Understanding local structure and redox chemistry of metal ions in nanoporous catalysts by X-ray absorption spectroscopy

E. Borfecchia

Dept. of Chemistry, University of Turin, INSTM reference center and NIS center, Via P. Giuria 7, 10125, Turin (Italy)

elisa.borfecchia@unito.it

X-ray absorption spectroscopy (XAS) has imposed as a powerful method to track structural and chemical dynamics of metal ions hosted in nanoporous frameworks, such as zeolites and metal-organic frameworks (MOFs), for selective redox catalysis applications [1]. Analysis of the XANES and EXAFS regions offers a highly complementary view with respect to diffraction-based methods guaranteeing a unique sensitivity to the local electronic and structural properties of metal centers. These are often disorderly distributed in the crystalline matrix, and occur as dynamic mixtures of different species, responding to the physico-chemical environment while undergoing a rich redox chemistry mediated by host-guest interactions. Continuous instrumental developments at synchrotron sources today enable *in situ/operando* XAS studies at high time and energy resolution, allowing to monitor such dynamic systems with unprecedented accuracy [1]. In this contribution, the potential of these methods, empowered by advanced data analysis strategies and synergic integration with multi-technique laboratory characterization and computational modelling, will be exemplified by selected research results.

A first example will focus on the Cu-exchanged chabazite (Cu-CHA) zeolite, currently representing the catalyst of choice for deNO$_x$ applications in the automotive sector via NH$_3$-assisted Selective Catalytic Reduction [2]. Here, the potential of Multivariate Curve Resolution (MCR) of time-resolved XANES datasets, quasi-simultaneous XANES/PXRD, and EXAFS Wavelet Transform analysis will be highlighted, to accurately quantify condition/composition-dependent Cu-speciation in CHA zeolites and therein establish robust structure-activity relationships, essential to design improved catalysts. A second case study will consider local structural and chemical transformations of Pt ions in Pt-functionalized UiO-67 MOFs [3], tracked by parametric refinement of time-resolved *operando* EXAFS under conditions yielding either isolated Pt^{II} sites anchored to the MOF framework (potentially interesting for C–H bond activation) or very small Pt^0 nanoparticles inside the MOF cavities (potentially interesting for hydrogenation reactions).

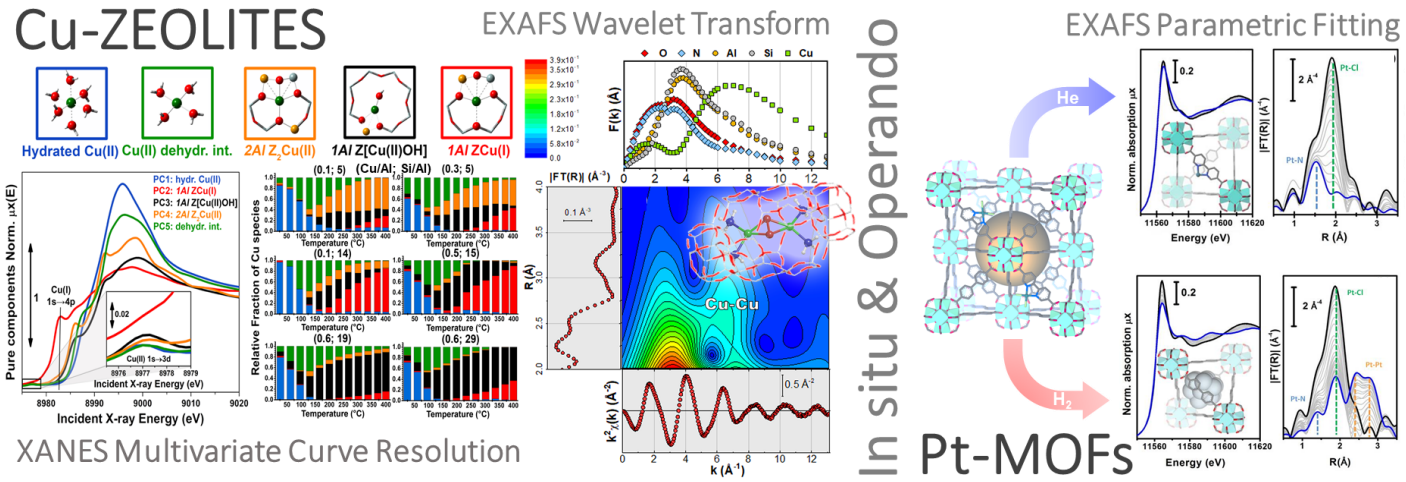

Figure 1. Selected examples and relevant keywords illustrating the potential of advanced analysis methods of *in situ/operando* XAS data to track structural/chemical dynamics of metal ions hosted in zeolites (left) and MOFs (right) for redox catalysis applications.

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[3] S. Øien, et al., *Chem. Mater.* **2015**, *27*, 1042. L. Braglia, et al., *Phys. Chem. Chem. Phys.* **2017**, *19*, 27489. L. Braglia, et al., *Faraday Discuss.* **2017**, *201*, 265.

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