



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: In situ sulphur poisoning and regeneration of Cu-CHA deNO_x catalysts

Experiment number:
CH-6181

Beamline: ID26	Date of experiment: from: 18/01/2022 to: 24/01/2022	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Detlefs Blanka Saveleva Viktoriia	
Names and affiliations of applicants (* indicates experimentalists): Anastasia Molokova* (ESRF) Kirill Lomachenko* (ESRF) Elisa Borfecchia (Laboratory Universita di Torino Dipartimento di Chimica) Gloria Berlier* (Laboratory Universita di Torino Dipartimento di Chimica) Andrea Martini (Laboratory Universita di Torino Dipartimento di Chimica) Silvia Bordiga (Laboratory Universita di Torino Dipartimento di Chimica) Ton Janssens (Laboratory Umicore Denmark ApS) Peter Vannestrom (Laboratory Umicore Denmark ApS) Fei Wen ((Laboratory Umicore Denmark ApS)		

Report:

Proposal summary:

Cu-exchanged chabazite zeolites (Cu-CHA) are efficient catalysts for NO_x removal from the exhaust gas of diesel vehicles, via the selective catalytic reduction of NO by NH₃ to N₂ and H₂O (NH₃-SCR). These catalysts show an unsurpassed low-temperature activity, but are also sensitive to SO₂. This limits the practical application as NH₃-SCR catalysts, since the small amount of sulphur in diesel fuel produces some SO₂, which significantly reduces the activity of Cu-CHA. The precise mechanism of this deactivation by SO₂ is unknown, but we have proof that SO₂ reacts very differently with different Cu species forming in the catalytic cycle. To understand the mechanism of deactivation we need to investigate resulting Cu-S species. In the first half of 2021, we will perform Cu K-edge XAS/XES experiments at BM23 and ID26 to shed light on the Cu side of the story (accepted proposal CH-5960). The necessary continuation of these experiments is the determination of the sulphur oxidation state and the local environment during the reaction in order to understand the interaction mechanism of Cu active sites with sulphur. **In this proposal, we want to determine which S complexes form during the interaction of SO₂ with different Cu intermediates of the SCR cycle in order to elucidate the role of the sulphur in the deactivation of Cu-CHA.** This requires *in situ* measurements of the oxidation state and local environment of the S ions under controlled conditions. HERFD-XANES at S K-edge is the best technique available to address these questions. This is a new approach to investigate the effect of SO₂ on Cu-CHA-based NH₃-SCR catalysts, to provide unique and crucial understanding of application of Cu-CHA catalysts in diesel exhaust systems

Experiment description

The idea of the experiment was to determine the oxidation state of S when Cu species forming in the Selective catalytic reduction (SCR) cycle interact with SO₂. Considering the results of CH-5960, we chose three Procedures with the most representative results. The Cu-CHA catalyst was activated in 10% O₂/He at 550 °C and then exposed to different gas compositions to get active Cu sites with different oxidation states and local environment (Procedures 1,2,5, Table 1). The experimental plan included three different pre-treatment procedures each ensuring the preferential formation of one of the

key intermediates of the SCR reaction indicated in the table. After the pre-treatment each sample was exposed to SO₂ for 3 hours at 200°C, and then regenerated in the flow of He by heating it up to 550°C. The measurements were conducted in flow conditions using an ESRF vacuum catalyse cell, compatible with the desired temperatures and gas compositions, and suitable for using in the Tender X-Ray Spectrometer (TEXS) at ID26. A mass spectrometer was used to monitor the effluent gas from the cell. During the interaction of the catalyst with SO₂ X-ray absorption spectra were measuring to track the evolution of the S oxidation state. After the stabilization of the spectra XES was measured to monitor the local geometry of S atoms.

Table 1. Experimental procedures details

Proc. number	Gas composition and conditions	Cu sites obtained
1	NO and NH ₃	[Cu ^I (NH ₃) ₂] ⁺ complex
2	As activated	Cu ^{II} -framework coordinated
5	Exposure to NO and NH ₃ , and then to 10% O ₂ /He	[Cu ^{II} ₂ (NH ₃) ₄ O ₂] ²⁺

We measured a sample with Cu content: 3.2 wt% (Cu_CHA_68E). Also we took the sample with the same Cu content pre-sulfated (pre-S) by the industrial partner (Umicore) and ran two deSO_x procedures (in O₂ and in O₂ + H₂O) on it to compare the state of sulfur in case of the *in situ* sulfation at the ESRF and *in situ* sulfation at the industry.

Results and discussion

We performed 3 Procedures listed in the Table 1 and measured S K-edge XANES during exposure the sample to SO₂, and S K-alpha XES at the end of the sulfation (Fig 1-4).

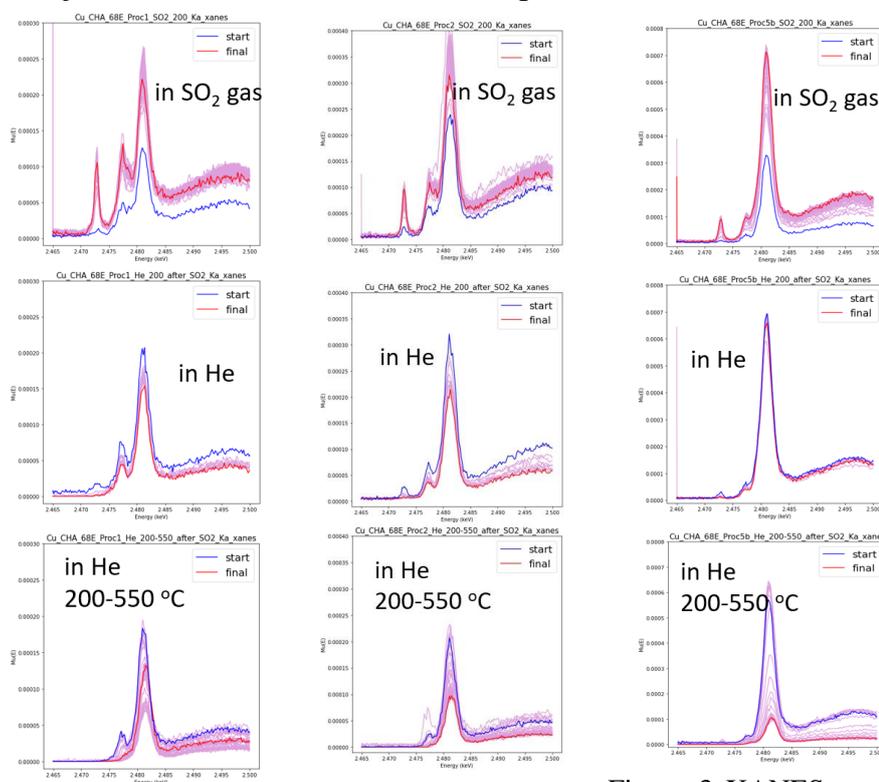


Figure 1 XANES spectra of the sample Cu_CHA_68E during exposure to SO₂ after pre-treatment procedure 1.

Figure 1 XANES spectra of the sample Cu_CHA_68E during exposure to SO₂ after pre-treatment procedure 2.

Figure 3 XANES spectra of the sample Cu_CHA_68E during exposure to SO₂ after pre-treatment procedure 5.

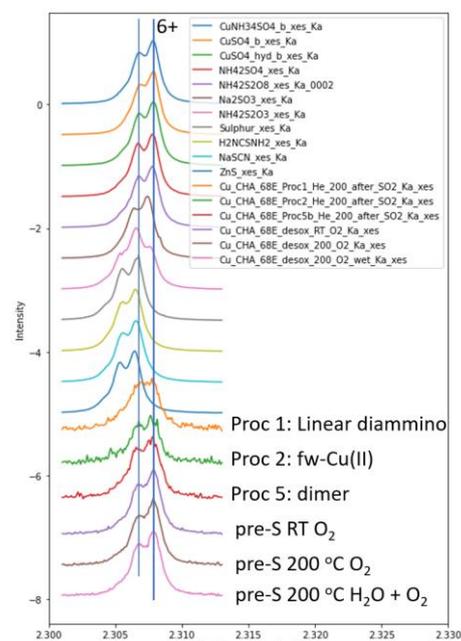


Figure 4 S K-alpha XES of a set of references containing S with different oxidation states and coordinations, S K-alpha XES of Cu_CHA_68E after sulfation in Procedures 1, 2, 5, and S K-alpha XES of pre-sulfated samples.

Conclusions

- 1) The experiments provided the first *in situ* characterisation of sulphur species formed during the poisoning of the active Cu sites of Cu-CHA catalysts
- 2) We found that in all our *in situ* sulfations and in the industrial sulfation the oxidation state of S is +6, XANES and XES spectra are similar to those that we have for references with SO₄ groups.