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:** Investigating the high T/low pressure and low T/high pressure routes to conversion of methane to methanol using copper/mordernite and copper/Omega Zeolites using	**Experiment number**: Ch-5330
Beamline: ID15A	**Date of experiment**: from: 25/07/2018 to: 30/07/2018	**Date of report**: 20/02/2020
Shifts: 18	**Local contact(s)**: Stefano Checchia*	*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, Paul Scherrer Institute

Report:

This work sought to use the novel combination of time resolved PDF and DRIFTS available at ID15 to investigate structure function relationships in copper-zeolites that have proven extremely difficult to resolve using other methods. To wit, the unambiguous establishment of the structure (specifically the nuclearity [1]) of the copper species that are active for the direct and selective conversion of methane to methanol using two copper-zeolite systems, mordenite [2] and mazzite [3].

It is worthy of note that this was very much a collaborative exercise. Even before we attempted to make these measurements a good deal of ground work was done by the main proposer and Dr Stefano Checchia (local contact for the experiment) in characterizing aspect of the DRIFTS set up, which itself is the product of a collaboration between the ESRF and the APS. [4] This sort of chemistry is extremely sensitive to numerous aspects of sample presentation, and specifically the accurate measurement of the sample temperature and any gradients that might exist with the sample bed.

Our studies, therefore, made extensive use of the resources available to ID15 at the ESRF: particularly, an infrared camera (Simon Benichou, ISDD) for imaging of the sample surface temperature, and then a diffraction based method for assessing the actual temperature of the sample being probed (Stefano Checchia, ID15A and Dimitry Chernyshov, SNBL-BM01). We then characterized, as best as possible, the thermal profile of the DRIFTS cell used. The results of these exercises and complementary others made on SNBL resulted in a publication on their own ([5], selected as one of the “hot” papers for Catal. Sci. Tech in 2019).

The experiments of the CH-5330 beamtime used the full allocation of shifts given to this experiment, and data was collected as foreseen on both zeolitic materials, though for mazzite a sealing problem in the gas handling system forced us to abandon the use of the combined PDF/infrared setup and to measure using only

PDF (along with mass spectrometry). However, this enforced rearrangement of the experimental set up did not prevent us from achieving most of what we have planned to achieve.

The voluminous results obtained are currently under analysis. For the purposes of this report it is sufficient to say that time resolved PDF does yield a new window into the behavior of these systems and one that comes without any significant perturbation of the materials due to X-ray induced damage. It has been recently demonstrated that radiation damage can affect spectroscopic measurements to the point where one cannot a priori trust the results obtained using focused X-ray sources at lower energies, e.g. experiments at the Cu K-edge in XAS [6, 7] or XES [8]. The use of much higher energy X-rays required for PDF has the intrinsic advantage of massively reducing absorption by the sample to the point that this issue can be practically neglected.

Interpretation of the PDF derived from this experiment, though time intensive, can be expected to be published in the near future in a high impact journal. This said, combined PDF/DRIFTS does not, of itself, provide a magic bullet for comprehension of the nature of the active sites in these materials. It is therefore likely that these results will be combined with the result of other in situ methods (e.g. XAS, and conventional XRD) in order to resolved this thorny, but rather important, issue.

References

[1] Newton, M. A.; Knorpp, A. J.; Sushkevich V. L; Palagin D.; van Bokhoven, J. A., *Chem. Soc. Rev*., **2020**, in press.
[2] 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.
[3] (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
[4] Beyer, K. A.; Zhao, H. Y.; Borkiewicz, O. J.; Newton, M. A.; Chupas, P.J.; Chapman, K.W., *J. Appl. Cryst.*, **2014**, 47, 95 - 101
[5] Newton, M. A.; Checchia, S.; Knorpp, A. J.; Stoian, D.; van Beek, W; Emerich, H; Longo, A; van Bokhoven, J. A., *Cat. Sci. Tech.*, **2019**, 9, 3081 – 3089
[6] *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? **"**
[7] 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*.
[8] See also report for CH – 5492, ID26, ESRF