

Experiment Report Form



Experiment title: The electronic structure of Cu-based molecular complexes hosted inside zeolite-frameworks: an in-situ XAS and XES study

Part 1: measurements at BM23

Experiment number:
CH-3796

Beamline: BM23	Date of experiment: from: 10/04/13 to: 15/04/13	Date of report: <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Olivier Mathon	

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Report:

Cu-exchanged zeolites [1] are attractive candidates for removal of hazardous NO_x gas compounds from the exhaust of lean-burn engines *via* selective catalytic reduction (SCR) using ammonia as reducing agent [2]. Experiment CH-3796 was devoted to monitoring the structural and electronic features of the Cu-active sites in the copper exchanged SSZ-13 and ZSM-5 zeolites with a combined XAS/XES strategy, exploiting the capabilities of the BM23 and ID26 beamlines of the ESRF. Hereinafter we report on the first part of the experiment, performed at BM23.

Figure 1a shows a scheme of the employed flow set-up, and its implementation in combination with the Microtomo reactor cell at BM23. It consists of the three main channels, each of them connected with stainless tubes to gas bottles with different content; the mass flow controller system allows to set the total flow rate and the composition of the reactor feed. For sake of security, each flow channel could be easily switched to venting by means of the dedicated valves. The gas composition of the outlet gas from the reactor is continuously monitored by means of a mass spectrometer.

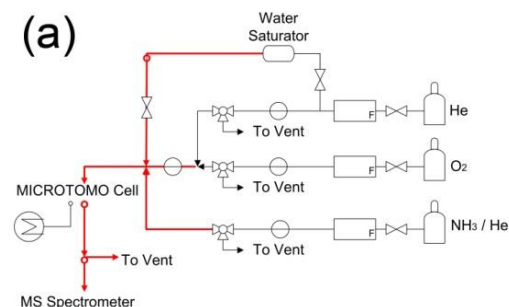


Figure 1 Experimental set-up for preliminary *operando* characterization employed in CH-3796. (a) Scheme of the flow set-up; (b) view of the gas-flow systems connected to the Microtomo reactor cell during experiments at BM23.

The system described above is very flexible, and it would be particularly suitable to monitor the real-time sample evolution in SCR conditions. In experiment CH-3796 we employed this setup to investigate and compare the two Cu-exchanged zeolites over different experimental conditions, including: i) hydrated as-such form; ii) activation process at 400 °C in O₂-atmosphere, *i.e.* lean conditions; iii) interaction of the activated samples with the reducing agent of the SCR reaction, *i.e.* NH₃ at 100 °C.

Data collection at BM23 included high-quality Cu K-edge XANES and EXAFS spectra (acquired in transmission mode) analyzable up to $k = 12 \text{ \AA}^{-1}$, with a time resolution of $\sim 12 \text{ min}$ while increasing the temperature and/or sending reagents in the gas phase. Higher statistics EXAFS spectra were also collected in steady-state conditions for the key-steps. A selection of the acquired data is reported in Figure 2. For both the hydrated Cu-zeolites, XANES features closely resembles that observed for aqueous Cu^{2+} ions [3]. Here, EXAFS fitting for Cu-CHA confirmed a square-planar Cu coordination, with 4 first shell Cu–O(H_2O) bonds of $(1.959 \pm 005) \text{ \AA}$, in good agreement with the recent literature [4,5]. Interestingly, the fit is improved considering a minor framework (fw) contribution at bond distances $> 2.5 \text{ \AA}$, despite the shielding effect due to the hydration shell. The gas-flow setup allowed us to appreciate the evolution of the XANES and EXAFS features during the activation in the Microtomo cell (gray spectra in Figure 2, each acquired in correspondence with a temperature variation of $\sim 35 \text{ }^\circ\text{C}$). XANES spectra reveal no substantial self-reduction of the Cu^{2+} centers after activation, as demonstrated by the persistence of the Cu(II) $1s \rightarrow 3d$ transition at $\sim 8977 \text{ eV}$ [5]. However, their significant modification suggests a strong perturbation in the Cu local coordination geometry/symmetry, consistent with the Cu coordination to the O(fw) upon dehydration. Correspondently, EXAFS spectra highlight a progressive lowering in the first-shell intensity, paralleled by the definition of a pronounced second shell in the 2–3 \AA R-range (phase uncorrected). Quantitatively, for activated Cu-CHA, we obtained a robust first-shell fit with three equivalent Cu–O(fw) bonds at $(1.926 \pm 0008) \text{ \AA}$. Among the configurations tested so far, the best fit up to 3 \AA was then obtained adding SS contributions from one O(fw) and two Si(fw) atoms, located at $(2.60 \pm 0.08) \text{ \AA}$ and $(2.67 \pm 0.04) \text{ \AA}$ from the Cu-centre, respectively. These results support the preferential location of Cu^{2+} ions in the $d6r$ ring of the SSZ-13 fw upon activation.

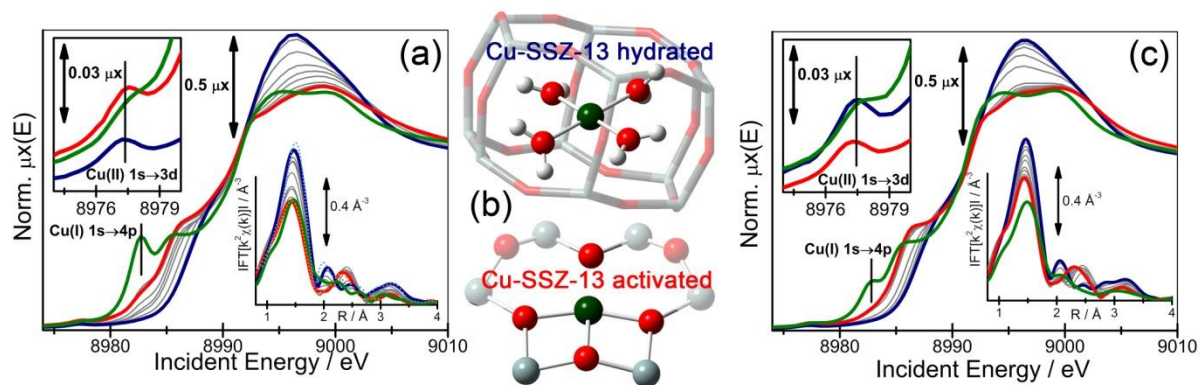


Figure 2. Summary of XAS characterization on Cu-zeolites performed at BM23 during CH-3796 experiment. Spectra color code: blue: hydrated sample; gray: evolution during activation; red: activated sample at $400 \text{ }^\circ\text{C}$; green: interaction with NH_3 at $100 \text{ }^\circ\text{C}$. (a) XANES and EXAFS data collected for Cu-SSZ-13; The EXAFS $|\text{FT}[k^2\chi(k)]|$ function are reported in the right inset, with preliminary fits for the hydrated and activated conditions, plotted as light blue and orange dotted lines, respectively. (b) Structural models obtained from preliminary interpretation of the data in part (a); atom color code: Cu green; O red; H white; Si gray. (c) As (a) for Cu-ZSM-5.

Upon interaction with NH_3 , for both the Cu-zeolites a significant fraction of the Cu-centers is reduced to Cu^+ , as evidenced by the strong pre-edge peak at $\sim 8982.7 \text{ eV}$, assigned to the Cu(I) $1s \rightarrow 4p$ transition. Furthermore, we observed the growth of an additional peak in the white line region ($\sim 8995 \text{ eV}$), previously associated to NH_3 coordination to Cu sites [5]. The EXAFS spectra of both the NH_3 -contacted Cu-zeolites are characterized by a less defined second shell, suggesting a reduced fw contribution, likely upon coordination of one (or more) NH_3 molecules. Quantitative EXAFS fitting is currently in progress, as well as simulation of the XANES spectra assisted by DFT-based calculations. Due to the difficulty of the EXAFS technique in distinguishing O(fw) and N(NH_3) neighbors, more insights with respect to the Cu-coordination environment in presence of NH_3 are expected from XES characterization (see CH-3796 report – Part 2).

References:

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- [2] (a) S. Brandenberger *et al.*, Catal. Rev. 50 (2008) 492-531; (b) D.W. Fickel *et al.*, J. Phys. Chem. C 114 (2010) 1633-1640; (c) S. Roy *et al.*, Appl. Ener. 86 (2009) 2283-2297.
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- [5] (a) Bordiga *et al.*, Chem. Rev. 113 (2013) 1736-1850; (b) U. Deka *et al.*, J. Phys. Chem. C 116 (2012) 4809-4818.

Experiment Report Form



Experiment title: The electronic structure of Cu-based molecular complexes hosted inside zeolite-frameworks: an in-situ XAS and XES study.

Part 2: measurements at ID26

Experiment number:
CH-3796

Beamline: ID26	Date of experiment: from: 03/07/13 to: 09/07/13	Date of report:
Shifts: 18	Local contact(s): Erik Gallo	<i>Received at ESRF:</i>

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Report:

The XAS data collected at the BM23 beamline for Cu-SSZ-13 and Cu-ZSM-5 in the first part of experiment CH-3796 (see CH-3796 report – Part 1: measurements at BM23) were subsequently complemented with a XES-RIXS characterization at the ID26 beamline. Remarkably, here we mounted and successfully exploited the same gas-flow set-up initially tested at BM23, integrated with the Microtomo reactor cell (see Figure 1). 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).

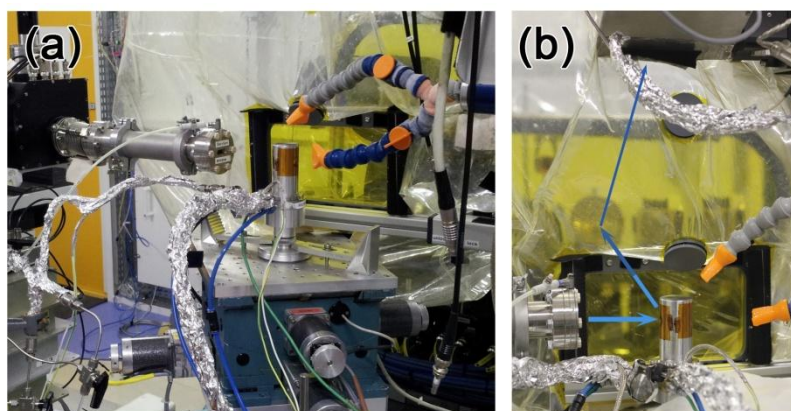


Figure 3 (a) Experimental set-up based on the Microtomo reactor cell for preliminary *operando* XAS/XES characterization of Cu-zeolites mounted in the experimental hutch of ID26 during the second part of experiment CH-3796. (b) Optical path of the X-ray during the measurements: source – sample cell – analyzer crystal – APD detector. Darker arrows correspond to the path inside the helium bag. See CH-3796 report – Part 1 for a more detailed description of the gas-flow system.

At ID26 we monitored the evolution of the Cu-SSZ-13 and Cu-ZSM-5 zeolites using TFY/HERFD XANES (~ 3 min time resolution), $K\beta_{1,3}$ and $K\beta_{2,5}$ emission spectra and $K\beta_{1,3}$ RIXS maps collected under the same experimental conditions previously investigated at BM23, *i.e.* hydrated form, activation process at 400 °C in O₂-atmosphere and interaction of the activated samples with NH₃ at 100 °C. Importantly, no radiation damage effects were observed for none of the considered experimental conditions even after prolonged exposure of the Cu-zeolites samples to the X-ray beam.

Figure 2 summarizes the collected RIXS and XES experimental data. Similarly to the XANES results, XES and RIXS of Cu-SSZ-13 resemble those of Cu-ZSM-5 acquired under the same experimental conditions, which indicates the similarity of the closest coordination of Cu atom in the two compounds. $K\beta''$ peak in the XES spectra, located around 8960 eV, is sensitive to the ligand environment of the absorber, since it arises from the transition between oxygen or nitrogen 2s orbitals and Cu 1s core level [1]. Due to the fact that the 2s binding energy of nitrogen is lower than the one of oxygen, the peak is blue-shifted for NH_3 -treated sample. Quantitative conclusions will be possible after DFT simulations, which will make the XES data highly complementary to EXAFS analysis, since the latter does not allow to unambiguously discriminate the signals from N and O.. In a similar way, the collected RIXS maps complement the conventional XANES data revealing more detailed information on the pre-edge region since not only the empty states, but also the occupied ones are probed [2],[3].

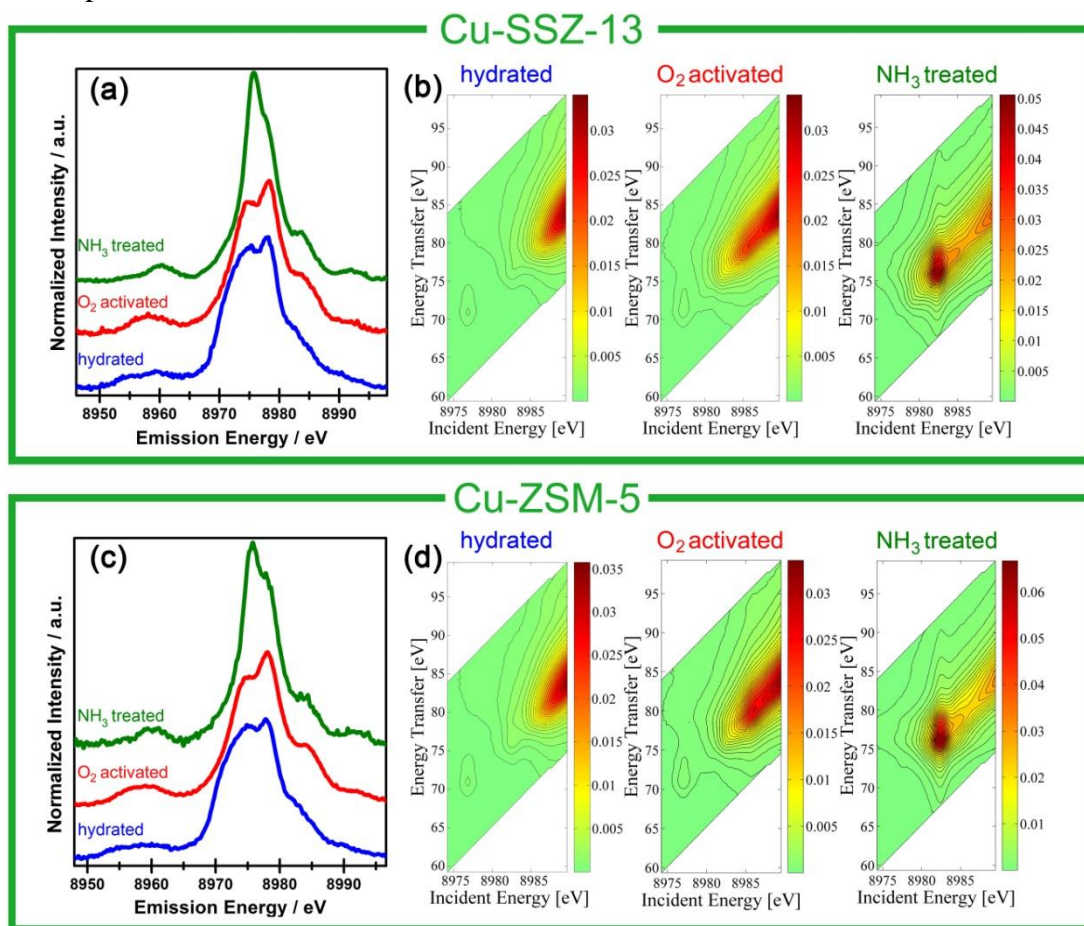


Figure 2 Selected RIXS/XES results obtained at ID26 during CH-3796 experiment. (a) Background-subtracted Cu $K\beta_{2,5}$ XES of hydrated Cu-SSZ-13 (blue curve), activated in O_2 at 400 °C (red curve) and in NH_3 flow at 100 °C (green curve). Spectra are shifted along vertical axis for the sake of clarity; (b) Cu $K\beta_{1,3}$ RIXS maps of hydrated Cu-SSZ-13 (left), activated in O_2 at 400 °C (center) and in NH_3 flow at 100 °C (right); (c) same as (a) for Cu-ZSM-5; (d) same as (b) for Cu-ZSM-5.

Moreover, during the beamtime several test measurements in standard SCR conditions (flow of 500 ppm NO/500 ppm NH_3 /10 % O_2 /5% H_2O) were performed for both samples. The goal was to check the feasibility of the *operando* experiment suggested in our new proposal (Ref. No 33552) tuning the gas-flow set-up and controlling the quality of the data. Preliminary results show that the expected differences in the spectra are observable and well-resolved. The whole gas system including the mass-flow controllers and the massspectrometer was functioning well, which sets the favourable ground for the following experiment.

References:

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- [2] P. Glatzel *et al.*, Catal. Today 145 (2009) 294-299.
- [3] J. Singh, C. Lamberti, J.A. van Bokhoven Chem. Soc. Rev. 39 (2010) 4754-4766.