



	Experiment title: Exploring the direct methane to methanol conversion on Cu-zeolites and Cu-MOFs: a combined XAS/XES study	Experiment number: CH4829
Beamline: BM26A	Date of experiment: from: 9 November 2016 to: 14 November 2016	Date of report:
Shifts: 15	Local contact(s): Alessandro Longo	<i>Received at ESRF:</i>
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Report:

The direct conversion of methane to methanol (MTM) is considered a ‘dream reaction’, since the development of an efficient process could profoundly alter the future of both energy sector and chemical industry. In this context, copper-exchanged zeolites (MFI [1a], MOR [1b] and more recently CHA [1d,e] frameworks) have shown interesting activity, even if the process requires multiple steps and is rather stoichiometric than a catalytic reaction [1b-e]. Catalysts are described as single-site, but the nuclearity and the nature of the active Cu-oxo centers formed as a function of the zeolite topology is still strongly debated in the literature [1].

Experiment CH4829 aimed at a comparative exploration, by *operando* XAS, of the structural and electronic properties of active Cu-sites in Cu-MOR and Cu-CHA catalysts during a stepwise protocol for the MTM conversion, previously proposed in the literature [1b] and optimized in our laboratories. The investigated platform of catalysts included two Cu-CHA and two Cu-MOR samples with comparable Si/Al ratio of 12-11, organized in a 2 X 2 matrix, according to topology (CHA, MOR) and Cu-loading (0.1, 0.5-0.4)

Operando XAS data were collected at the BM26A beamline in transmission mode. We employed the Microtomo reactor cell designed by the ESRF Sample Environment Group integrated in a devoted gas-flow setup, as described in detail in our previous works on Cu-CHA [2]. The gas composition of the outlet gas from the reactor has been continuously monitored by means of a mass spectrometer (MS). The stepwise process monitored by XAS included the following steps: (i) O₂-activation: heating from RT to 500°C (5°C/min) in O₂ and keeping the samples in O₂ at 500 °C for 2h; (ii) ‘cool & flush’: cooling to 200 °C in O₂ and flushing with dry He; (iii) CH₄-activation: exposing the activated catalyst to CH₄ at 200 °C; (iv) H₂O-extraction: after a dry He flush, exposing the catalyst to a 10% H₂O/He gas flow.

The samples were prepared in the form of self-supporting pellets (~ 100 mg/1.3 cm², resulting in edge jumps Δμ_x in the 0.2-0.7 range, depending on Cu-loading, for a total absorption after the edge of μ_x = 2.5) and fixed inside the Microtomo reactor cell. Our measurement strategy combined (i) fast scans (~ 10 min/scan) to efficiently track the modifications in Cu-speciation during the protocol by XANES and quick EXAFS and (ii) longer steady-state scans (30 min/scan, repeated 2-4 times depending on the Cu-loading), aimed at the collection of higher-quality EXAFS spectra upon stabilization for each of the four steps.

Fig.1 compares the steady state XANES and FT-EXAFS spectra obtained for each of our 2 X 2 catalysts’ matrix at the key process steps, including O₂ flow at 500°C, and subsequent He, CH₄, 10% H₂O/He flow at 200°C. The XAS features of both CHA- and MOR-based catalysts observed in each of the relevant conditions, strongly supporting the presence of equivalent average Cu-environments in both topologies.

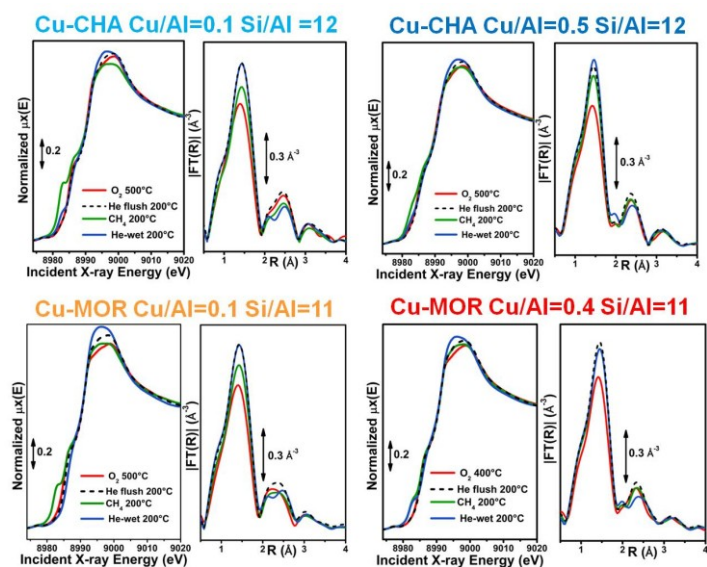


Fig. 1 Operando XANES (left panels) and phase uncorrected k^2 -weighted FT-EXAFS spectra (right panels, k -range for the FT: 2.4–12.4 \AA^{-1}) collected on Cu-CHA and Cu-MOR catalysts with Si/Al = 11/12 and different Cu/Al ratios in steady state conditions at key steps during the MTM process.

detectable for high-loading ones. We possibly connect such effect to the formation of end-on Cu(II)-superoxo moieties from reaction of O_2 with Cu(I) sites *e.g.* transiently formed from self-reduction of $[\text{CuOH}]^+$ species: DFT-assisted data modelling is currently in progress.

During the CH_4 -activation step, all catalysts reduce to some extent, as demonstrated by the rise of the XANES peak at ca. 8983 eV, assigned to the $1s \rightarrow 4p$ transition in Cu(I) sites (green curves in Fig. 1 and Fig. 2a). Preliminary linear combination fit analysis allowed us to quantify the Cu(I) fraction, obtaining values in the 20–40% range. Noteworthy, the relative fractions of Cu(I) do not correlate with the productivity of the investigated samples. As demonstrated by the MS data collected during *operando* XAS (Fig. 2a, bottom), the formation of Cu(I) during interaction with CH_4 is accompanied by the release of significant amounts of CO and CO_2 , suggesting a connection with the Cu(I) formation and possible ‘spectator’ Cu-sites capable to activate C-H bond, but unable to protect the product from further oxidation steps. H_2O -assisted extraction (Fig. 1 blue curves, Fig. 2b) yielded a partial reoxidation in all the samples, together with modifications in the XANES white-line region consistent with the formation of partially hydrated Cu(II) species. In the EXAFS, it is clear a substantial degradation of the second-shell peak, supporting mobilization of the Cu-cations. During extraction we detected MeOH (Fig. 2b, bottom), demonstrating that the catalysts were effectively active in our *operando* XAS conditions. Nonetheless, the big dead volume of the Microtomo cell and the not-passant gas flow prevented quantitative analysis of MS data.

References

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The good quality of the collected EXAFS spectra allowed us a reliable comparison of the O_2 -activated catalysts (red curves in Fig.1) in the second shell region, which in the current literature tends to be assigned differently in Cu-CHA (Cu-Si/Al paths in framework-interacting mononuclear Cu-species [2, 3]) and Cu-MOR (Cu-Cu paths in multi-nuclear Cu-species [1a-c]). The strong similarity of the FT-EXAFS spectra in the 2–3 \AA region for all the investigated samples and the absence of any detectable trend as a function of the Cu-loading discourage for both Cu-CHA and Cu-MOR a substantial contribution from Cu-Cu paths. Although the final XANES of the O_2 -activated catalysts reveals in all cases a virtually total Cu(II) state, we observed a transient reduction during the heating phase of the O_2 -activation step. The development of Cu(I) features is observed for all catalysts in the 160–350 $^\circ\text{C}$ range. The effect is clearly visible for low-loading samples and barely

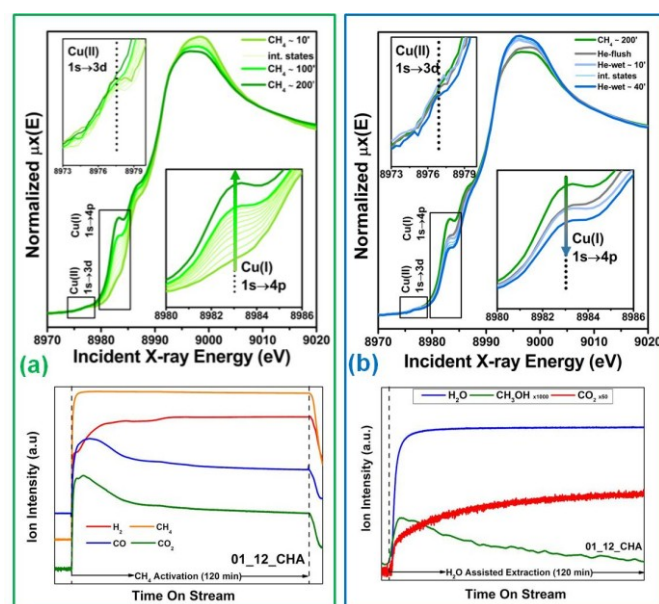


Fig. 2 Temporal evolution of XANES spectra for a representative Cu-zeolite catalyst (Cu-CHA, Cu/Al = 0.1, Si/Al = 12) in isothermal conditions at 200 $^\circ\text{C}$ during (a) the CH_4 -activation and (b) the H_2O -assisted extraction steps. Bottom panel reports the corresponding qualitative MS data collected during the *operando* XAS experiment.