# XAS reveals structure-activity relationships for the methane to methanol conversion over Cu-SSZ-13 zeolites

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A process allowing energy-effective methane to methanol (MTM) conversion would represent a major breakthrough for chemical industry. Although nature does the work masterfully with Cu-enzymes, an industrially-viable process for this conversion remains an ongoing challenge. In recent years, Cu-exchanged zeolites have been shown to possess Cu active sites able to cleave the C−H bond of methane at temperatures $\leq 200$ °C, enabling its stoichiometric transformation into methanol [Ravi *et al.*, *Angew. Chem. Int. Edit.* **56**, 16464 (2017)]. The conversion is performed through a stepwise process, involving high-temperature activation in $O_2$ to generate the active sites, methane loading at 200 °C, and steam-assisted methanol extraction.

We have combined laboratory performance testing with *in situ*/*operando* Cu K-edge XAS at the BM23 and BM26A beamlines of the ESRF to establish structure-activity relationships for the MTM conversion over Cu-SSZ-13 zeolites [Pappas *et al.*, *J. Am. Chem. Soc.,* **139**, 14961 (2017)]. By *operando* XAS, we tracked the oxidation state and average coordination of Cu ions during each step of the process. To obtain deeper insights in the nature of the active sites, we explored the impact of different pretreatments and compositional characteristics by *in situ* XAS. Our previous results from multivariate analysis of a large XANES dataset [Martini *et al., Chem. Sci.,* **8**, 6836 (2017)] enabled an accurate determination of Cu-speciation after activation.

*Operando* XAS reveals tri-coordinated framework-interacting $Cu^{II}$ centers as the dominant species in the $O_2$-activated state at 500 °C, while cooling to 200 °C promotes an increase in the first-shell coordination number. During methane loading, XANES linear combination fit indicates the $Cu^{II}$ to $Cu^{I}$ reduction in 27% of the Cu sites. During $H_2O$-assisted methanol extraction, the $Cu^{I}$ fraction diminished to 13%, together with the formation of 27% of mobile $Cu^{II}$ aquo complexes. High-temperature reaction with $O_2$ is evidenced as a key requirement to form the active sites. Moreover, a positive linear correlation between the methanol productivity and the composition-dependent self-reducibility under high-temperature treatment in He is found.

These results demonstrate how high populations of bare $Cu^{II}$ sites charge-balanced by two proximal Al, favored at low Si/Al ratios, inhibit the MTM performance by being inactive for the conversion. $[Cu^{II}OH]^{+}$ complexes are instead identified as the precursors to the active sites, though their ability to self-reduce. As also supported by FTIR and Raman, $[Cu^{II}OH]^{+}$ species progressively deplete during high-temperature oxidative treatment, evolving towards different mono- and multimeric $O_2$-derived $Cu^{II}$ moieties, among which the active sites should be researched. The study highlights the XAS role in understanding reaction routes in Cu-zeolites, and paves the way for rationalized material synthesis to develop an industrial MTM process.