

## Beamline report: CH-5231

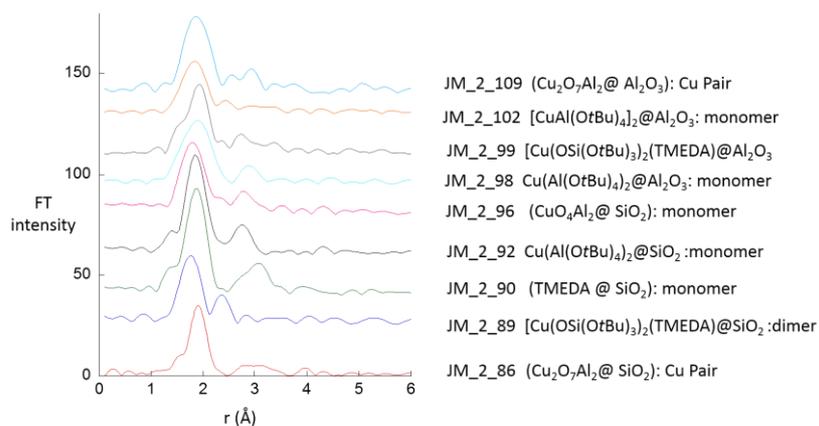
### ***Operando EXAFS/PDF investigation of structure and reactivity in supported FeOx and CuOx clusters for selective conversion of methane to methanol***

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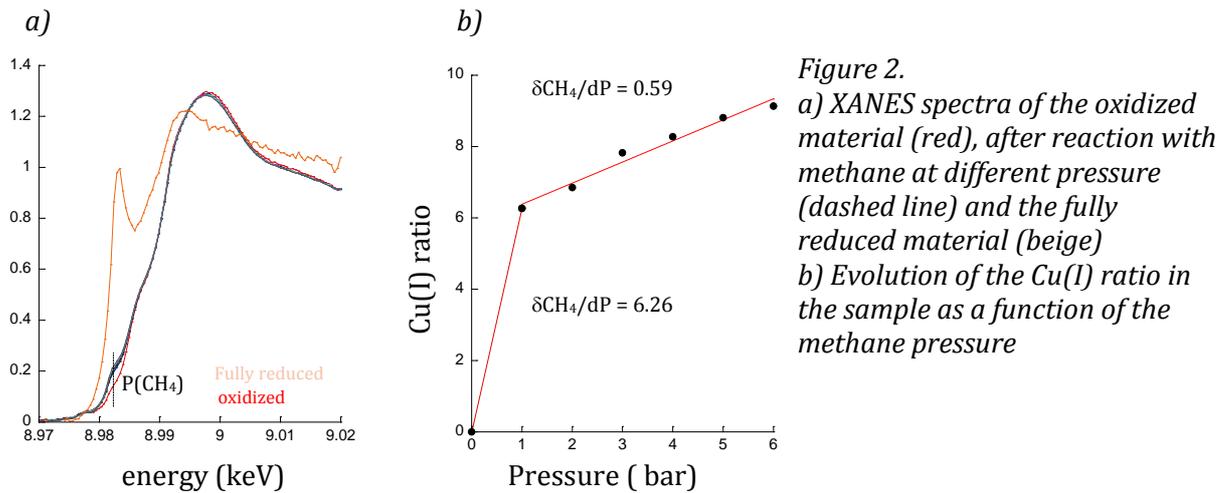
This experiment involving in situ reactivity studies of metal oxide clusters supported on oxide supports for the selective conversion of methane to methanol was, in the end, successful. The measurements originally planned were made, despite the complexity of the sample preparation, which required the use of the ESRF glovebox in the central chemical lab and setting up a high purity gas system, due to the high air and moist sensitivity of the supported material. In addition to in situ measurement, we were able to look at ex situ samples before and after the calcination step and so compared the chemical rearrangement of the copper center. Due to the low loading of some materials studied (~ 0.5 wt%) along with the use of transmission acquisition, probing the chemical environment around the copper passing the first coordination sphere was not possible. For a future characterization of such low loaded material, the requirement of a fluorescence detector would be needed to assess the full picture of the isolated copper clusters.

The ex situ sample present significant variation in the first shell (Cu-O/N) and at higher shell (Cu-Al, Cu-Si, Cu-Cu) for the grafted material, due to the different nuclear environment at the copper center (*figure 1.*). After calcination of the material, none of the sample show the formation of particles (Cu nanoparticle or bulk CuO domains).



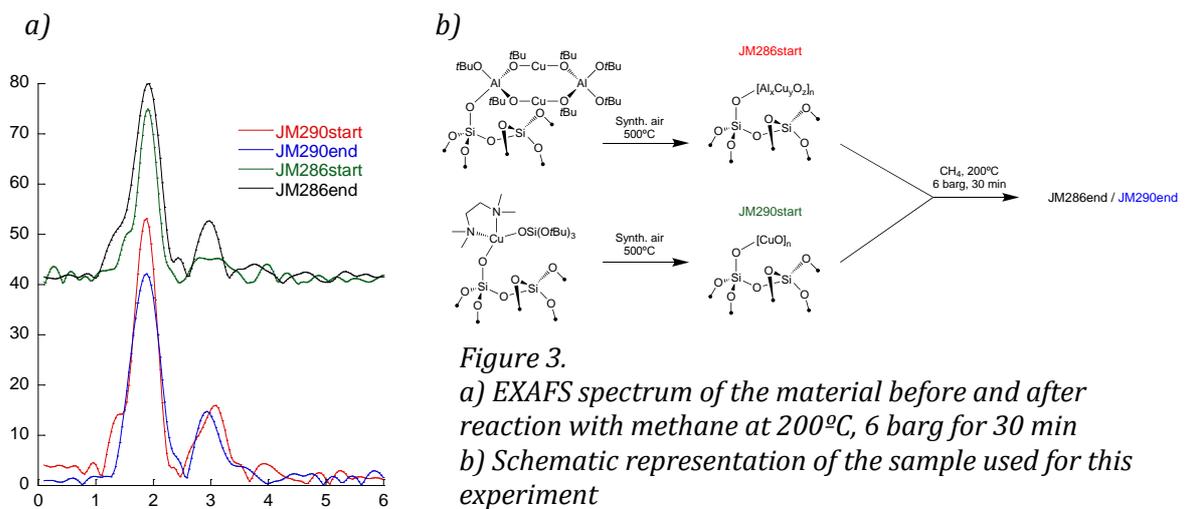
*Figure 1. ex situ EXAFS measurement of different precursor grafted (blue) and calcined at 500°C (red). These spectra show a wide variation in Cu-O/N sphere as well as in higher shell (Cu-Al, Cu-Si, Cu-Cu) in the grafted material. No clustering to Cu nanoparticle could be evidence for the calcined materials*

When contacting to the previously oxidized material with an increasing pressure of methane at 200°C, a clear change in the XANES region assessing the reduction of the copper center could be spotted and analyzed to have an idea of the amount of copper centers involved in the partial oxidation of methane (*figure 1.a*). This rough quantification of the amount of copper sites reduced during the reaction with methane and so compares it to the production of methanol from the studied material (*figure 2.b*). These values of reduced copper (I) site are higher than expected (considering a 2 electron process: 2 Cu center responsible for the partial oxidation of methane), possibly implying a different selectivity of the material toward over oxidized product.



**Figure 2.**  
 a) XANES spectra of the oxidized material (red), after reaction with methane at different pressure (dashed line) and the fully reduced material (beige)  
 b) Evolution of the Cu(I) ratio in the sample as a function of the methane pressure

Finally, when comparing EXAFS spectrum of two materials after calcination prepared with different molecular precursors, some disparity, mainly in the second shell, exists indicating a different nuclear / chemical environment around the copper core. Interestingly, after reaction with methane, both material show similar EXAFS spectrum, especially a new feature in the second shell (*figure 3.*). This information suggest a similar structure of the reduced copper center independently of the initial structure of the oxidized material.



**Figure 3.**  
 a) EXAFS spectrum of the material before and after reaction with methane at 200°C, 6 barg for 30 min  
 b) Schematic representation of the sample used for this experiment