



## 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> Time-resolved XAFS/XRD study of low-temperature WGS catalysts : effect of cesium substitution on the structure, stability and performance.	<b>Experiment number:</b> CH-6286
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 16/06/2022 to: 20/06/2022	<b>Date of report:</b> 28/08/2023
<b>Shifts:</b> 12	<b>Local contact(s):</b> Cesare Atzori	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Prof. Andrew Michael Beale* Professor Gopinathan Sankar Mr Sebastian Stockenhuber* Mr Kallum Mehta* Miss Maria Asuncion Molina Esquinas*		

### Report:

The first run was to determine the changes observed in a typical catalyst, that is, 60:30:10 ratio of Cu:Zn:Al. To do this, a 1.5 mm diameter borosilicate capillary was loaded with ~100 mg of 250 – 150 µm catalyst which was diluted with SiO<sub>2</sub> to avoid too much self-absorption. The beamline furnace was then installed and the initial XAFS/XRD taken to see whether the dilution worked. Once we were satisfied with this, we ran 40 mL/min He through the capillary, and increased the temperature to 160 °C. Once at this temperature another XAFS/XRD was taken and H<sub>2</sub> concentration increased to 4 vol %, while keeping the flowrate at 40 mL/min. Once this was reached, the temperature would slowly go up, taking XAFS/XRD as the temperature increased. Once at 230 °C, multiple XAFS/XRD were taken and then the temperature brought back to room temperature to passivate in 1,5,10 and 20 % O<sub>2</sub>. Each time, XAFS/XRD were taken.

To confirm not only gases that were detected successfully but leaks weren't present, the Mass Spectroscopy (MS) machine measured Hydrogen, Helium, Oxygen, Carbon Dioxide and Water. All relevant experiments, besides the 5 wt. % Dry which due to mechanical failure didn't record, had their Mass Spec responses recorded successfully. It is noted that for Dry, the hydrogen is consistent and almost immediate, mainly owing to the high GHSV. In the case of the wet experiment's response was relatively sporadic, owing to the fact no condenser was installed down-stream. For future experiments involving water, it may be prudent to install a condenser with a reservoir as the mass spectroscopy isn't well equipped to handle that amount of water.

The XANES are shown in Figure 1 below. Unfortunately, the XRD were also as in Figure 3, which indicates that during preparation or operation the beamstop location could have been moved. This could also be exacerbated by the dilutant silica, thus making XRD impractical for size and strain calculations. This causes the Cu and Zn to be overwhelmed by SiO<sub>2</sub>, resulting in difficult to discern XRD plots. In both cases, the copper reduces above 150 °C, however, the XRD suggests that Cu metal continues to form until 230 °C which is difficult to observe in the XAS. However, it should be noted that the silica had shifted, making direct comparisons difficult to nigh-on impossible, with some XRD measurements not available. This makes the XAS the main focus of the investigation.

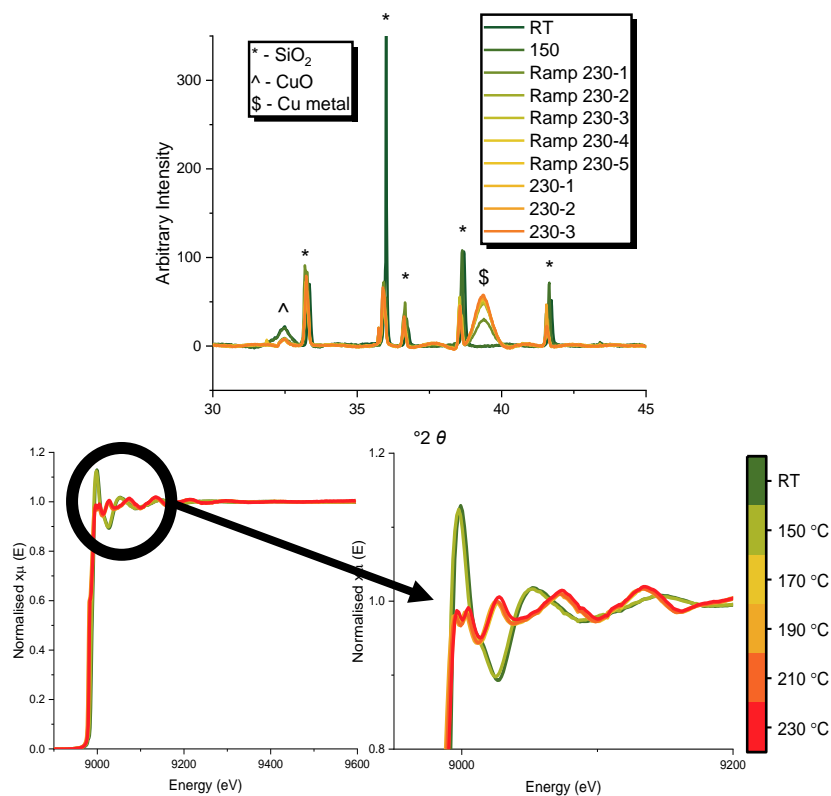


Figure 1. XRD of 0 wt. % Cs<sub>2</sub>O CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (Top) and XAS/XANES of the same experiment (Bottom)

The data collected has shown that there is an obvious difference between the nature of reduction in 0, 1 and 5 wt. % Cs<sub>2</sub>O, but the electronic state seems to change a lot quicker than any phase, as was shown in the XRD that could be understood. The effect of even saturated water vapour is also drastic, with copper and water vapour interacting at reducing temperatures to reform Cu<sup>1+</sup>, when without Cs<sub>2</sub>O. When a high concentration of Cs<sub>2</sub>O was involved, the onset of full reduction was delayed drastically, essentially requiring harsher conditions to achieve the same active sites. For zinc, as of now, there seems to be little known difference before and after reduction, along with little difference between the Cs<sub>2</sub>O concentrations. Using the fourier transform and k-spacing the Zn-O distances can be determined which could provide further information. Additionally, changes in copper will be determined using this and Linear Combination Analysis (LCA). This data will act as the cornerstone for the electronic interaction aspect of understanding how water and high Cs<sub>2</sub>O concentration affects real-world WGS pellets, with data taken from ID31 and BM28 recently complimenting this. This work will be aimed to be published together, as part of a comprehensive picture.