

Experiment Report Form



	Experiment title: Investigating the nitrate-mediated limiting step in the SCR pathway by operando XAS/DRIFT	Experiment number: CH-5561
Beamline: BM23	Date of experiment: from: 24/10/2018 to: 30/10/2018	Date of report: 31/01/2020
Shifts: 18	Local contact(s): Dr. Kirill A. Lomachenko	<i>Received at ESRF:</i>
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Report:

The Selective Catalytic Reduction with ammonia (NH₃-SCR) reaction is the state-of-the-art technology to abate NO_x emissions from lean burn heavy-duty and passenger car vehicles. Currently, Cu-exchanged chabazite zeolites (Cu-CHA) are the catalysts of choice, with a good performance over a wide range of temperatures.[1] Notwithstanding many in-depth studies about the nature and location of Cu^{II} (present as a mixture of Z[Cu^{II}(OH)]/Z[Cu^{II}(O₂)]⁺ and Z₂Cu^{II}, where Z represents a framework negative charge) and Cu^I sites [2], some aspects of the NH₃-SCR mechanism over Cu-CHA are still debated. A kinetically relevant step is activation of O₂, necessary to re-oxidize Cu^I to Cu^{II}. This has been proposed to be mediated by NO, and to involve solvated [Cu^I(NH₃)₂]⁺ pairs, forming [Cu₂(NH₃)₄O₂]²⁺ mobile complexes.[3] These dimeric Cu moieties are proposed to be responsible for the low temperature catalytic performances as well as for the loss in activity on the 250-350 °C range, ascribed to their thermal instability. On the other side, the possible role played by different Cu^{II}-(N,O) species (Cu-nitrate and Cu-nitrite, formed by reaction with NO/O₂ and/or NO₂) and their reactivity with NO and NH₃ in the low-temperature regime, relevant for the performance in the cold start of diesel engines, is still an intriguing research playground.[4]

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. To shed some light on the debated topic, we performed the experiment CH-5561 on BM23, studying a series of Cu-CHA samples of different composition: Cu:Al/Si:Al = 0.1/5; 0.5/15; 0.6/29. These samples were already being characterized in terms of Cu location and local environment in various experiments at BM23, ID24 and ID26 (CH-4661 on BM23, CH-5289 on ID24 and CH-4960 on ID26). The acquired detailed knowledge on Cu speciation as a function of sample composition allowed us to deeply investigate some selected SCR-relevant states at different temperatures in the 50°C - 400°C range. We performed *in situ/operando* measurements collecting XANES/EXAFS data for this set of samples.

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 several previous experiments (see also CH-4796, CH-4080 Experimental Reports). Cu K-edge XAS measurements were performed in transmission mode, employing a double-crystal Si(111) monochromator for the incident energy scan and ionization chambers to detect incident and transmitted photons. We have performed XANES measurements (time resolution 6 min/scan) during activation, cooling and stabilization under the applied reaction conditions (different percentage of the SCR reactants) and longer acquisitions (~30 min/scan) in order to obtain higher quality EXAFS data for steady states after activation and at selected key states at 200 °C and 50 °C.

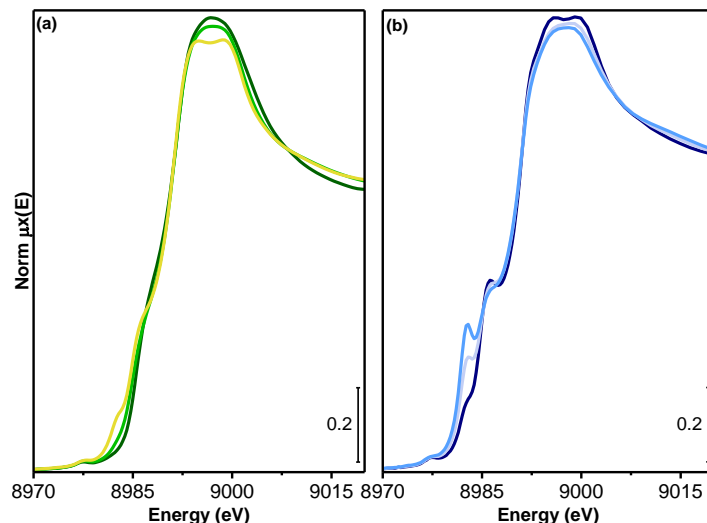


Figure 1 (a) *Operando* XANES Cu K-edge spectra of Cu-CHA15_05 during NO/NH₃ interaction (green: intermediates; yellow lines: final state) after equilibration in NO/O₂ (dark green curve). (b) *Operando* XANES Cu K-edge spectra of Cu-CHA5_01 (dark blue), Cu-CHA15_05 (grey) and Cu-CHA30_06 (blue curve) exposed to O₂/He at 200 °C after reduction in NO/NH₃/He at 200 °C.

Figure 1a presents the evolution of the XANES spectra upon exposure of Cu-nitrate species (highlighting a virtually pure Cu^{II} oxidation state, dark green curve) in Cu-CHA15_05 to a NO/NH₃ feed, at 50 °C. We observe important modifications during the reaction (green and yellow lines in Figure 1a) as the intensity of the white-line peak at ca. 8997 eV progressively decreases, while evolving towards a characteristic broadened doublet shape. While most of the Cu ions remain in the Cu^{II} oxidation state, a very minor Cu^I contribution become appreciable (< 10% total Cu) through the development of a rising-edge shoulder at ca. 8982 eV. Noteworthy, at 200 °C under the same gas feed and pre-treatment conditions, the NO/NH₃ mixture has been shown to completely reduce Cu^{II}-nitrates to Cu^I species:[4c] it is clear that operation temperature strongly influences the reduction kinetics and the Cu^{II}/Cu^I ratio in the final state. These findings resulted in the recently published paper Negri *et al.*, *ChemCatChem* 2019, **11**, 3828, featured as a cover.

Figure 1b shows the XANES data of NO/NH₃-reduced Cu-CHA with different Si/Al and Cu/Al, obtained after the exposure to 10%O₂/He. The final state clearly differs among the three catalysts, demonstrating a different response to re-oxidation (depending on the Si/Al ratio and Cu speciation) and also the formation of different Cu complexes, as visible from the differences in the white line shape (dark blue vs grey and blue curve). We hypothesize that the reaction promotes the formation of the mobile [Cu₂(NH₃)₄O₂]²⁺ complex proposed in literature for the two sample with Si/Al=15 (grey curve) and Si/Al=30 (blue curve), as the spectra closely resemble each other; the higher residual amount of Cu^I in Cu-CHA30_06 is in good agreement with the Cu density reported in literature for this Si/Al ratio. On the contrary, the Cu-CHA5_01 spectrum is different both in the shape of the rising edge features, with a well defined Cu^{II} 1s → 4p at ~8986 eV, and in the shape of the white line, which closely resemble that of a four-coordinated Cu^{II} amino-complex. These results are of an outstanding quality and would be the basis of further studies on the topic, as well as of two papers which are currently in preparation. It would be of a great interest now to further investigate the reactivity of the so-formed mobile complexes, when exposed to the SCR feed. Therefore, a dedicated proposal on the topic will be submitted in one of the next rounds.

[1]Beale A.M., *et al.*, *Chem. Soc. Rev.* 2015, **44**, 7371.

[2]Borfecchia E., *et al.*, *Chem. Soc. Rev.* 2018, **47**, 8097.

[3]a)Gao F., *et al.*, *J. Am. Chem. Soc.* 2017, **139**, 4935. b) Paolucci C., *et al.*, *Science* 2017, **357**, 898.

[4]a)Ruggeri M.P., *et al.*, *Catal. Today* 2018, **307**, 48. b) Colombo M., *et al.*, *Catal. Today* 2012, **197**, 243. c) Janssens T.V.W., *et al.*, *ACS Catal.* 2015, **5**, 2832. d) Marberger A., *et al.*, *Nat. Catal.* 2018, **1**, 221.