

Experiment Report Form



Experiment title: Structure-activity relationship in the deNO_x Cu-CHA catalyst: exploring the effect of composition tuning by HERFD-XANES and XES.

Experiment number:
CH-4960

Beamline: ID26	Date of experiment: from: 02/11/2016 to: 08/11/2016	Date of report: 06/03/2017
Shifts: 18	Local contact(s): Rafal Baran	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

NH₃-assisted selective catalytic reduction of NO_x (so called NH₃-SCR) is one of the most efficient ways to remove environmentally harmful nitrogen oxides (NO, NO₂) from the exhaust of lean-burn engines [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.

Recently Paolucci *et al.* have employed experiment in conjunction with *ab initio* approaches to correlate the composition parameters in Cu-CHA and different types of Cu-sites formed after dehydration and in SCR-relevant conditions [2]. It was suggested that during dehydration Cu(II) ions first populate 2Al sites in the six-membered rings (6r) of the CHA framework, because they are considered as the most energetically favored exchange sites for “naked” Cu(II) ions. When this lowest-energy sites are saturated, Cu cations are stabilized in proximity of isolated 1Al sites as redox-active complexes, representing the dominant coordination environment at high Cu-loading. Consistently with previous reports [3,4] during SCR at 200 °C *operando* XANES revealed the presence of a 50/50% Cu(I)/Cu(II) mixture. To confirm these theoretical results the experiment CH-4661 on BM23 was performed with Cu-CHA samples of different composition: Cu:Al/Si:Al = 0.47/15; 0.13/14; 0.56/19; 0.56/29; 0.5/5; 0.1/5. We performed *in situ/operando* measurements collecting XANES/EXAFS data for this set of samples.

The experiment CH-4960 at ID-26 was aimed to investigate local environment of active Cu-species as a function of material composition (different value for Cu:Al and Si:Al) by HERFD XANES and valence-to-core XES under conditions previously employed at BM23, i.e. hydrated form, activation process at 450 °C in He atmosphere and selected SCR-relevant states at different temperatures in the 150°C - 400°C range.

We used 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, CH-4080 (see also CH-4796, CH-4080 Experimental Report). We used cryogenically-cooled fixed-exit double-crystal Si (311) monochromator with $\Delta E/E = 0.3 \times 10^{-4}$ eV. For fluorescence yield detection with high energy resolution we used emission spectrometer equipped by four spherically bent analyzer crystals. We have performed fast XANES measurements (time resolution 3min/scan) for activation, cooling and stabilization under SCR feed and long XES acquisitions (~ 1 h) for steady states after activation and during SCR at 400 °C and 150 °C.

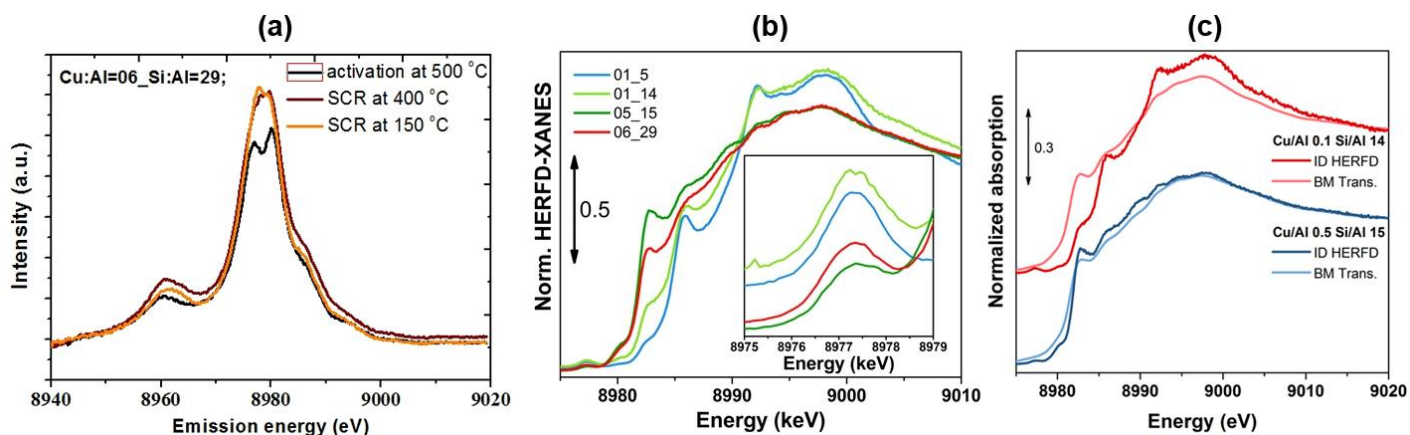


Figure 1 (a) Cu $K\beta_{1,3}$ and $K\beta_{2,5}$ emission spectra collected after activation in O_2+He and under SCR conditions at 400 °C and 150 °C for high-loading sample Cu:Al = 0.6 and Si:Al = 29; (b) HERFD XANES Cu K-edge spectra obtained for the activated in O_2+He samples with different Cu:Al and Si:Al ratios; (c) Comparison Cu K-edge XANES spectra collected at bending magnet (BM) beamline in transmission mode and at undulator beamline (ID) in high energy resolution fluorescence detection mode for high-loading Cu:Al = 0.5 and low-loading Cu:Al=0.1 Cu-CHA samples.

In the Figure 1a XES data for the high-loading Cu:Al=0.6 and high Si:Al ratio are presented. The same set of data were obtained for all the samples with different stoichiometry under study. Figure 2b shows HERFD XANES Cu K-edge spectra for activated states of all samples. It was clearly revealed that composition of Cu-CHA has strong effect on the local environment of Cu ions in the activated material. It means that we form different Cu-species for different stoichiometry and high-resolution XANES makes differences in the spectra more pronounced. We have observed intensive peak related with Cu(I) 1s-4p transition for high-loading samples Cu:Al=0.5 and Cu:Al=0.6, while increasing intensity of pre-edge peak related with 1s-3d transition for low-loading Cu:Al=0.1 samples can be considered as a robust evidence of Cu(II) species formation.

However, Figure 1c shows that XANES collected in high energy resolution fluorescence detection mode for low-loading sample with Cu:Al=0.1 and Si:Al = 14 is completely different compared with the previous measurements at BM23 in transmission mode. We assumed that in our experiment we have observed, that under intense undulator beam in Cu-CHA sample with low copper loading Cu ions relocate to a different site inside CHA pores compared to the case when they are probed by much less intense bending magnet radiation. From our previous studies we can unambiguously identify that the one measured at BM is typical for the dominant fraction of Cu(I) species coordinated to 1Al site, while the HERFD data which lack intensity in the low-energy edge region evidence the formation of Cu(II) at 2Al sites. This might indicate, that under intense X-ray beam the Cu ions can migrate inside the CHA cavities to energetically more favorable sites and undergo a change of oxidation state. The effect which was observed can be interesting for further investigation of Cu-species in Cu-CHA in particular and the influence of intense X-ray light on chemical processes in general. Therefore, a dedicated proposal aimed to shed light on this “site-flip” phenomena will be submitted in one of the next rounds.

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