



## 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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.



	<b>Experiment title:</b> “Kinetics of fundamental steps in methane to methanol conversion using high temperature activated copper hosted in zeolites using Quick XAFS”	<b>Experiment number:</b> 31 -01-70
<b>Beamline:</b> BM31	<b>Date of experiment:</b> from: 20/06/2018 to: 26/06/2018	<b>Date of report:</b> 20/02/2020
<b>Shifts:</b> 18	<b>Local contact(s):</b> Wouter van Beek	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Amy Knorpp Professor Jeroen Van bokhoven Dr Mark Newton* Dr. Ana Pinar Dr. Vitaly Sushkevich*  ETJ, Zurich and Paul Scherrer institut  Dr Drago Stoian, Swiss Norwegian beamlines*		

## Report:

This beamtime, as with that described for exp 31 -01-70 was extremely successful. It should be noted that the success of this experiment is in good part due to Dr Dragos Stoian who went out of his way, and far beyond his local contact remit, in helping the author to get these tricky experiments completed in the time allotted. All 18 shifts, as a result were very effectively used.

Whereas in exp 31 -01-70 we had concentrated upon Cu/MOR, in this experiment we investigated another promising candidate system for the selective conversion of methane to methanol: Cu/MAZ [1].

In this experiment we used Cu K-edge XANES (17 seconds per spectrum) allied to downstream and mass spectrometry (MS) to quantitatively assess all aspects of the high temperature activation step-wise approach to methane conversion to methanol as facilitated by Cu/MAZ. This process requires initial high temperature activation of the zeolite system (723 K, O<sub>2</sub>) before reaction with methane conducted in the 413 – 498 K temperature range. Post reaction with methane the products of that reaction must be steamed from the zeolite before a new reactive cycle can begin. The objective of this time was therefore, as it was for Cu/MOR, in exp 31-01-70, to be able to understand the copper speciation involved throughout the overall step-wise process and investigate the durability of the reactive system over numerous such cycles.

The results of this beamtime may be summarized as follows:

- (I) The kinetics of the reaction of methane with activated Cu/MAZ are, within experimental error the same as found for Cu/MOR and the reaction results in the formation of two spectroscopically discrete Cu(I) centres. In Cu/MAZ, however, a greater variability in the overall extent of reaction (if not the apparent activation energy) was found.
- (II) Steaming of the products in MAZ, and as with Cu/MOR, was also revealed to be a three stage process comprising: (a) zeolite hydration wherein no changes in copper speciation were observed;

(b) product desorption, wherein the two Cu(I) centres were found to transiently behave in different manners; and, (c) slow re-oxidation of the copper by the water.

However, in MAZ one of the Cu(I) species found to be present is shown to be significantly less stable toward re-oxidation by water than its counterpart in MOR which leads to a very different kinetic character to this stage of the process that leads to closure of the reactive cycle.

- (III) Quantitative cross referencing of the copper speciation observed in time resolved Cu XANES with the products evolved in MS shows that Cu/MAZ is a far more selective for this conversion than Cu/MOR and that virtually no higher oxidation products (such as carbon monoxide and carbon dioxide) are formed by this system.
- (IV) Subsequent reactive cycling, however, revealed that unlike Cu/MOR Cu/MAZ cannot be quantitatively recycled within the high temperature activation scheme and undergoes systematic degradation in terms of methanol yields achieved. Equally however, the superior selectivity toward methanol and dimethyl ether is retained.
- (V) Whilst this degradative behavior was followed and quantified it also became apparent that Cu K-edge XANES could shed no direct light on the mechanism of the degradation.

This extremely rich information regarding the behaviour MAZ leads to both positive and negative conclusions regarding this material. On the one hand these data clearly show that Cu/MAZ is not a viable material within the conventional reactive protocols applied. However, they also show that if the degradation can be managed, through for instance, adopting different reaction protocols (see also report for 31-01-96 (Knorpp) which has used BM31 to investigate this issue further), then the superior selectivity of MAZ and the reduced stability of one of the Cu ion formed in the stepwise process toward oxidative reactivation could be used to some significant advantage from a process perspective.

In summary, the combination of time resolved Cu K-edge XANES and quantitative downstream MS has proved very powerful and extremely informative as to the timescales, speciation, kinetics, and stability of Cu/MAZ in the selective conversion of methane to methanol. The copious results that have resulted from these studies are currently being written up for submission to a high impact journal in the near future.

## References

- [1] A. J. Knorpp, A. B. Pinar, M. A. Newton, V. L. Sushkevich, J. A. van Bokhoven, *ChemCatChem*, (2018), 10, 5593-5596
- [2] A. J. Knorpp, A. B. Pinar, M. A. Newton, V. L. Sushkevich, P. P. Zimmermann, A. B. Pinar, J. A. van Bokhoven, *Cat. Sci. Tech.*, (2019), 9, 2806-2811
- [3] A. J. Knorpp, A. B. Pinar, M. A. Newton, S. C. M. Mizuno, J. Zhu, H. Mebrate, A. B. Pinar, J. A. van Bokhoven, *Chem. Comm.*, (2019), 55, 11794 - 11797