

## Experiment Report Form



	<b>Experiment title:</b> Understanding of the Fe(II) active site in mixed-metal MOFs for the conversion of methane to methanol	<b>Experiment number:</b> CH-6110
<b>Beamline:</b> ID26, BM31	<b>Date of experiment:</b> from: 15 February 2022 to: ' February 2022	<b>Date of report:</b> 11 March 2023
<b>Shifts:</b> 30	<b>Local contact(s):</b> Kenneth Marshall, Sami juhani Vasala	<i>Received at ESRF:</i>
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### Report:

Experiment CH-6110, performed at the ID26+BM31 beamlines, aimed to get information on the methane to methanol process catalysed by MIL-100(Fe) MOF [H<sub>3</sub>BTC= Benzene-1,3,5-tricarboxylic acid]. Iron-based enzymes efficiently activate molecular oxygen to carry out methane oxidation to methanol (MTM).[1] MIL-100(Fe)[2] features isolated Fe(II) sites to accomplish the same process using O<sub>2</sub> under mild conditions. In the planned experiment, we applied a diverse set of advanced operando X-ray techniques to unveil how MIL-100(Fe) shows a promising reactivity towards the direct MTM conversion under mild conditions using O<sub>2</sub> as the oxidant. We employed operando X-ray absorption (XAS) and emission (XES) spectroscopies together with resonant inelastic X-ray scattering (RIXS) (ID26 beamline) and coupled X-ray absorption (XAS) - X-ray diffraction (XRD) measurements (BM31 beamline) to fully characterize the MIL 100(Fe) MOF along activation and under conditions relevant to the O<sub>2</sub> based MTM reaction.

In a typical procedure, about 50 mg of a mixture of as-prepared MIL-100(Fe) and boron nitride (BN) at a 1:4 MOF:BN ratio were pressed into a wafer and lodged into a reactor cell connected to the beamline gas lines. For all the experiments, once the sample is mounted in the sample holder, it has been activated up to 250°C prior to the flow of the reaction mixture. Operando high energy resolution fluorescence detected (HERFD) XAS, 1s3p RXES, and valence-to-core (VtC) XES measurements were then performed at beamline ID-26 following both the thermal activation of the material and the MTM process. Radiation damage was assessed by determining the dwell time per sample spot through the collection of short energy range XAS scans of 10 sec/scan. The dwell time per sample spot avoiding radiation damage effects, was employed for all experiments. HERFD-XAS spectra were collected in an energy range between 7100-7150 eV in 0.1 eV steps. Resonant K $\beta$  and VtC XES measurements were collected in energy ranges of 7030-7068 eV and 7060-7120 eV, respectively, in 0.2 eV steps. The incident energies for the 1s3p RXES measurements (7113.7, 7115.1 and 71124.5 eV) during the thermal activation of the pristine MIL-100(Fe) sample were selected based on the HERFD-XAS measurements.

Operando XAS-XRD measurements were performed at BM31 beamline (Swiss-Norwegian beamlines, SNBL). In a typical procedure, about 50 mg of a mixture of as-prepared MIL-100(Fe) and boron nitride (BN) at a 1:4 MOF:BN ratio were pressed into a wafer and then disrupted, sieving out the fraction with a size above 125  $\mu\text{m}$ . About 5 mg of the resulting powder were loaded in a 1 mm (0.02mm wall thickness) quartz capillary reactor, plugged with quartz wool, and hooked to the gas lines on the BM31 sample stage. The sample was first heated to 250°C at 1 atm in a 12 mL/min He flux while measuring EXAFS and XRD to properly characterize the activation stage, then the activated sample was cooled to 200°C in He and exposed to a mixture of 12 mL/min He, 3mL/min CH<sub>4</sub> and 3 mL/min O<sub>2</sub> flux at 1 atm to perform the MTM reaction. The spent catalyst was subjected to one more cycle of activation at 250 °C in He, reaction at 200°C with methane and oxygen, and reactivation at 250°C in He. The sample was then cooled to 100°C and exposed again to CH<sub>4</sub> and O<sub>2</sub>, using the same fluxes as above. Finally, the MTM reaction was performed on the activated sample at room temperature. EXAFS and XRD measurements were collected during each reaction and activation step to monitor the state of the sample. During all experiments, the outlet gas was fed to a Pfeiffer Omnistar GSD 301 C mass spectrometer to detect and monitor methanol production at different temperatures. The extended X-ray absorption fine structure (EXAFS) spectra were collected at the Fe K-edge, continuously scanning between 7000 and 7900 eV with a step size of 0.3 eV. The XRD patterns were collected with a 2D DEXELA detector at a wavelength of 0.3386Å using a Si(111) channel-cut monochromator. EXAFS spectra and XRD patterns were alternately recorded by automatically switching between the DEXELA detector and the XAS-dedicated ion chambers. Phase purity and unit cell parameters were validated by performing whole powder pattern refinements (TOPAS-Academic V6) on the data collected during all the experiments described.

We have exploited the complementarity of the employed experimental techniques to propose consistent assignments for the key reaction species. Thanks to the experimental setup available at BM31, indeed, it has been possible to monitor, almost at the same time, both the diffraction and the X-ray absorption of the sample under in situ conditions.

MIL-100(Fe) activity for the O<sub>2</sub>-based MTM reaction is demonstrated for two consecutive reaction cycles in the essayed conditions, proving the MOF potential towards active site regeneration.

## References:

- [1]: Banerjee, R., et al., Nature 2015, 518, 431
- [2]: Shi, J. et al. J. Chem. 2013, 1–4 (2013).