EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.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 form 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.

ESRF	**Experiment title: In situ sulphur poisoning and regeneration of Cu-CHA deNOx catalysts**	**Experiment number**: CH-6268
Beamline: BM23	**Date of experiment**: from: 21/07/2022 to: 27/07/2022	**Date of report**:
Shifts: 18	**Local contact(s)**: Anastasia Molokova	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Peter Vannestroem (Laboratory Umicore Denmark ApS)

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Report:

Proposal summary:

Cu-exchanged chabazite zeolites (Cu-CHA) are excellent catalysts for NO_x removal from the exhaust gas of diesel vehicles, via the selective catalytic reduction of NO by NH_3 to N_2 and H_2O (NH_3-SCR). However, their low-temperature activity decreases after prolonged exposure to sulphur, ever-present in diesel fuel. In our recent *in situ* experiment (CH-5960) we proved that SO_2 actively reacts only with some particular SCR-relevant Cu intermediates, being virtually unreactive to others. Now, when the Cu species that are the most vulnerable to SO_2 are identified, we are prepared to face the challenge of determining the mechanism of Cu reactivity towards SO_2 under real SCR conditions. **In the proposed experiment we will reveal the mechanisms of sulphur poisoning and regeneration of Cu-CHA by characterising Cu complexes that form in Cu-CHA during interaction with SO_2 under *operando* SCR conditions.** This requires *operando* Cu K-edge XANES and EXAFS measurements for monitoring the electronic structure and local environment of active Cu centres during the adsorption and desorption of sulphur in presence of other components of the SCR mixture. Obtained results will be crucial to optimize regeneration procedures for the catalysts, increasing thus their efficiency.

Experiment description

The idea of the experiment was to expose the Cu-CHA catalyst to the SCR mixture at different temperatures and then add SO_2 to the mixture to observe the effect of SO_2 on the active Cu species in the real operando conditions. The Cu-CHA catalyst was activated in 10% O_2/He at 550 ℃ and then exposed to the SCR mixture (500 ppm NO, 600 ppm NH_3, 10% O_2, 4% H_2O). Then the sample was cooled down to one of the three temperatures: 200, 250, 500 ^oC. 200 and 250 ^oC correspond to the low-temperature SCR which is the main subject of our studies. We chose also 500 ^oC to compare the effect of SO_2 on the high-temperature SCR. After the state of Cu stabilized at the sertain temperature, we add SO_2 to the gas mixture to see the effect of it in the catalyst performance and on the oxidation state and local environment of Cu. The measurements were conducted in flow conditions using a new ESRF operando cell, compatible with the desired temperatures and gas compositions. A mass spectrometer was used to monitor the catalytic activity of the samples and quantity of sulphur uptake and relese. During the experimental protocol X-ray absorption spectra were measuring to track

the evolution of the Cu oxidation state and local environment. We measured a sample with Cu content: 3.2 wt% (Cu_CHA_68E).

Results and discussion

We performed operando SO_2 poisoning of the catalyst at three different temperatures (200, 250, 500 ^oC) and measured Cu K-edge XANES during exposure the sample to SO_2 (Fig 1-3).

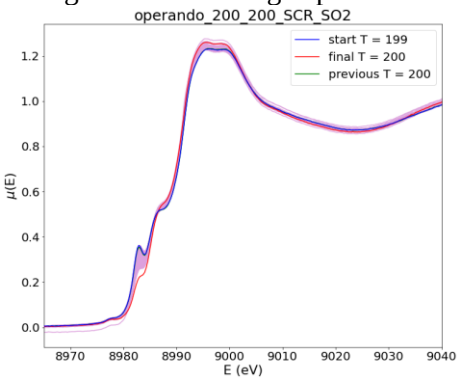

Figure 1 XANES spectra of the sample Cu_CHA_68E during exposure to SO_2 and the SCR mixture at 200 ^oC.

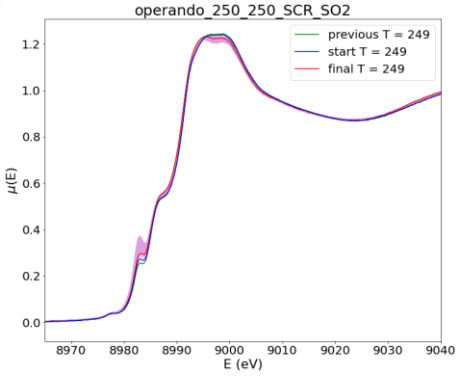

Figure 1 XANES spectra of the sample Cu_CHA_68E during exposure to SO_2 and the SCR mixture at 250 ^oC.

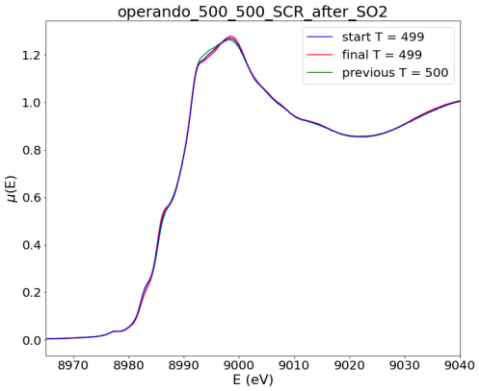

Figure 3 XANES spectra of the sample Cu_CHA_68E during exposure to SO_2 and the SCR mixture at 500 ^oC.

Conclusions

1) The experiments provided the first *operando* characterisation of suplhur species formed during the poisoning of the active Cu sites of Cu-CHA catalysts.
2) We found the Cu species forming during the SO_2 poisoning of the catalyst in operando conditions for the low-temperature SCR. The SO_2 for the high-temperature SCR does not have such a high impact on the performance and the Cu species participating in the reaction cycle are different.
3) The results will be further analysed with advanced mixture-resolving techniques such as principal component analysis (PCA) and multivariate curve resolution (MCR) to provide the full characterization of the SO_2 poisoning.