

Experiment Report Form



Experiment title: The structural and electronic configuration of Cu active sites in Cu-SSZ-13 and Cu-ZSM-5 under SCR conditions: a combined operando XAS and XES study. *Part 1 – Measurements on BM23*

Experiment number:
CH-4080

Beamline: BM23	Date of experiment: from: 30/04/2014 to: 06/05/14	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Suresh Gatla	

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Report:

Cu-CHA is an outperforming catalyst for the NH₃-assisted selective catalytic reduction (SCR) of the harmful nitrogen oxides (NO_x, x=1, 2), but despite two decades of intensive research efforts, a comprehensive picture of the structure-activity relationship in these promising catalysts is still missing [1]. Since the catalytically active sites for this reaction are mainly represented by the isolated Cu ions incorporated into the zeolitic framework, the element-selective study of Cu local environment is crucial for understanding of the enhanced catalytic properties of this material. In experiment CH-4080 we combined XAS (on BM23) and XES (on ID26, see below CH-4080 report – *Part 2*) spectroscopies, complemented by FTIR and EPR characterization, and DFT computational analysis, to elucidate the nature and location of the most abundant Cu-sites for an highly active Cu-CHA catalyst formulation (Si/Al and Cu/Al ratios of 13.1 and 0.444 respectively) for the dehydrated material and upon different reaction-relevant conditions [2a,b]. On this basis, we were able to suggest a consistent, experimentally-validated, mechanism for the NH₃-SCR reaction [2c].

We performed *in situ/operando* measurements on both BM23 and ID26 beamlines, adopting the same gas flow/sample environment setup based on the MICROTOMO reactor cell developed at the ESRF, successfully tested and employed also in the previous experiment CH-4796 (see also CH-4796 Experimental Report).

On BM23 we collected in transmission mode high quality XANES and quick EXAFS spectra analyzable up to $k = 12 \text{ \AA}^{-1}$, with a time resolution of ~ 12 min while increasing the temperature and/or sending reagents in the gas phase, together with high-quality EXAFS scan analyzable up to $k = 16 \text{ \AA}^{-1}$ with typical integration time of 1 h upon stabilization of the spectral features at key reaction points.

Firstly, Cu species that form in Cu-CHA upon activation in 50% O₂/He were characterized in more details. It was found that, upon heating, Cu(II) centers undergo progressive dehydration, while interacting more closely with the framework, with no significant modification of their oxidation state. Features typical for Cu (II) in low-symmetry environment are observed in XANES (Fig. 1a), while EXAFS witnesses the marked decrease of the first shell intensity due to the loss of the coordinated water molecules (Fig. 1b). DFT-assisted EXAFS fits were carried out for several theoretical models for Cu(II) sites: it was found, that the dominant Cu species

in the activated material are $[\text{Cu}^{2+}(\text{OH})]^{+}$ complexes situated in the 8-member rings of the CHA framework, in the vicinity of a single Al atoms (Fig. 1c,d). An equivalent characterization protocol was applied to the He-activated catalyst, revealing how an inert atmosphere promotes reduction to Cu(I), concomitantly to the loss of the OH extra-ligand in the first coordination shell of Cu (equivalently but more efficiently with respect to what has been previously observed during thermal treatment in vacuum). We also performed preliminary tests on the XAS characterization of a low Cu-loading Cu-CHA sample (ca. 0.8 w% Cu) in the hydrated and O_2 -activated condition. With enhanced, but still reasonable, collection time (2.5 h, with respect to 1h for the high-loading catalyst), EXAFS spectra analyzable up to ca. 12.5 \AA^{-1} were obtained in transmission mode (Fig. 1e).

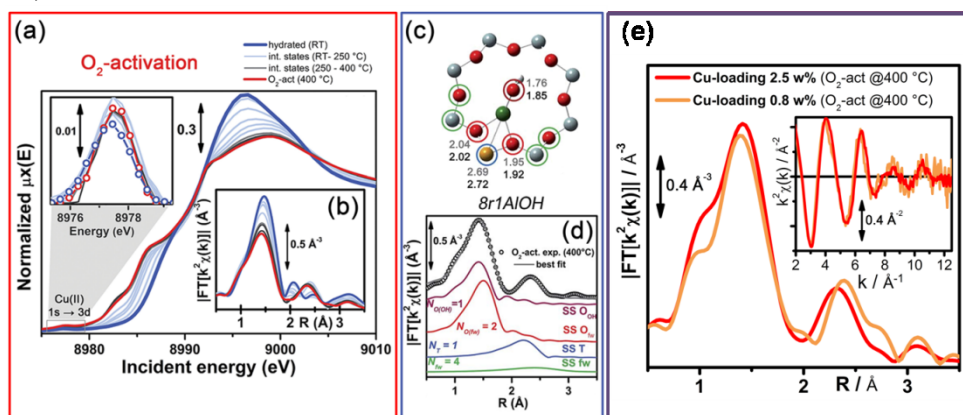
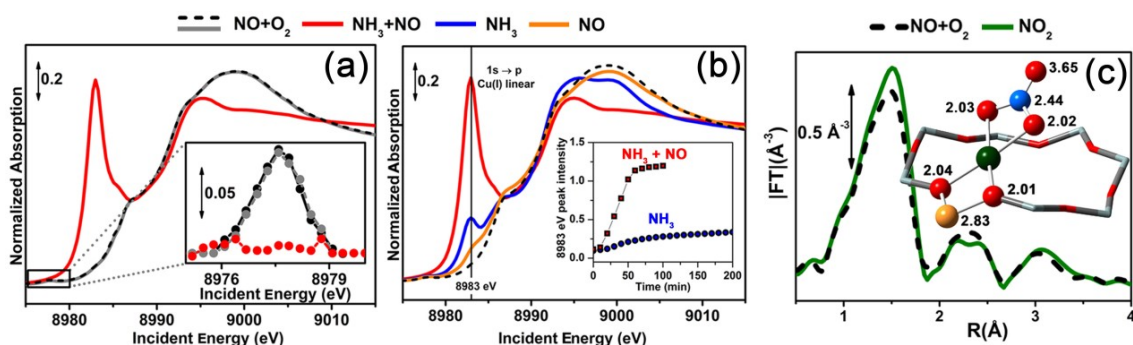


Fig.1 Spectroscopic data for Cu-CHA activated in 50% O_2/He . (a) XANES and (b) EXAFS spectra collected while heating from RT (blue curve, hydrated material) to $400 \text{ }^\circ\text{C}$ (red curve, activated material); (c) DFT model of the dominant Cu-site in the activated material, that resulted in (d) the best EXAFS fit. (e) Preliminary comparison between EXAFS spectra for low (ca. 0.8 w% Cu) and high Cu-loading O_2 -activated CHA samples. Both $\text{FT}[k^2\chi(k)]$ spectra calculated in the $(2.4-12.4) \text{ \AA}^{-1}$ range.

A second stage of the experiment was designed to validate a consistent scheme of the SCR reaction [2c], by testing different SCR-relevant conditions in the reactor while collecting XAS spectra *in situ*. In particular, it was proved possible to decouple the oxidation and reduction parts of the SCR reaction, by exposing the catalyst alternately to a mixture containing NO and O_2 and a mixture containing NH_3 and NO . Indeed, it was witnessed by a very pronounced pre-edge XANES peak that the sample was reduced upon interaction with NH_3+NO and reoxidized after switching back to $\text{NO}+\text{O}_2$ (Fig. 2a,b). Conversely, the interaction with NH_3 alone did not lead to such prominent reduction (Fig. 2b), converting only about a quarter of $\text{Cu}(\text{II})$ sites to $\text{Cu}(\text{I})$. Reduction upon interaction with NO alone was even less likely, resulting in purely $\text{Cu}(\text{II})$ species. This study also revealed that the interaction of both $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ species with NO_2 and $\text{NO}+\text{O}_2$ results in the same $\text{Cu}(\text{II})$ species (Fig. 2c), in full agreement with the suggested mechanism. The obtained complex was a bidentate $\text{Cu}-\text{NO}_3^-$, as evidenced by the EXAFS and XANES analysis. All these findings confirm the proposed scheme of the SCR reaction, resulting in greatly improved understanding of its chemistry.

Fig.2. *In situ* Cu K-edge XAS data collected at $200 \text{ }^\circ\text{C}$ under different SCR-relevant conditions. (a) XANES upon initial oxidation in 1000 ppm $\text{NO} + 10\% \text{ O}_2$ (dashed black curve), reduction in 1200 ppm $\text{NH}_3 + 1000 \text{ ppm NO}$ (solid red curve) and reoxidation in 1000 ppm $\text{NO} + 10\% \text{ O}_2$ (solid grey curve). (b) XANES showing the reducing capability of 1200 ppm NH_3 (solid blue curve), 1000 ppm NO (solid orange curve) and a mixture of 1200 ppm NH_3 with 1000 ppm NO (solid red curve) on the $\text{Cu}(\text{II})$ state obtained after initial oxidation in a mixture of 1000 ppm NO and $10\% \text{ O}_2$ (dashed black curve). (c) Fourier-transformed EXAFS after exposure of dehydrated Cu-SSZ-13 to 1000 ppm NO_2 (solid green curves), and to a mixture of 1000 ppm NO and $10\% \text{ O}_2$ (dashed black curve) together with the structural model of the bidentate $\text{Cu}-\text{NO}_3^-$ species forming at these conditions.




(a) XANES upon initial oxidation in 1000 ppm $\text{NO} + 10\% \text{ O}_2$ (dashed black curve), reduction in 1200 ppm $\text{NH}_3 + 1000 \text{ ppm NO}$ (solid red curve) and reoxidation in 1000 ppm $\text{NO} + 10\% \text{ O}_2$ (solid grey curve). (b) XANES showing the reducing capability of 1200 ppm NH_3 (solid blue curve), 1000 ppm NO (solid orange curve) and a mixture of 1200 ppm NH_3 with 1000 ppm NO (solid red curve) on the $\text{Cu}(\text{II})$ state obtained after initial oxidation in a mixture of 1000 ppm NO and $10\% \text{ O}_2$ (dashed black curve). (c) Fourier-transformed EXAFS after exposure of dehydrated Cu-SSZ-13 to 1000 ppm NO_2 (solid green curves), and to a mixture of 1000 ppm NO and $10\% \text{ O}_2$ (dashed black curve) together with the structural model of the bidentate $\text{Cu}-\text{NO}_3^-$ species forming at these conditions.

References

- [1] (a) S. Brandenberger *et al.*, *Catal. Rev.* **2008**, 50, 492; (b) U. Deka *et al.*, *ACS Catal.* **2013**, 3, 413; (c) A. M. Beale *et al.*, *Chem. Soc. Rev.* **2015**, doi: 10.1039/c5cs00108k.
- [2] (a) F. Giordano *et al.*, *J. Phys. Chem. Lett.* **2014**, 5, 1552. (b) E. Borfecchia *et al.*, *Chem. Sci.* **2015**, 6, 548; (c) T. V. W. Janssens *et al.*, *ACS Catal.* **2015**, 5, 2832.

Experiment Report Form

	Experiment title: The structural and electronic configuration of Cu active sites in Cu-SSZ-13 and Cu-ZSM-5 under SCR conditions: a combined operando XAS and XES study. <i>Part 2 – Measurements on ID26</i>	Experiment number: CH-4080
Beamline: ID26	Date of experiment: from: 10/06/2014 to: 14/06/2014	Date of report:
Shifts: 12	Local contact(s): Kristina Kvashnina	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Filippo Giordanino ^{1*} , Prof Alexander Soldatov ³ , Andrea Lazzarini ¹ , Kirill Lomachenko ^{1,3*} , Prof. Carlo Lamberti ^{1,3*} , Prof. Silvia Bordiga ^{1*} , Dr. Elisa Borfecchia ^{1*} , Pablo Beato ⁴ , Anna Puig-Molina ^{4*} ¹ Department of Chemistry, NIS Centre of Excellence, INSTM Reference Center, University of Turin, Turin, Italy ² European Synchrotron Radiation Facility (ESRF), Grenoble, France ³ Research Center for Nanoscale Structure of Matter, Southern Federal University, Rostov-on-Don, Russia ⁴ Haldor Topsøe A/S, Kgs. Lyngby, Denmark		

Report:

The XANES and EXAFS data collected at the BM23 beamline for the Cu-CHA catalyst monitored during O₂- and He-activation processes, as well as in SCR-relevant conditions, (see above, CH-4080 report – *Part 1*) were subsequently complemented with HERFD XANES and XES characterization at the ID26 beamline. Remarkably, here we mounted and successfully exploited the same gas-flow set-up employed at BM23 integrated with the MICROTOMO reactor cell, as in previous experiment CH-3796. The overall experimental arrangement demonstrated an excellent stability and control of the measure conditions, allowing for high-statistics data collection with quite prolonged acquisition times (> 6 h).

At ID26 we monitored the Cu-CHA catalyst using TFY/HERFD XANES (~ 3 min time resolution) and Kβ_{1,3} and Kβ_{2,5} emission spectra collected under the same experimental conditions previously investigated at BM23, *i.e.* hydrated form, activation process at 400 °C in O₂- and He-atmosphere and selected SCR-relevant states, at different temperatures in the 150 °C-400°C range.

Importantly, no radiation damage effects were observed for the considered experimental conditions even after prolonged exposure of the Cu-zeolites samples to the X-ray beam. Nevertheless, in a specific case, *i.e.* while probing with the intense ID26 undulator beam the effect of NH₃ on the O₂-activated catalyst at 200 °C (containing a majority of Cu(II) sites), we observed a significantly increased formation of linear Cu(I) species with respect to what observed while measuring at the BM23 beamline. Indeed, the major contribution to XANES spectra collected on BM23 was represented by Cu(II)-tetrammino complexes, with a minor contribution from the Cu(I)-diammino moieties. The presence of a correlation between the incoming flux and the the Cu(II) → Cu(I) reduction kinetics was assessed by collecting HERFD XANES in exactly the same experimental conditions but using a progressive numbers of attenuators. Further studies will be conducted to clarify this interesting effect, where a very high photon flux seems to facilitate Cu site reduction.

Fig. 2 summarizes the HERFD XANES and XES data collected during experiment CH-4080 on the O₂- and He-activated Cu-CHA catalyst. These data, after a thorough DFT-assisted simulation work, played a key role in understanding the nature and location of the most abundant Cu sites in the activated material [1a].

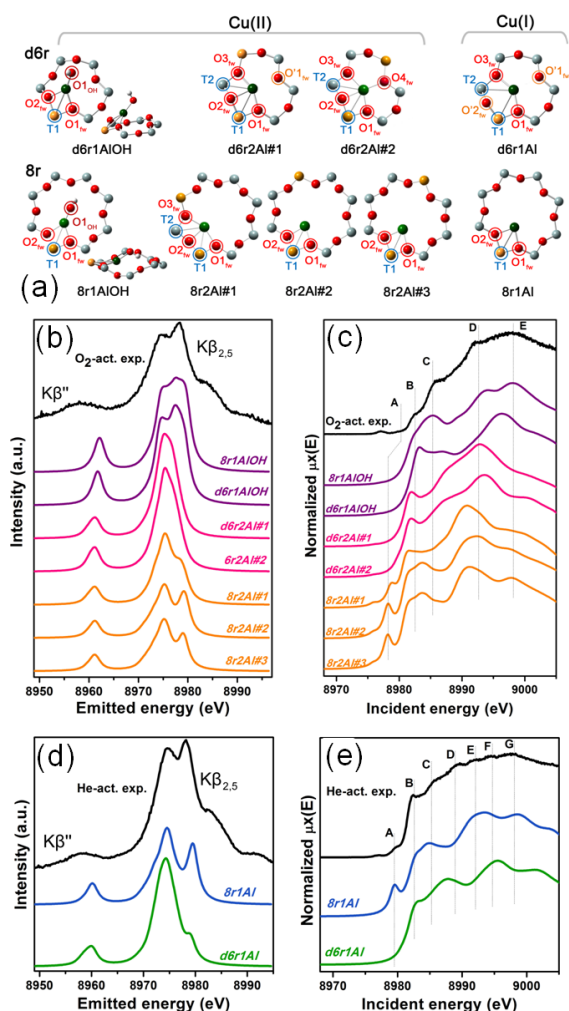


Fig.1. DFT-optimized structures (a) highlighting the local coordination environment of Cu(II) and Cu(I) sites in the d6r and 8r units of the CHA framework, and comparison between experimental XES and HERFD XANES spectra and simulated ones, obtained from structures in (a), for the Cu-CHA dehydrated catalyst after O₂-activation, parts (b,c), and He-activation, part (d,e).

Remarkably, looking at the HERFD XANES of the He-activated material, the 1s → 3d peak can still be observed suggesting a residual contribution of oxidized Cu(II) species as well. However, their amount should be rather low, since the peak is so weak that it is visible only in the high-resolution mode due to a very low background, and completely absent in the conventional XANES spectrum. XES and HERFD XANES data supported the findings of DFT and EXAFS. The performed simulations suggested that copper is more likely to dwell in the larger 8-membered ring cavities than in smaller 6-membered rings. Likewise, the formation of [CuOH]⁺ complexes is favored in the case of the activation in O₂ compared to the alternative of “bare” Cu²⁺ ions in the rings that contain two Al atoms. Despite the fact that the aforementioned presence of many rather different Cu species in the material worsens the agreement of the simulated XES and XANES spectra with the experimental, these methods proved to be an invaluable complement for the EXAFS and DFT data, which is particularly important when studying such complex systems like Cu-CHA.

Moreover, during the beamtime, the high-Cu-loading Cu-CHA sample was monitored both sending separate mixtures

of reactants (NO+O₂, NH₃+NO, NH₃) and the complete standard SCR conditions (flow of 500 ppm NO/500 ppm NH₃/10 % O₂/5% H₂O) at 400, 300 and 150°C. TFY/HERFD XANES was used to monitor sample evolution, while the catalyst was characterized by longer XES acquisition once stabilization of the spectral features was reached. DFT-assisted simulations and data analysis is currently in progress. These are expected to provide novel insights on the NH₃-SCR mechanism [1b], complementing the XAS results reported before. Figure 2 reports a selection of the XES data collected during experiment CH-4080.

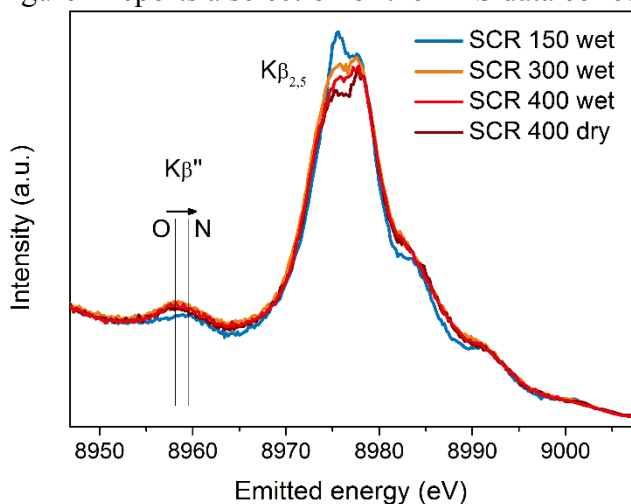


Fig.2. Cu valence-to-core XES of Cu-CHA catalyst under SCR conditions at different temperatures. At 400 °C the sample was measured also in “dry” SCR conditions, that is without water in the gas feed. Blue-shift of Kβ'' satellite at 150 °C indicates the formation of Cu–N bond.

The good data quality achieved for these *in situ* XES measurements together with the stability and robustness of the whole gas system (including the mass-flow controllers and the mass spectrometer) sets a favourable ground for a future experiment aiming at investigating the effect of composition tuning (Cu/Al and Si/Al ratios) on Cu-speciation in the Cu-CHA catalyst, for the dehydrated material, in SCR conditions at selected

temperatures. In particular, monitoring the Kβ'' peak (at ca. 8960 eV) in our XES spectra, we will achieve improved sensitivity on Cu ligands, allowing e.g. to discriminate atomic neighbours with similar Z [2], such as O and N [1c], which is hardly possible with EXAFS, especially in *operando* conditions with high-T collection.

References

- [1] (a) E. Borfecchia *et al.*, *Chem. Sci.* **2015**, 6, 548; (b) T. V. W. Janssens *et al.*, *ACS Catal.* **2015**, 5, 2832. (c) F. Giordanino *et al.*, *J. Phys. Chem. Lett.* **2014**, 5, 1552.
- [2] P. Glatzel, and U. Bergmann, *Coord. Chem. Rev.* 249 (2005) 65-95.