

Development of in situ X-ray diffraction techniques for characterization of stimuli-induced dynamics in MOFs

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Metal–organic frameworks (MOFs) exhibit extraordinary flexibility and dynamic behavior in response to external stimuli such as guest adsorption, temperature, pressure, and light [1]. Understanding these phenomena at the atomic scale requires advanced structural techniques capable of capturing transient and metastable states under non-ambient conditions. To address this challenge, we have developed a suite of in situ X-ray diffraction (XRD) methods tailored for probing stimuli-responsive dynamics in MOFs with high temporal and spatial resolution [2].

These developments encompass both synchrotron-based and laboratory-scale setups designed for gas/vapor adsorption, temperature variation, and mechanical compression experiments. In particular, the integration of in situ powder XRD with gas-dosing systems and variable-temperature stages has enabled the real-time monitoring of structural transformations during guest-induced breathing, gate-opening, and negative gas adsorption. Complementary single-crystal in situ XRD approaches further allow precise determination of framework deformation mechanisms and the role of host–guest interactions in driving phase transitions [3].

Using these tools, we have uncovered critical insights into structure–property relationships in flexible MOFs such as DUT-8(Ni) [4, 5], DUT-49 [6, 7], and MIL-53(Al) [8], including their energy landscapes, phase coexistence, and metastability. These findings not only advance our fundamental understanding of MOF responsiveness but also provide a rational basis for the design of stimuli-adaptive materials for gas storage, separation, and sensing applications.

This contribution will highlight key instrumental advancements, exemplary case studies, and future perspectives on dynamic crystallography in MOFs, emphasizing the need for operando methodologies in the era of smart materials.

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