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:** Can operando valence to Core (V2C) X-ray emission spectroscopy identify the true nature of the active sites in copper containing zeolites in methane to methanol conversion?	**Experiment number**: CH4592
Beamline: ID26	**Date of experiment**: from: 18/04/2018 to: 22/04/2018	**Date of report**: 20/02/2020
Shifts: 12	**Local contact(s)**: Rafal Baran	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. J. A. van bokhoven, A. J. Knorpp*, Dr M. A. Newton*, Dr A. Pinar, ETH Zurich

Dr V. L. Sushkevich, Dr. G. Smolentsev, Paul Scherrer Institute

Report:

This work sought to use the valence to core (V2C) emission spectroscopy to establish the nature of the active Cu(II) oxo centres, present in high temperature activated copper ion exchanged mordenite (MOR), and mazzite (MAZ), which are responsible for the selective activation of methane within established step-wise approaches to the direct and selective oxidation of methane to methanol [1,2].

We are happy to report that we received excellent support from the local contact (Dr Rafal Baran) and the ID26 team and that all of the allocated shifts were effectively used. V2C data was successfully collected for Cu/MOR, both high and low loaded Cu/MAZ, and for a third system, Gmelenite (GME), under all the conditions required, that is to say, after activation to 723 K in flowing oxygen and under methane (reacted state) and 473 K.

The systems were specifically chosen to represent examples of Zeolite topologies that result, either in highly active systems (Cu/MOR and high loaded Cu/MAZ) or systems that show no activity at all within this type of stepwise approach to activation and reaction (low loaded Cu/MAZ and Cu/GME).

Whilst the beamline performed very well and the data of excellent quality it was noted that, especially after the exposure of methane to these systems at 473 K, the footprint of the X-ray beam could clearly be observed on the sample as black stripes (most likely due to carbon deposition as aresult of the X-ray indiced cracking of the methane). This being the case even when implementation of a rastering of the beam over many different sample positions was used to build up spectra. This approach has been developed on ID26 in order to minimize exposure of the sample at any given point and thereby minimizes the possibility of the powerful X-rays that the ID26 undulator produces may induce changes in the sample that are not the result of the chemistry but of the presence of the X-rays themselves.

Subsequent XAS studies made at SNBL (BM31) and SuperXAS (Swiss light source) have revealed that the flux, and specifically the power density of X-rays of similar energies (in and around the Cu K-edge), can have very considerable effects upon the apparent behavior of these materials once methane is introduced into the system. It has also latterly been found that in order to study these materials in a meaningful manner in the presence of methane, that the photon flux at SuperXAS has to be attenuated and then defocused as completely as possible (to reduce the applied power density by a factor of ca 1500).[3,4]

It seems likely therefore, give the evidence, that the measurements we have made under methane on the considerably more powerful ID26 source have been compromised in a similar manner.

However, this does not mean that the results obtained from the beamtime allocation for the activated systems maintained under oxygen – wherein no evidence of a distortion of the system is apparent- may not be successfully used to understand whether the V2C approach can in fact discriminate between active and inactive copper in these systems. That said, analysis/modelling of these results, to properly determine the nature of the active, and indeed inactive sites present, and are still on going.

References

[1] See for instance: (a) Vanelderen, et al., *J. Am. Chem. Soc*., **2015**, *137*, 6383 – 6392; (b) Grundner, S., et al., *Nat. Commun.*, **2015**, *6*, 7546; (c) Sushkevich, V. L. et al., *Science*, **2017**, *356*, 523 -527; (d) Pappas, D. K.et al., *J. Am. Chem. Soc*., **2018**, *140*, 15270-15278.
[2] (a) Knorpp, A. J., et al., *Catal. Sci. Tech*, **2019**, 9, 2806 – 2811; (b) Knorpp, A. J.; Pinar, A. B.; Newton, M. A.; Sushkevich, V. L.; van Bokhoven, J. A., *ChemCatChem*, **2018**, 10, 5593-5596; (c) Knorpp, Amy J.; et al., Chem. Commun., **2019**, 55, 11794 -11797
[3] *EBS workshop - Sample modulation by high photon densities: desired and undesired effects*: Mark Newton, **"**How to tame your beamline: Unwanted effects of X-rays in surface grafted copper (II) organometallics and copper exchanged zeolites, how they manifest, and what might be done about them?**"**
[4] Newton, M. A.; Knorpp, A. J.; Meyet, J.; Stoian, D.; Nachtegaal, M; Clark, A. H.; Safonova, O. V.; Emerich, H; van Beek, W.; Sushkevich, V. L.; van Bokhoven, J. A., **2020**, submitted to *Phys. Chem. Chem. Phys*.