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:** μ-XRD-CT studies of low-temperature water-gas shift catalysts during activation and reaction: Effect of catalyst and gas composition on the crystalline phase and deactivation	**Experiment number**: CH-6402
Beamline: ID31	**Date of experiment**: from: 09/02/2023 to: 13/02/2023	**Date of report**: 12/09/2023
Shifts: 12	**Local contact(s)**: Veijo Honkimaki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Andrew Michael Beale*

Professor Gopinathan Sankar

Mr Sebastian Stockenhuber*

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Miss Antonia Bobitan*

Report:

Before the beamtime, preparation of the catalyst required using a reactor of length 20 cm (containing approximately 10 pellets per section, 4 sections) was performed, under conditions described in Table 1. The Gas Hourly Space Velocity (GHSV) was approximately 5600 hr^{-1} with 2 vol % H_2 at 220 °C over 24 hours. After reaction, the reactor was flushed with Argon and taps on the edges would trap the pellets inside the stainless-steel tube, after which placement in an Argon glovebox could prevent any interaction in air and thus, passivation/oxidation. The pellets for each condition would then be placed in a 10 cm glass capillary, with one pellet per section being held up by quartz wool on either end. Using the natural Fischer-Tropsch reaction as inspiration, paraffin wax was then melted and placed on top of the quartz wool on either end, trapping the pellets on either end. The capillaries were then removed and transported safely for the beamtime.

Table 1. Samples and their experimental conditions and whether they were run at the beamline.

Sample	Experimental Condition	Capillary name	Successful Beam scan
CZA-PS-1	20 Bar Dry	D	Yes
	Atm Dry	A, O	Yes
	20 Bar Wet	G, J, M	Yes
	Atm Wet	P	Yes
CZA-PS-2	20 Bar Dry	E, L	Yes
	Atm Dry	B, H	Yes
CZA-PS-3	20 Bar Dry	F	Yes
	Atm Dry	C	Yes
	20 Bar Wet	I, K	Yes

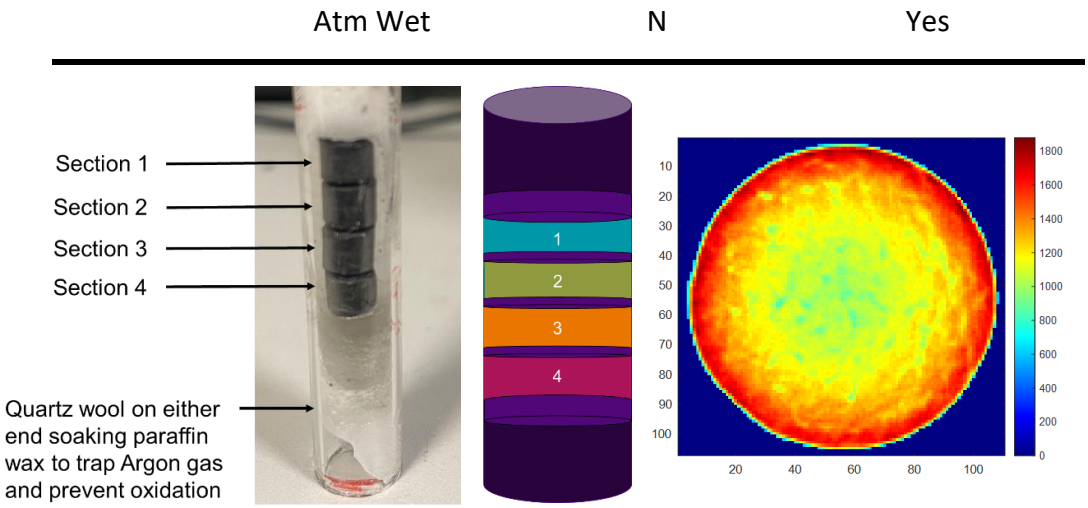

Figure 1. Pellets trapped in the capillary (Left), along with their relative positions in the large-scale reactor (middle) and an example of the total intensities for each scan in an unreacted pellet with 1 wt. % Cs_2O (right).

It was desired to determine how the pellets after different reduction environments was affected, by preventing oxidation/passivation using a novel method of trapping the pellets. At the beamline, the 4x5 mm pellets were to be scanned at 90.856 keV by rotating the tubes described in Figure 1 at 180 °, with the conditions as described in Table 1. All conditions in this table were successfully scanned, with each pellet scanned twice. To achieve these positions, heights for each catalyst scan were found by raising the plate and using the Y-level. It was confirmed that the beam would hit the right place as the capillary tubes used would leave a "burn" mark where the incident beam occurred, since the capillary seems to contain some Fe. Initially, it seemed that the scans would completely penetrate the pellets, but there appears to be some dampening of the intensity as it gets closer to the centre of the pellet, as seen in Figure 1. While it might have been useful to see peak intensities initially for specific 2 θ values, this wasn't as important as determined the specific phases present of CuO, Cu metal and ZnO and their subsequent crystallographic properties. Using Rietveld analysis, Figure 2 shows the preliminary analysis of conditions D and E in Table 1.

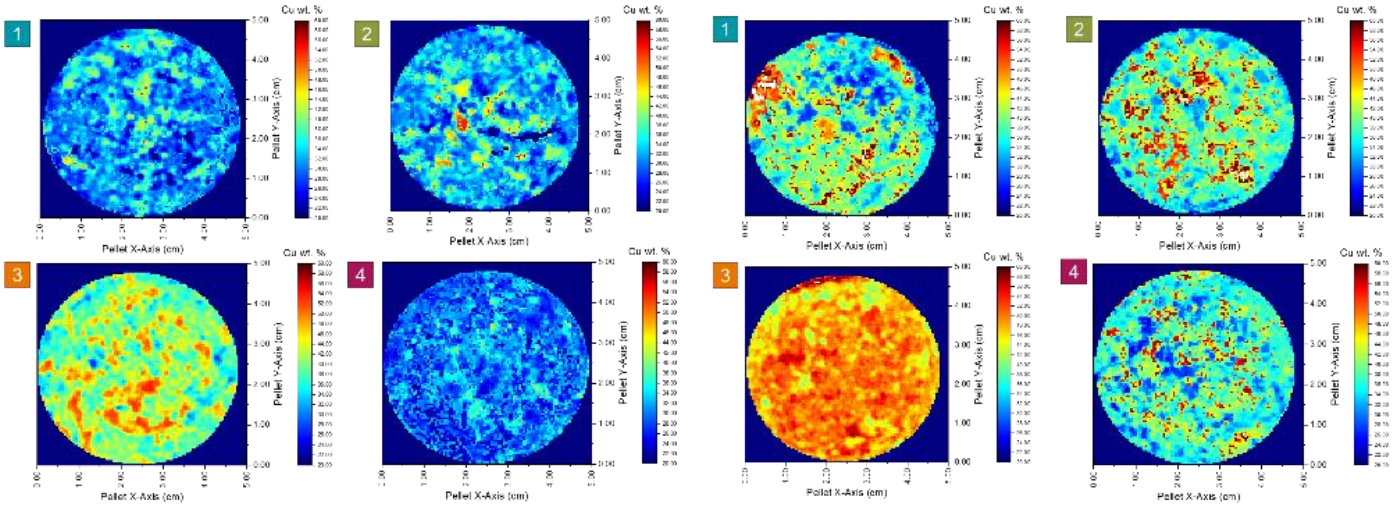

Figure 2. Cu wt. % after Rietveld fitting for conditions D (left) and E (right) from Table 1.

From preliminary visual analysis, it is clear that the Cu metal is more intense when Cs_2O is introduced, even before any water is added. The pockets of Cu formation (which typically indicate sintering) are more drastic, especially for the centre of the reactor where the temperature is 220 °C. Since there is a small temperature profile of ± 10 °C in the bed, the extremes can also pinpoint the drastic effect even a small temperature change can have. This phenomenon will be studied further and can set the basis for detailed publications on how real-world pelletised catalysts are affected by the addition of these alkali metals and in-particular, why the sintering and subsequent strength loss is observed. Additionally, this method of analysis also prevents the need for general intensities to be kept the same and can be used in many other hard materials.