Breathing behaviour of CALF-20 MOF during gas sorption: *in situ* XRPD study

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Metal-organic frameworks (MOFs) have gained significant attention as materials for gas separation due to their tuneable porosity and selective adsorption properties. For the development of this field, it is important not only to modify the structure of the MOFs for specific applications, but also to understand their sorption mechanism.
In this work, we studied one of the most promising MOFs large scale industrial application, called CALF-20, and its ability to physically absorb various gases. The main structure characterization method used was laboratory *in situ* X-ray powder diffraction (XRPD) with a home-built gas loading setup. The setup allows to measure a sample in Debye-Scherer geometry under a dynamic vacuum, or in a chosen gas atmosphere up to 1 bar. The typical experimental series involved isobaric measurements in the temperature range from 130°C to -70°C. Fully weighted Rietveld refinements [1] were employed to determine the lattice parameter changes and an amount of absorbed gas in the pores. The conventional gas sorption measurements at 298K were also performed, validating XRPD results.

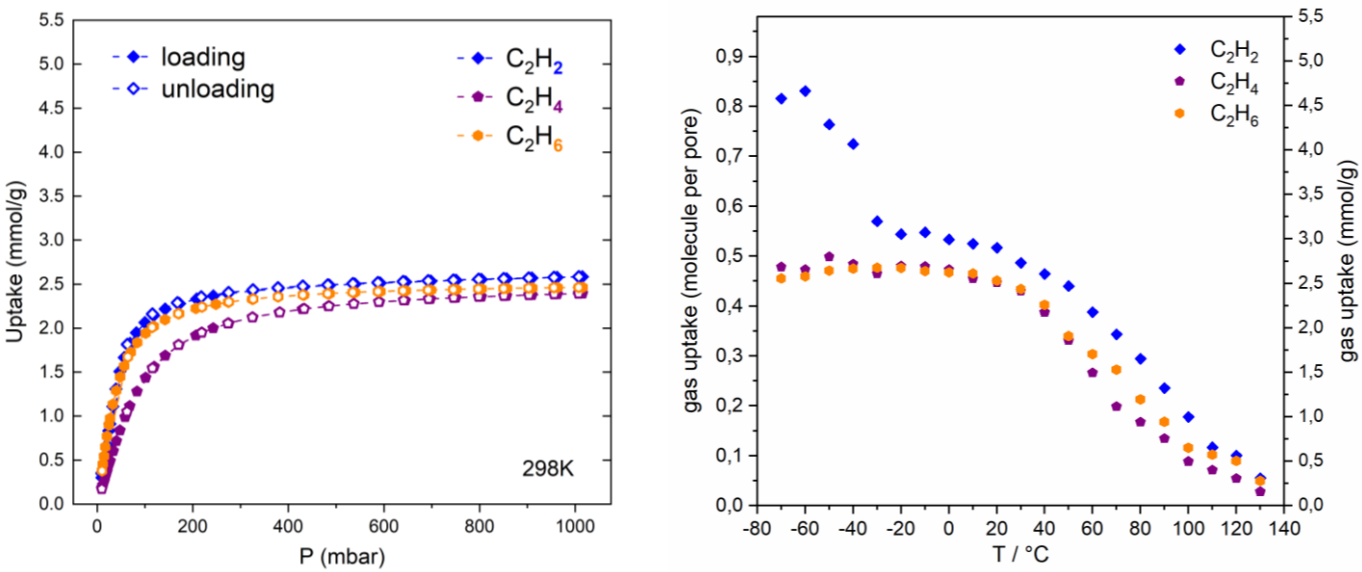


Figure 1. *Sorption measurement (left) and calculated gas uptake from in situ XRPD (right).*

In situ isobaric measurements (fig.1, right) showed a similar behavior at high temperatures for all light hydrocarbons (C_2H_2, C_2H_4, C_2H_6) – the amount of absorbed gas increases while cooling and reaches a plateau below the room temperature with ~2.5 mmol/g, which corresponds to 0.5 molecule per pore. These results are confirmed by sorption measurements approaching the full loading above 400 mbar (fig.1, left). However, below -30°C acetylene uptake started to increase and reaches 0.85 molecule per pore. It is most likely related to the smaller molecule size of acetylene, which leads to higher maximal gas loading values, compared to the other gases.

[1] H. Rietveld, J. Appl. Cryst. (1969). 2, 65-71.