



	Experiment title: Combined in situ XRD/XAS characterization of the direct oxidation of alkanes to alcohols over bioinspired Cu-MOFs	Experiment number: A31-1-150
Beamline: BM31	Date of experiment: from: 09/11/2021 to: 16/11/2021	Date of report: 07/09/2023
Shifts: 9	Local contact(s): Dragos Stoian, Wouter Van beek	<i>Received at ESRF:</i>
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Report:

This proposal aimed to characterize a selection of bioinspired metal-organic frameworks (MOFs) containing exposed Cu cations by XAS, to investigate the local structure of the metal site under different redox conditions, a key step to unravel their reactivity in the direct oxidation of alkanes to alcohols (DATA). Such materials were rationally designed to mimic the active sites, thus the outstanding catalytic performances, of Cu enzymes, while circumventing the stability and scalability limitations typical of biological systems. Specifically, we analysed a histidine-modified UiO-66 and a UiO-67 containing a biomimetic N,N,N ligand. Both systems were exchanged by Cu to give the final materials. We investigated them by combined in situ XAS/XRD under desolvation/activation/reaction conditions relevant to the methane to methanol conversion, the most iconic DATA process. Initially we considered the thermochemical protocol reported by Baek et al. [1] on similar materials, which proposed an isothermal process at 150 °C, featuring N₂O as the oxidant. The samples, in form of powder, were loaded in a flow-through capillary of optimized diameter for transmission XAS (typically 1-1.5 mm) The sample is initially exposed to inert and warmed to 150 °C, then kept to this temperature for 1 h, afterwards N₂O was dosed. In the following steps, the sample has been exposed first to CH₄ and, finally, to H₂O for the sake of products extraction, in analogy with DMTM on zeolites [2]. During the thermal treatment a Cu reduction process was observed, as testified by the occurrence of typical pre-edge fingerprints of Cu⁺ (e.g. the intense 1s→4p transition). As oxidation wasn't observed on any sample in N₂O, we resorted to attempt O₂ dosage, showing in this case a partial reversion of Cu⁺ to Cu²⁺. This behaviour was particularly relevant for the UiO-66-his-Cu sample, as depicted in Figure 1.

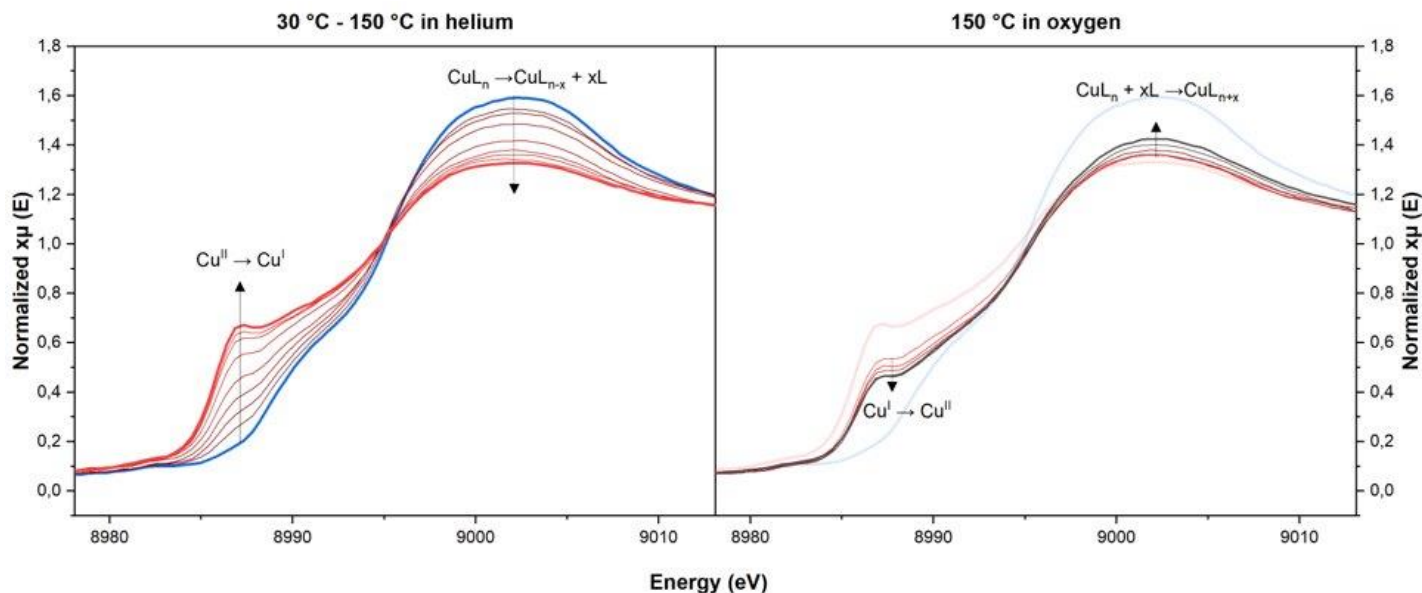


Figure 1. Evolution of XANES spectra of UiO-66-his-Cu during heating in He (left) and upon dosage of O₂ at 150 °C (right).

Upon contact with CH₄, again a partial reduction is observed, suggesting that reactivity on oxidized Cu species could have occurred. Finally, during steam assisted extraction, Cu returned mostly to the 2+ state, closing the redox cycle. A small trace of methanol was detected in the product stream by mass spectroscopy. Finally, all investigated samples remained crystalline over the whole protocol, accounting on the renown robustness of the UiO-6X frameworks. These results allowed us to verify the potential of novel Cu-MOFs catalysts in DMTM, and helped us in designing the next generation of materials, as foreseen in the ERC-SyG “CUBE” project [3].

References

- [1] J. Baek et al., *J. Am. Chem. Soc.* **2018**, *140*, 18208-18216
- [2] a) D.K. Pappas et al., *J. Am. Chem. Soc.* **2017**, *139*, 14961-14975; b) D.K. Pappas et al., *J. Am. Chem. Soc.* **2018**, *140*, 15270–15278. b) 2018, c) K.T. Dinh, K. T et al., *ACS Catal.* **2018**, *8* (9), 8306-83133
- [3] CUBE - Copper Based catalysts for selective C-H activation, *ERC-Synergy*, grant n° 856446

