CO_2 and H_2O sorption induced bulk-phase changes of CALF-20 captured using *in situ* laboratory X-ray powder diffraction

Sebastian Bette[1], Anastasiia Sleptsova[1], Robert E. Dinnebier[1]

[1]Max Planck Institute for Solid State Research, Heisenbergstr. 1 70569 Stuttgart, Germany

s.bette@fkf.mpg.de

The CALF-20 [Zn_2(1,2,4-triazolate)$_2$(oxalate)] metal organic framework (MOF) exhibits a remarkably selective and high carbon dioxide uptake capacity and high chemical and thermal stability, which enables its application for carbon dioxide sequestration on a large industrial scale, e.g., for cement production plants [1]. In this process the MOF is activated by heating, exposed to a hot (approx. 90 °C) exhaust gas stream, where it removes carbon dioxide. Unloading of the MOF is subsequently performed by extraction with hot water vapour and followed up by a heating step for regeneration. Accordingly, data on lattice expansion, deformation and water or carbon dioxide uptake into the bulk structure are of fundamental importance.
We performed a detailed investigation [2] on the thermal expansion behaviour and the water and carbon dioxide uptake of the CALF-20 MOF by using various *in situ* setup for laboratory X-ray powder diffraction (XRPD). *In situ* heating measurements under dynamic vacuum and gas loading measurements were performed using a home-built gas loading setup for diffraction experiments in Debye-Scherrer geometry, which enables as oscillatory rotation of the capillary. The lattice parameters of the CALF-20 MOF and the amount of disordered gas molecules within it pores were derived from fully weighted Rietveld refinements. Under dynamic vacuum, the MOF exhibits an anisotropic, negative thermal expansion that is driven by an expansion of the 001 lattice plane distance and by a contraction of the *b*-lattice parameter (Fig. 1, (a)). During the heating process, kinetically hindered lattice deformations can lead to a large volume expansion upon relaxation, which can be accompanied by a reduction of the monoclinic lattice symmetry. The gas loading was investigated by both isobaric and isothermal experiments. A CO_2-uptake initially leads to a contraction of the 001 lattice plane distance and to an expansion of the b-axis, whereas the *a*-axis is hardly affected (Fig. 1, (b)). When more than 0.5 molecules of CO_2 per zinc cations enter the framework, the lattice deformation is reverted, i.e. the 001 lattice plane distance starts expanding and the *b*-axis starts contracting. The water uptake and released was studied by using a commercially available humidity chamber (Anton Paar) operated in Bragg-Brentano geometry. The water uptake capacity increases with increasing humidity and surprisingly is independent of the temperature. Overall, an uptake of water molecules leads to a contraction of the MOF framework (Fig. 1, (d)), that is mainly driven by interactions of the guest molecules with the oxalate linker (Fig. 1, (e, f)). Due to the increase in packing density, the water-loaded state is more stable than the CO_2-loading, which explains why water vapour can be utilized for unloading CO2 from the CALF-20 MOF.

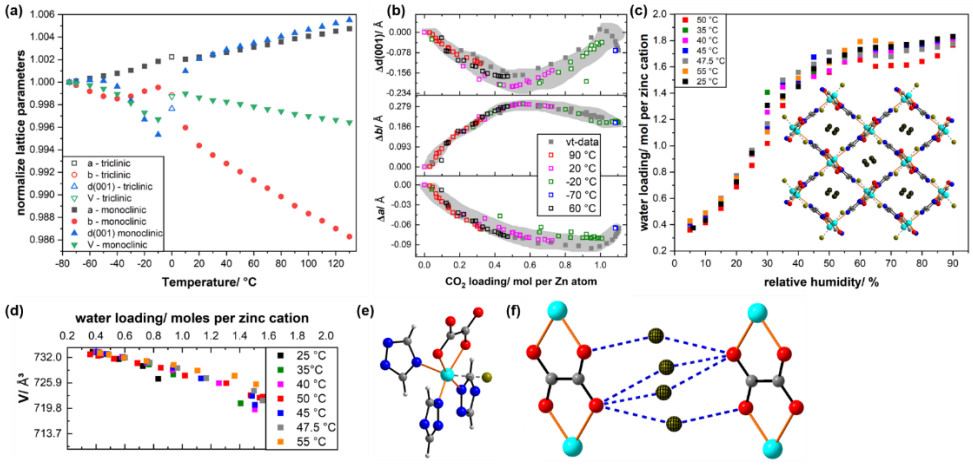


Figure 1. *CALF-20 MOF: (a) Thermal expansion under vacuum, (b) lattice distortion during CO_2 loading, (c) water uptake capacity at different temperatures, (d), volume contraction during H_2O loading, interaction of H_2O with (e) zinc cations, (f) oxalate linkers.*

[1] J.-B. Lin *et al.* Science (2021) 374, 1464-1469.
[2] S. Bette *et al.* J. Am. Chem. Soc. (2025), 147, 28799-28809.