In situ monitoring of guest-assisted mechanochemical synthesis of porous materials

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Porous materials inherently containing empty spaces within their structures are very important for technologies of the future, such as liquid and gas storage, separations, catalysis and more [1]. Their many possible applications heavily depend on the shape, size and properties of their pores. Unfortunately, porous materials are inherently thermally unstable, and often collapse into their densely packed counterparts. Inclusion of guests can provide significant stabilization to the porous frameworks, but traditional solvothermal synthetic methods are limited in scope of guests that can be used.

Mechanochemistry is a quantitative, fast, sustainable and energy-efficient synthetic method used in all areas of chemistry, including the preparation of porous materials [2]. Since solubility restrictions are of no importance in this solid-state method, inclusion of different guests, including those providing novel functionalities, into porous frameworks is possible. We have recently shown that a fast and easy mechanochemical screening can reliably produce multiple forms of zinc imidazolate, including new forms of the **crb** topology, and that the thermodynamic stabilization effect of guest inclusion can be quantified by periodic DFT calculations [3].

We now demonstrate that these mechanochemical reactions can be monitored *in situ* using several techniques, such as synchrotron powder X-ray diffraction, Raman spectroscopy, and calorimetry, giving complementary insight into their kinetics and mechanisms. We discover short-lived intermediates and observe the interactions of guests with the host structures. We hope these studies will help inform and improve the future synthesis of functional guest-stabilized porous materials.

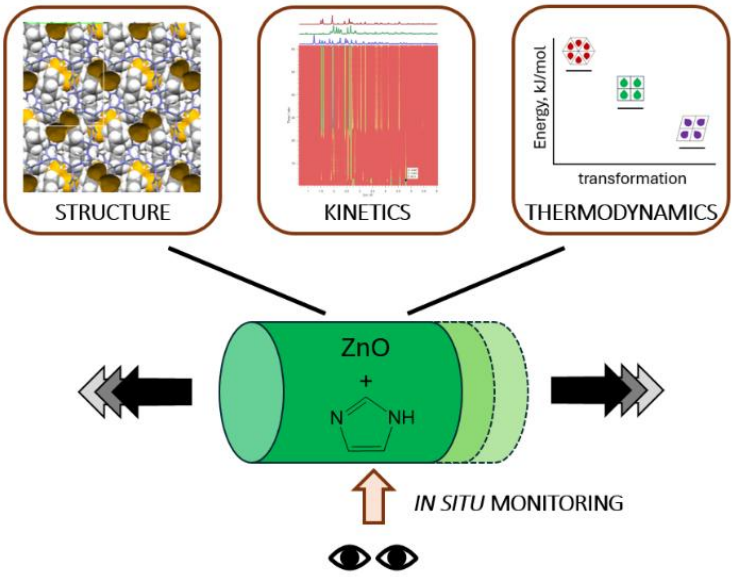


Figure 1. *In situ* monitoring of the mechanochemical synthesis of zinc imidazolate provides insight into intermediate structures, reaction kinetics and thermodynamics.

[1] D. Zhao, et al. ACS Sustainable Chem. Eng. (2019). 7, 7997.
[2] T. Stolar, et al. Chem (2026). 12, 102880.
[3] I. Brekalo, et al. J. Am. Chem. Soc. (2025). 147, 27413.

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