



	Experiment title: Combined in situ XAS-XES of bioinspired Cu-MOFs as methane partial oxidation catalysts	Experiment number: CH-6440
Beamline: BM23/ID26	Date of experiment: from: 24/11/2022 to: 28/11/2022 (BM23) from: 21/02/2023 to: 28/02/2023 (ID26)	Date of report: 07/09/2023
Shifts: 12 (BM23) + 18 (ID26)	Local contact(s): Cesare Atzori (BM23), Vinod Paidi (ID26)	<i>Received at ESRF:</i>
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Report:

Cu-based catalysts proved their effectiveness in direct methane to methanol conversion (DMTM), a highly desirable process for methanol production from economical feedstocks. Examples of active materials include heterogenous (e.g., Cu-zeolites [1]), homogeneous [2] and enzymatic (e.g., pMMOs and LPMOs [3]) catalysts. Each class of materials present specific (dis)advantages compared to others, however none of them is nowadays applicable to DMTM in an industrial perspective. A promising route, envisaged in the framework of the ERC-Syg project “CUBE” [4], aims at the development of improved catalysts through the synthesis of hybrid materials, e.g. MOFs, where all the desirable features from the materials mentioned above are available in a single system.

This proposal aimed at providing a detailed spectroscopic characterization of a selection of bioinspired metal-organic frameworks (MOFs) containing exposed Cu cations by combining in situ XAS and XES, in order to unravel the finest details of the local coordination and electronic structure of Cu sites upon their exposure to different thermo-chemical conditions. The final goal of this activity is to capture the intermediate stages involved in the direct oxidation of methane to methanol (DMTM), performed by exploiting such Cu-MOFs as catalysts. Within this new proposal, we performed a fully spectroscopy-oriented experiment, by collecting spectroscopic data of outstanding quality we exploited for a thorough quantitative analysis on the local geometry and electronic structure of Cu sites involved in the catalytic process.

In detail, we performed *in situ* Cu K-edge XAS in BM23 and in situ HERFD/vtc-XES in ID26 to characterize Cu-MOFs at relevant reaction steps. We focused on materials based on the Zr-based UiO-66 and UiO-67 frameworks. In detail, a defective UiO-66 sample has been post-synthetically modified with histidine and then loaded with Cu²⁺ ions, in order to reproduce the coordination environment of Cu in the active site of LMPO

enzymes. Another class of materials was based on the larger UiO-67 framework, where some of the biphenyl dicarboxylic acid linkers were replaced during synthesis by isostuctural bipyridine dicarboxylic acid. The introduction of the bipyridine motif offered an anchoring site for Cu^{2+} ions, with a different coordination geometry. Both in XAS and vtc-XES measurement, a similar thermichemical protocol was explored to investigate the redox behavior of Cu sites and their impact on subsequent reaction stages: i) initial heating to the optimal desolvation temperature (150 °C); ii) pre-reduction in H_2 at 150 °C; iii) O_2 activation at 150 °C; iv) reaction with CH_4 at 150 °C; and v) extraction of CH_3OH by steaming. At each protocol stage, we collected XAS and vtc-XES spectra. In the case of XAS, the spectral evolution was monitored continuously (time resolution 2.5 min) until spectral invariance was achieved, testifying complete reactivity was reached. In vtc-XES measurements, due to the extreme sensitivity of the samples and consequent long acquisition time, the protocol was explored only until step iii).

In Figure 1, an example of XAS dataset obtained on two histidine modified UiO-66 samples with different Cu loading is presented.

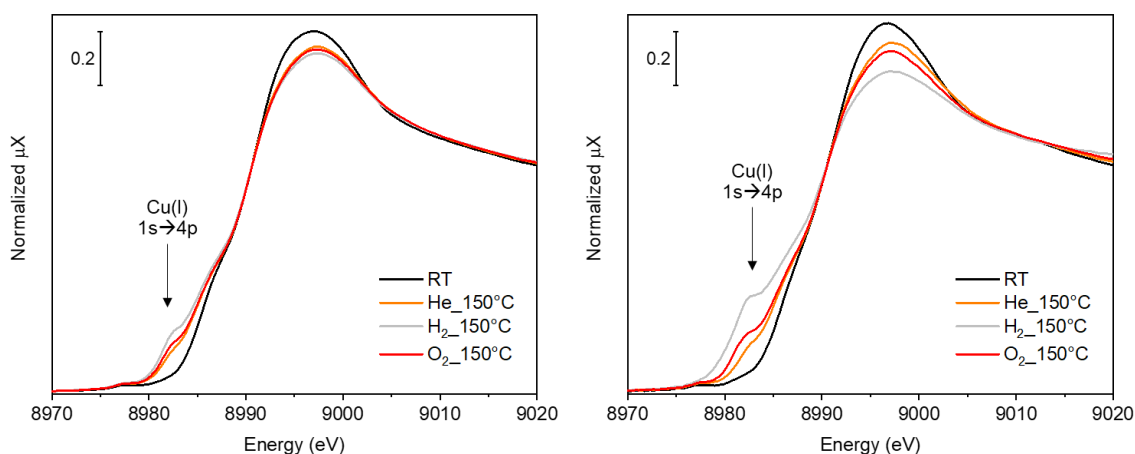


Figure 1. Comparison of redox behavior of two histidine modified UiO-66 samples under different reactive conditions, characterized by a high (left) and low (right) Cu loading.

The *in situ* XAS measurements we performed allowed getting useful insights to drive the design of next-generation of MOF-based catalysts. In both samples, Cu is entirely found in its 2+ oxidation state (a clear $1s \rightarrow 3d$ transition is observed at 8978 eV) in the pristine form of the materials, showing a XANES spectral profile typical for 4-5 coordinated Cu ions, often observed in hydrated systems. Upon desolvation, a decrease in the intensity of the whiteline can be attributed to the progressive lost of weakly-bound ligands, e.g. solvent molecules coordinating the Cu ion. In parallel, a new pre-edge features rapidly grows at 8982 eV, that is attributed to the $1s \rightarrow 4p$ transition of Cu^+ formed by reduction of initial Cu^{2+} . This process is obviously enhanced in presence of a reducing agent (H_2), but interestingly the fraction of Cu^{2+} involved in the reduction is much higher in the low Cu loading sample. Even more intriguing is the response of the latter sample to O_2 , showing a partial reoxidation of Cu^+ to Cu^{2+} . Furthermore, the intensity of the whiteline is not restored to that of the pristine sample, inferring different Cu^{2+} (possibly bearing active oxo species) are formed along the treatment. The reported data (as well as the remainder of the dataset) are currently under analysis, aiming at both disclosing redox kinetics (via MCR-ALS treatment of the data) and the local structure of most abundant states (through EXAFS fitting). Concerning the HERFD-XANES and vtc-XES data collected on ID26, several difficulties were encountered during data collection because of the extreme beam-sensitivity of the MOF samples. Accordingly, we had to significantly limit the photon flux at the sample, hampering both time resolution and data quality. We are currently working on data pre-treatment and XES simulation, in order to identify trends useful for the sake of data interpretation.

References

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