Multivariate analysis of *in situ* XAS to determine Cu-speciation in zeolite catalysts

A. Martini (1,2), E. Alladio (1), C. Negri (1), K. A. Lomachenko (3), G. Berlier (1), S. Bordiga (1), C. Lamberti (1,2), E. Borfecchia (1,4)
(1) Department of Chemistry and NIS Centre, University of Turin, Turin, Italy; (2) The Smart Materials Research Center, Southern Federal University, Rostov-on-Don, Russia; (3) European Synchrotron Radiation Facility, Grenoble, France; (4) Haldor Topsøe A/S, Kgs. Lyngby, Denmark
andrea.martini@unito.it

Cu-exchanged chabazite (Cu-CHA) is currently the object of intensive research efforts due its outstanding performance in deNO_x catalysis [Beale *et al.*, *Chem. Soc. Rev.* **2015**, 44, 73712] and its activity in the partial oxidation of methane to methanol (MTM) [Pappas et al., *J. Am. Chem. Soc.* **2017**, 139, 14961]. Understanding at the atomic scale how the catalyst composition influences the Cu-species formed during activation is fundamental to unleash the potential of this promising catalyst. To shed light on this aspect, we explored by *in situ* XAS the impact of the catalyst composition on the temperature-dependent Cu-speciation and reducibility. Here, the use of multivariate data modelling [Jaumot *et al., Chemometr. Intell. Lab*. **2015**, 140, 1] allowed us to access an unprecedented level of understanding in a complex multi-component system, yielding novel insights into the birth of Cu-active sites in the cages of the CHA zeolite.
We monitored by *in situ* XANES (BM23 ESRF) the He-activation, from room temperature (RT) to 400 °C, in a series of six Cu-CHA samples with Si/Al and Cu/Al ratios in the 5−29 and 0.1−0.6, respectively. We applied a factorial procedure called Multivariate Curve Resolution (MCR) on the entire temperature-dependent multi-composition XANES dataset to isolate chemically meaningful spectra and concentration profiles of common, 'pure' Cu-species [Martini *et al*, *Chem. Sci.*, **2017**, 8, 6836]. Moreover, to obtain insights on the formation of O_2-derived species, we focused on a selected Cu-CHA sample (Si/Al=12, Cu/Al=0.5), resulting in an optimal performance for the MTM process [Martini et al., *Top. Catal.,* **2018**, submitted]. In this case we performed MCR analysis on High Energy Resolution Fluorescence Spectra Detected (HERFD) XANES (ID26 ESRF) during thermal treatment in both He and O_2 gas flow, exploiting the superior energy resolution in the detection of minor Cu-species.
Starting from He-activation, the trends in Cu-speciation evolution show that the decreasing of the fully hydrated Cu(II) population correlates with the appearance of four-coordinated Cu(II) dehydration intermediates. At higher temperatures two major Cu-sites progressively appear, whose relative abundance strongly depends on the Si/Al ratio in the parent zeolite. These include reduction-resistant Cu(II) species, charge balanced by two proximal Al (*i.e* 2AlCu(II)), and redox-active 1Al[Cu(II)OH] complexes. 2AlCu(II) reach a steady population in the 200-300 °C range and remain stable until 400 °C. On the other hand, 1Al[Cu(II)OH] peak around 200 °C and therein start to progressively decrease in favor of 1AlCu(I) species. During O_2-activation, MCR analysis evidences the existence of additional Cu(II)-oxo species originated from 1Al[Cu(II)(OH)] precursor, which most likely plays a crucial role in the MTM process.
For the first time, MCR approach allowed us to rationalize in a quantitative frame the complex dynamics of Cu-cations in the CHA cages during the activation process in He and O_2. Overall, the reported results for Cu-CHA evidence how synergizing the structural/chemical sensitivity of synchrotron-based X-ray spectroscopy with multivariate techniques results in an enhanced quantitative understanding of conditions- and composition-dependent metal speciation in complex nano-catalysts.