

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

- 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.



	Experiment title: Structural elucidation of atomically precise catalytic Cu/ZrO ₂ clusters on MgO with high activity for CO ₂ hydrogenation by operando XAS characterization	Experiment number: A31-1-184
Beamline: SNBL-BM31	Date of experiment: from: 25th of October, 2022 to: 1st of November, 2022	Date of report:
Shifts: 18	Local contact(s): STOIAN Dragos Constantin MARSHALL Kenneth	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Seongmin Jin, *Bartu Karakurt, *Yu-Cheng Lin, and Jeremy Luterbacher Laboratory of sustainable and catalytic processes, Ecole Fédérale Polytechnique de Lausanne, Lausanne, Switzerland		

Report:

The experiments were carried out with Cu/MgO, Cu/ZrO₂, and Cu/MgOZrO₂ prepared via a liquid phase atomic layer deposition and CuZrO₂(I)/MgO prepared by an impregnation method. The oxidation states and coordination environment of Cu and Zr and the change of crystalline structure were studied using *operando* XAS and XRD. Cu and Zr XAS spectra were collected at the K-edge in fluorescence mode under reaction conditions (250 °C and 15 bar). The catalyst was loaded into a quartz capillary reactor cell, initially reduced at 350 °C under dilute H₂ flow for 0.5 h, and then cooled down to 250 °C to introduce the feed gas (CO₂/H₂=1:3).

The fresh Cu/MgOZrO₂ showed the first peak for Cu-O shell and a broad but highly shifted second peak in comparison to the second shells in Cu/MgO and Cu/ZrO₂, whereas the fresh CuZrO₂(I)/MgO catalyst prepared via impregnation exhibited two obvious peaks corresponding to Cu-O and Cu-(O)-Cu shells in **Figure 1a**. In Cu K-edge EXAFS fitting of the fresh Cu/MgOZrO₂, the first peak was fitted to Cu-O shell having 2.6 of coordination number (CN) whereas the fresh CuZrO₂(I)/MgO exhibited 3.8 of CN. The second shell of the fresh Cu/MgOZrO₂ broadly appeared and was displaced from the Cu-(O)-Cu shell of CuO or Cu₂O in **Figure 1a**. Therefore, the second shell was fitted to Cu-(O)-Zr shell having two different bonding lengths. As a result, the low coordination number of Cu-O shell and the absence of the peak from Cu-(O)-Cu shell in the fresh Cu/MgOZrO₂ suggest that Cu species in Cu/MgOZrO₂ were atomically dispersed.

After the reduction, the first shell resulting from Cu-O scattering in Cu K-edge EXAFS spectra substantially decreased in all catalysts as presented in **Figure 1b**, indicative of the reduction to metallic Cu. In the catalyst prepared via the ALD method, the peak close to Cu-Cu shell of Cu foil was observed but it was shifted to the lower bonding length in R-space in comparison to CuZrO₂(I)/MgO prepared via the incipient wetness impregnation. This shift could result from either existence of Cu cluster consisting of several atoms¹ or the bonding with other metals^{2,3} (*i.e.* Cu-Zr). The derivative of Zr K-edge XANES data in **Figure 2** also shows that

the structure of ZrO_2 in Cu/MgOZr_2 was considerably changed during reduction, compared with the structure in MgOZrO_2 and $\text{CuZrO}_2(\text{I})/\text{MgO}$. This result indicates the formation of oxygen vacancies or structural distortion of ZrO_x cluster, thereby evidencing that the structural change of Cu and ZrO_2 is highly correlated in the Cu/ZrO_x cluster structure of Cu/MgOZrO_2 .

Under CO_2 hydrogenation reaction condition, a stable methanol production was confirmed via the mass spectrometer and no noticeable change in oxidation states and coordination environment of Cu in Cu/MgOZrO_2 was observed, suggesting that the structure of Cu/ZrO_x in Cu/MgOZrO_2 was retained during 10 h of reaction.

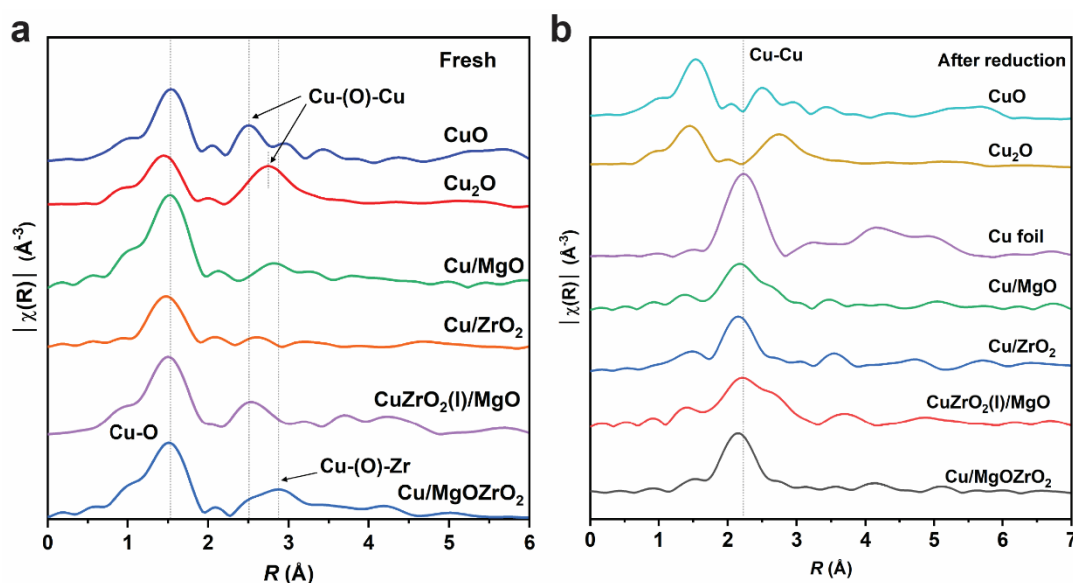


Figure 1. Fourier-transform of the k^2 -weighted Cu K-edge EXAFS of catalysts (a) before and (b) after reduction.

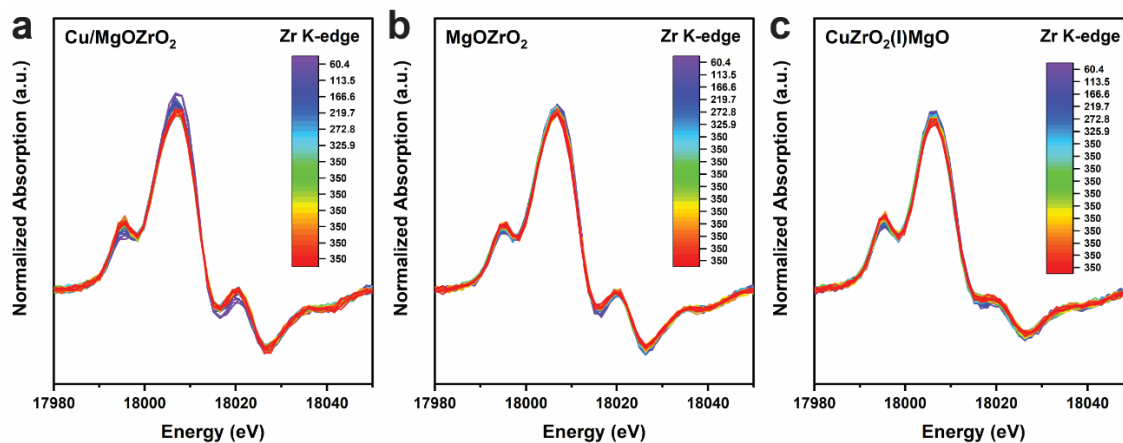


Figure 2. The first derivatives of in situ Zr K-edge XANES data of (a) Cu/MgOZrO_2 , (b) MgOZrO_2 , and (c) $\text{CuZrO}_2(\text{I})/\text{MgO}$ obtained during in situ reduction of catalysts to $350\text{ }^\circ\text{C}$ under $20\%\text{H}_2/\text{N}_2$ flow. (Numbers next to the color scale indicate the temperature at which the spectra were obtained)

References

1. Jaque, P. & Toro-Labbé, A. Characterization of copper clusters through the use of density functional theory reactivity descriptors. *J. Chem. Phys.* **117**, 3208–3218 (2002).
2. Shan, J. *et al.* NiCu single atom alloys catalyze the CH bond activation in the selective non-oxidative ethanol dehydrogenation reaction. *Appl. Catal. B Environ.* **226**, 534–543 (2018).
3. Sadoc, A. EXAFS study of amorphous $\text{Cu}_{33}\text{Zr}_{66}$ alloy. *J. Non-Cryst. Solids* **61–62**, 403–407 (1984).