Theoretical investigation of Cu oxo species in Cu-exchanged CHA and MOR zeolites by means of DFT-assisted Cu K-edge XANES simulations.

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Transition metal-exchanged zeolites are efficient catalysts in the decomposition of harmful NO_x [M. H. Groothaert, et al., *J. Am. Chem. Soc.*, **125** (2003) 7629] and have shown promising performance in the selective oxidation of methane to methanol (MTM) [M. H. Groothaert *et al.*, *J. Am. Chem. Soc.* **127** (2005) 1394]. In this context, Cu-exchanged zeolites have shown interesting activity, even if the process requires multiple steps and is rather stoichiometric than a catalytic reaction [P. Tomkins, et al., *Angew. Chem. Int. Edit.* **55** (2016) 5467]. XAS has been largely used to characterize Cu-zeolites after high-temperature O_2-activation [M. H. Groothaert *et al.*, *J. Am. Chem. Soc.* **127** (2005) 1394; S. Grundner *et al.*, *Nature Comm.* **6** (2015) 7546], but the nature of the active Cu-oxo centers formed as a function of the zeolite topology is still debated. The present study aims to get theoretical insights on the XAS fingerprints for different Cu-oxo species formed in CHA and MOR zeolites.

DFT simulations were performed using plane wave pseudopotential approach as implemented in the VASP 5.2 package. Cell volume, cell shape and atomic positions were used as variable parameters in the geometry relaxation procedure. A kinetic energy cutoff of 450 eV was used to restrict plane wave basis set. All calculations were performed in reciprocal space employing Monokhorts-Pack algorithm for sampling the Brillouin zone. For Cu K-edge XANES simulations finite difference method and full potential approximation implemented in the FDMNES software [Y. Joly, *Phys. Rev. B* 63 (2001) 125120] was employed. Sparse solvers for the finite difference matrix were used in order to decrease the required computational time [S. A. Guda, *J. Chem. Theory Comput.* **11** (2015) 4512].

We built up several structural models aimed to mimic mono and multimeric Cu_xO_y species formed in small pore Cu-CHA and large pore Cu-MOR zeolites upon O_2-activation. For all models cell shape and volume as well as atomic positions were subsequently optimized. For both frameworks, structural parameters are in a good agreement with a recent theoretical report [Viella and Studt Eur. J. Inorg. Chem. **2016** (2016) 1514]. Comparative analysis of correspondent Cu K-edge DFT-assisted XANES simulations evidence that it is very difficult to distinguish mono- and di-copper species if they show the same first-shell environment, three-fold or four-fold coordinated Cu sites. Cu Kβ vtc-XES simulations are currently in progress, to explore the potential of the technique in the identification of Cu-active sites for the MTM.

The study provides a robust theoretical background to assess potential and limitations of X-ray spectroscopy applied to the identification and structural analysis of Cu-oxo active species for the MTM conversion over Cu-zeolites. I.P., A.G. and A.S. acknowledge the Mega-grant of the Russian Federation Government (No. 14.Y26.31.0001) for financial support of the research.