

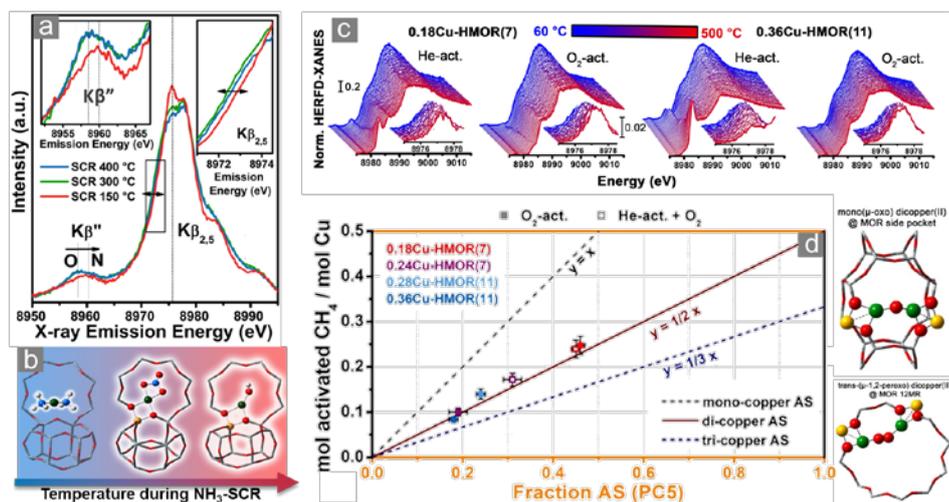
# Selective redox catalysis over Cu-zeolites: insights by HERFD-XANES and vtc-XES

E. Borfecchia

Dept. of Chemistry, University of Turin, Via P. Giuria 7, 10125, Turin (Italy), [elisa.borfecchia@unito.it](mailto:elisa.borfecchia@unito.it)

Cu-exchanged zeolites are attracting increasing attention as platforms for high-impact selective redox chemistry, including  $\text{NH}_3$ -mediated selective catalytic reduction of harmful nitrogen oxides ( $\text{NH}_3$ -SCR) and direct selective oxidation of methane to methanol (DMTM) [1]. Quantitative determination of Cu-speciation in the zeolite framework under realistic reaction conditions and robust correlation between spectroscopic and catalytic observables are essential to keep advancing the field.

This contribution will focus on the role of HERFD-XANES and vtc-XES applied under *in situ* and *operando* conditions at the ID26 beamline of the ESRF to accomplish this task, in synergy with conventional XAS, laboratory-based multi-technique characterization, computational modelling and systematic performance evaluation.



**Figure 1:** (a) Vtc-XES during temperature-dependent  $\text{NH}_3$ -SCR over Cu-CHA providing direct evidences for preferential N-ligation of Cu-centers at 150 °C, as illustrated in part (b). (c) Time-resolved HERFD-XANES during  $\text{O}_2$  and He-activation of Cu-MOR zeolites with different composition. (d) Quantitative correlation between DMTM activity and Cu-speciation derived from MCR analysis of spectra in part (c), unambiguously indicating a di-copper active site, such as the mono-( $\mu$ -oxo) or the trans( $\mu$ -1,2-peroxo) dicopper(II) species.

The presented results will highlight the unique sensitivity of vtc-XES in discriminating among almost-isoelectronic ligands, such as O and N, crucial in the context of  $\text{NH}_3$ -SCR [2]. The great potential of HERFD-XANES combined with the emerging multivariate curve resolution (MCR) approach [3, 4] will be also exemplified, to resolve the finest details of Cu-speciation during the activation of Cu-CHA [4] and Cu-MOR [5]. In the latter case, quantitative correlation of MCR results with DMTM activity measurements provided, for the first time, unambiguous evidence of a di-copper (II) active site for  $\text{CH}_4$  activation [5].

## References

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