of minutes milling, the reflections belonging to ZIF-8 started to fade away indicating slow amorphisation (Fig. 1a,d). Complete amorphisation of ZIF-8 left a featureless diffraction image with small contribution from the unreacted ZnO. As demonstrated by solid state NMR, the amorphous matrix however, kept the connectivity between Zn(II) and imidazolate anions reminiscent of ZIF-8, but with much broader peaks indicating the loss of long-range order upon amorphisation. Surprisingly, upon continued milling treatment, this amorphous matrix served as the precursor for the recrystallisation into the new phase, which turned out to be a nearly-close-packed polymorph of ZIF-8 (Fig. 1). The new phase is metastable and would readily transform to the close-packed polymorph of ZIF-8 with diamondoid topology upon further milling (Figure 1c). In general the new phase was sensitive to heat, moisture or solvent vapour but could nevertheless be stored for months in closed vials.

Even though the formation of the new phase could not be exactly reproduced in each experiment, knowledge acquired from in situ experiments allowed this new phase to be isolated in the laboratory and characterised. Its crystal structure was solved from laboratory powder diffraction data using direct space methods of structure solution and employing rigid bodies for MeIm fragments. Katsenite crystallises in the tetragonal system in the $P-42c$ space group. It contains four crystallographically independent Zn(II) atoms which all but one lie on special positions and four crystallographically independent MeIm ligands forming tetrahedral environment around each Zn(II) atom (Figure 2). The crystal structure revealed also a new topology for this phase which we name katsenite (kat).

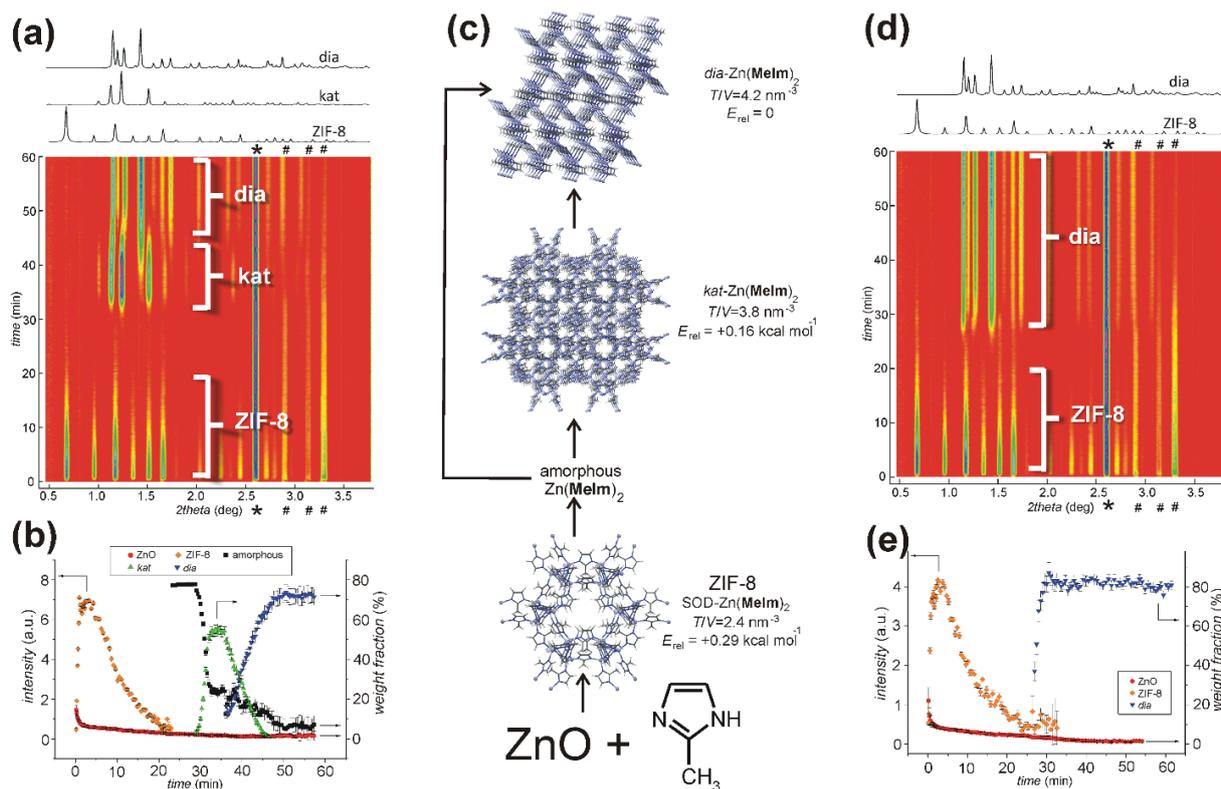


Figure 1. (a) Time-resolved X-ray diffractogram for the LAG reaction of ZnO and **HMeIm** with aqueous acetic acid as the milling liquid showing formation and amorphisation of ZIF-8 followed by the crystallisation of katsenite and its transformation to diamondoid-topology polymorph of ZIF-8. Reflections of the silicon standard are denoted by the asterisk sign '*' while ZnO reflections are denoted with the hash sign '#'. (b) Corresponding plot for the evolution of weight fractions of participating phases extracted from quantitative Rietveld refinements. (c) Representation of the observed reaction pathway. (d) Time-resolved X-ray diffractogram for LAG reaction of ZnO and **HMeIm** in the presence of aqueous acetic acid and (e) a corresponding plot of the evolution of each phase, demonstrating that recrystallisation can take place without the katsenite intermediate.

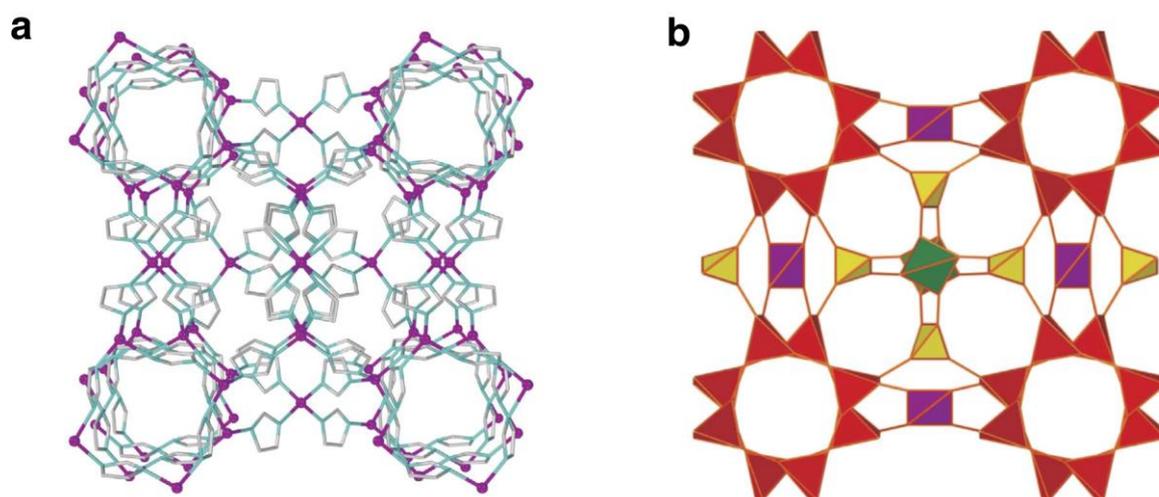


Figure 2. a) Representation of the crystal structure of katsenite viewed along the crystallographic c direction and b) the katesenite framework represented by its vertex figure with different colouring for each type of vertex.

The course of the reaction from highly porous ZIF-8, over slightly porous katsenite to the non-porous diamondoid topology $\text{Zn}(\text{MeIm})_2$ follows the order of stabilities of the polymorphs, as

shown by ab initio calculations. The discovery of a new-topology MOF which is additionally obtained in the well explored system such as ZIF-8, gives sway to in situ and real-time monitoring of milling reactions not only for understanding and optimisation of mechanochemical processes, but also for the discovery of new phases and unusual transformations such as recrystallisation after amorphisation during milling treatment.

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