



Contribution ID: 40

Type: **Poster contribution**

Elucidating the structural evolution of a highly porous responsive metal-organic framework (DUT-49(M)) upon guests desorption by time-resolved in-situ powder X-ray diffraction

Metal-organic frameworks (MOFs) are 3-dimensional architectures constructed via the coordination of metal ions or cluster as nodes and organic linkers as struts, resulting in crystallographically well-defined porosity.[1] After removing the guest molecules from the pores, record values of surface area and pore volumes can be reached.

A unique type of adsorption-induced phenomenon has been discovered in the hierarchical mesoporous Cu₂(BBDCDC) framework, further denoted as DUT-49(Cu).[2] The MOF is constructed from the coordination of tetratropic carbazole-based linker with Cu-Cu paddlewheel, forming three distinct types of pores: cuboctahedral MOPs with 10 Å in diameter, interconnected by edges via biphenyl moieties and form additional tetrahedral (17 Å) and octahedral (24 Å) cages.[3] The framework can be desolvated by exchange with supercritical CO₂ without losing crystallinity. Variation in the metal centres of M-M paddle-wheel SBU results in the formation of isostructural DUT-49(M) [DUT-49(M); M= Ni, Mn, Fe, Co, Zn, Cd] frameworks. However, the porosity of the framework was found to be different for each of the structures. All attempts to regain the structure by resolution at elevated temperatures were unsuccessful and only DUT-49(Cu) and DUT-49(Ni) retain the structural integrity after the supercritical drying procedure. Thus, herein, we aimed to study the detailed structural transformations that are possibly occurring during the removal of the subcritical fluid from the framework by time-resolved synchrotron PXRD at P23 beamline aiming to access the structural pathways of the framework collapse.[4]

Figure 1. Structural transformation of DUT-49(Cu) MOF during solvent removal through (a) supercritical CO₂ activation approach to retain the highly porous (op) phase that can undergo further structural transition during gas adsorption process; and (b) conventional activation approach. (c) Typical adsorption isotherm from op phase of the framework (green line) and amorphous phase (red line).

References

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Primary authors: BON, Volodymyr (Technische Universität Dresden); Dr GARAI, Bikash (Technische Universität Dresden); Mr WALENSZUS, Francesco (Technische Universität Dresden); Dr KHADIEV, Azat (P23 Beamline, PETRA-III, DESY); Dr NOVIKOV, Dmitri (P23 Beamline, PETRA-III, DESY); Prof. KASKEL, Stefan (Technische Universität Dresden)

Presenter: BON, Volodymyr (Technische Universität Dresden)

Session Classification: Framework structures: MOFs, COFs, etc.

Track Classification: Framework structures: MOFs, COFs, etc.