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:** "Revisiting the autoreduction process in copper-exchanged mordenite: unraveling the role of water"	**Experiment number**: **31-01-70**
Beamline: BM31	**Date of experiment**: from: 18/07/2018 to: 24/07.2018	**Date of report**: 20/02/2020
Shifts: 18	**Local contact(s)**: Wouter van Beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jeroen Van Bokhoven, Mark A. Newton,* Amy J. Knorpp, ETH Zurich

Vitaly Sushkevich, Maxim Zabilisky, Paul Scherrer Insttute

Dr Dragos Stoian*, Swiss Norwegian beamlines

Report:

Please note: somehow, in the ESRF this system, the above listed experiment has become listed under Mark Newton. However, proposal as titled above, was submitted by Vitaly Sushkevich. This confusion has no doubt arisen due to a swapping of another accepted experiment in the schedule at the time and that the beamtime was shared.

This report therefore only refers to work carried out regarding one half of this beamtime which was dedicated to understanding the kinetics and speciation of the reaction of methane with activated copper-mordenite (Cu/MOR) using time resolved Cu K-edge XANES. It is therefore also related to the report for exp 31 -01-65 wherein similar experiments were conducted concerning the copper-mazzite (Cu/MAZ) system.

To summarise, this beamtime was successfully used to quantitatively assess both the copper speciation that results from the exposure of high temperature activated Cu/MOR, and the kinetic nature of the reaction of the activated copper with methane in the temperature range 413 – 498 K. Moreover, we also succeeded in quantitatively investigating the process of steaming of the products formed within this zeolite as a result of reaction with methane and, for the first time, quantitatively cross referencing the time resolved Cu K-edge XANES data to the product distributions obtained from parallel acquisition of mass spectrometry.

The results obtained from this novel approach are far reaching in a number of ways.

Firstly, we have been able to quantitatively assessment kinetics associated with the reaction of methane with activate Cu/MOR. The results can be compared with those obtained previously using UV-vis spectroscopy [1] to study this chemistry and lead to the conclusion that transmission Cu K-edge XANES cannot distinguish between the two types of active Cu(II) species present in the activated materials that could be discriminated in UV-vis. The Cu K-edge XANES therefore averages over these sites but is in excellent agreement with these previous studies in terms of the kinetics parameters restored from analysis.

Secondly, comparison with identical measurements made at the SuperXAS beamline, at the Swiss light source, subsequently revealed that in these inorganic and dehydrated systems unwanted effect due to the X-rays themselves can manifest when the applied X-rays are focused. This comparison led to a subsequent investigation, which has shown that for materials of this nature, and under the reactive conditions applied, the X-rays at the SuperXAS beamline are required to be significantly defocused and attenuated before the kinetics and speciation of the copper that result from reaction with methane are found to correspond with that observed at BM31. This important observation and investigation was reported at the ESRF by the author at the workshop held in Grenoble in December 2019 that concerned itself with unwanted effects due to the application of ever more powerful and brilliant X-rays. [2] It has also resulted in a paper, currently under consideration for publication by Physical Chemistry Chemical Physics [3]

Thirdly, and for the first time, we were able to see within the process of the steaming of the products resulting from reaction with methane. Using time resolved Cu K-edge XANES allied to online MS we now understand that, far from being a single process, product release is found to be comprised of three, kinetically distinct, phases. Application of Principal component analysis (PCA) to this data has further revealed that two, rather than one, spectroscopically distinct Cu(I) species can be observed to be present during this chemistry and that they behave in very different manners in the presence of steam.

This observation has led to a complete reassessment of the reaction of methane itself (which has previously been supposed only to result in the formation of a single Cu(I) species), and revealed new details concerning the manner in which methoxy species are created and then removed from the zeolites. At present, these results are being written up for submission to a high impact journal given the entirely new and varied insights that these measurements have given to this important conversion. [4]

In summary this beamtime (along with the subsequent exp 31 -01-65, wherein this methodology was extended to study the Cu/MAZ system) was extremely successful and all f the shifts allotted to it were used. It remains only to thank the beamline staff, Hermann Emerich and Dragos Stoian, for the excellent job that they did. In the latter case, the degree of help given to MAN to get these measurements made in the manner that they eventually were, and which constituted going well beyond the basic remit of “local contact”.

References

[1] P. Vanelderen, P.; B. E. R. Snyder, M. –L. Tsai,; R. G. Hadt; J. Vancauwenbergh, O. Coussens, R. A. Schoonhedyt, B. F. Sels, E. I. Solomon, *J. Am. Chem. Soc*., 2015, 137, 6383-6392.

[2] *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? **“**

[3] M. A. Newton, A. J. Knorpp, J. Meyet, D. Stoian, M Nachtegaal, A. H. Clark, O. V. Safonova, H. Emerich, W. van Beek, V. L. Sushkevich, J. A. van Bokhoven, submitted to *Phys. Chem. Chem. Phys*.

[4] M. A. Newton, D. Stoian, A. J. Knorpp, H. Emerich, V. L. Sushkevich, J. A. van Bokhoven, manuscript in preparation