

Cu-oxo Species in Zeolites: Preliminary Results by Wavelets Analysis

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Recently, Cu-exchanged chabazite (Cu-CHA) and mordenite (Cu-MOR) are attracting increasing attention for the direct conversion of methane to methanol (MTM). A key step to understand their potential in this reaction is the reliable determination of Cu-speciation in O₂-activated materials. From a qualitative analysis, the experimental XAS data reported in the literature for O₂-activated Cu-CHA and Cu-MOR do not show sharp differences. However, the interpretation of the EXAFS signal significantly differs for the two topologies. While the first peak of the EXAFS Fourier transform (FT-EXAFS) is commonly associated to Cu-O single scattering paths (SS), the interpretation of the second peak seems to be more uncertain. In particular, in Cu-CHA this feature has been associated to the SS path involving the second-shell Al/Si atoms in monomeric Cu-complexes [Pappas et al., *J. Am. Chem. Soc.*, **2017**, 139, 14961]. Conversely, for Cu-MOR, the second-shell region is modelled by Cu-Cu (SS) paths in multimetric Cu species [Alayon et al., *Phys. Chem. Chem. Phys.*, **2015**, 17, 7681]. We employed Wavelet Transform (WT) analysis on EXAFS spectra in order to visualize a given spectrum in three dimensions: the wavevector (k), the interatomic distance R and the WT modulus. This new kind of signal representation should be able to single out different contributions from scattering atoms with different Z that, from classical FT-analysis, could appear of ambiguous identification.

We collected EXAFS spectra (BM26A and BM23, ESRF) on a series of Cu-CHA and MOR samples with Si/Al ratios in the 5-12 range and Cu/Al ratios from ~ 0.1 to ~ 0.4 after O₂-activation at 500 °C. After the definition of a common apodization window (hanning type with a Δk range from 2.4 to 11 Å), we applied WT on each k^2 -weighted EXAFS spectrum. For our study, we chose as “mother” function the Cauchy wavelet characterized by a Cauchy order n of 200, which ensures a good resolution in both k and R space [Muñoz et al., *Am. Mineral.*, **2003**, 88, 694].

Through graphical analysis of WT modulus, we find similarities and differences among samples. All of them have highly a symmetric first-shell maxima peaking at low k , which is safely assigned to SS involving framework and extra-framework oxygen neighbors. In the second shell, more differences appear as a function of topology and composition. Every Cu-MOR presents a peak characterized by two lobes extending along the k direction. In line with the k -dependence of the scattering amplitudes for the involved scattering atoms (O, Si/Al, Cu), the first one, at low k , can be associated with Al/Si scattering contributions, while the second lobe to Cu ones. These evidences lead to the conclusion that at 500 °C monomeric and dimeric Cu moieties could coexist. The same features, although less pronounced, can be identified in CHA with Si/Al=11, while at Si/Al=5 the second shell peak is more compact at low k , denoting the dominance of monomeric Cu-sites.

These results highlight that WT approach could represent a promising technique if compared with conventional FT, both for visualization and interpretation of EXAFS signals, permitting to discriminate contributions from heavy and light scatterers in the Cu local environment in zeolite-based catalysts, thus shedding light on the long-standing question about nuclearity of Cu-species.