



## 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> Rh-based bimetallic catalytic catalysts for the selective synthesis of ethanol from CO <sub>2</sub> hydrogenation	<b>Experiment number:</b> A31-1-168
<b>Beamline:</b> SNBL-BM31	<b>Date of experiment:</b> from: 19.04.2022 to: 25.04.2022	<b>Date of report:</b> 06.09.2022
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Wouter van Beek, Dr. Dragos Stoian	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Wei Zhou*, Scott Docherty*, Xiaoyu Zhou*, Christian Ehinger*  Laboratorium für Anorganische Chemie, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland		

## Report:

## Overview

The Rh-based catalysts has been recently shown promising selectivity towards ethanol in CO<sub>2</sub> hydrogenation. Via surface organometallic chemistry (SOMC), a powerful tool for the construction of well-defined model catalysts for an array of reactions, we have synthesized size-homogeneous Rh nanoparticles doped with Mn or Fe on SiO<sub>2</sub> (RhMn@SiO<sub>2</sub> and RhFe@SiO<sub>2</sub>) with tailored interfaces to rationalize the effect of various metal promoters. By conducting *ex situ* as well as *in situ* x-ray absorption spectroscopy experiments to identify the speciation of these bimetallic catalysts especially under working state, we hope to elucidate the interplay between structure and catalytic performance for Rh-based catalyst. In combination with other spectroscopic (IR, XPS), microscopic (TEM, STEM-HAADF, EDX) techniques and computational approaches (AIMD or static DFT) on these catalysts, we hope to clarify the promotional effect of metal promoters and the associated reaction mechanism. The outcomes of this proposal will enable to rationally design the next generation of catalysts for CO<sub>2</sub> hydrogenation, which would have an important impact on decarbonizing our economy.

## Data obtained and experimental parameters

In situ X-ray adsorption spetrac data were collected on powered sample of Rh@SiO<sub>2</sub>, RhMn@SiO<sub>2</sub> and RhFe@SiO<sub>2</sub>, packed into the quartz capillaries (1.5 mm for Rh, 1.0 mm for Mn and Fe). Data were collected at beam energies range from 23.1-24.1 keV for the Rh K, from 6.4-7.1 keV for the Mn K, and from 7.0-8.0 keV for the Fe K. Flow rates (Ar, H<sub>2</sub>, CO<sub>2</sub>) were controlled using mass-flow controllers (Bronkhorst), and pressure was set at 20 bar using a back pressure regulator (Bronkhorst, EL-PRESS). The temperature for H<sub>2</sub> reduction (400 °C) and CO<sub>2</sub> hydeogenation (230 °C) were maintained using a nitrogen blower. Prior to measurements, a K-type thermocouple mounted inside a sample cell was used for the temperature calibration. Outlet gas was detected using a mass spetrometer (MS, Pfeiffer vacuum) mounted after the back-pressure regulator.

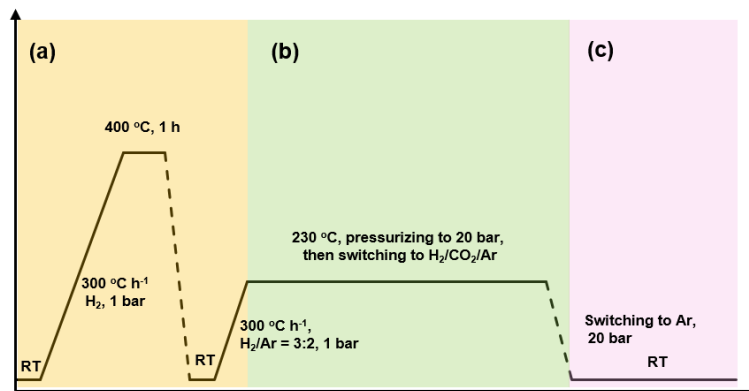


Figure 1. Scheme for the temperature profile for a typical experiment.

In a typical experiment, EXAFS spectra were first collected after the sample was mounted and exposed to air. Subsequently, H<sub>2</sub> pretreatment was carried out under 10 mL/min of H<sub>2</sub> for 1 h at 400 °C (300 °C h<sup>-1</sup> ramp), while continuously collecting XANES spectra. After the pretreatment and cool down room temperature, EXAFS spectra were collected for the reduced sample. Then, heating to reaction temperature (230 °C) under 10 mL of H<sub>2</sub>/Ar mixture (300 °C h<sup>-1</sup> ramp), followed pressurizing to 20 bar and keeping 20 min. Subsequently, switching to CO<sub>2</sub>/H<sub>2</sub>/Ar mixture for CO<sub>2</sub> hydrogenation 2 h. Notably, the XANES spectra were continuously collected during this entire protocol. After CO<sub>2</sub> hydrogenation, the gas was switched to Ar and the temperature was cooled to room temperature for the post-CO<sub>2</sub>-hydrogenation EXAFS spectra. Regarding the bimetallic sample, Rh K XAS spectra and Mn or Fe K XAS spectra due to the great difference in beam energies were separately collected under the identical *in situ* conditions.

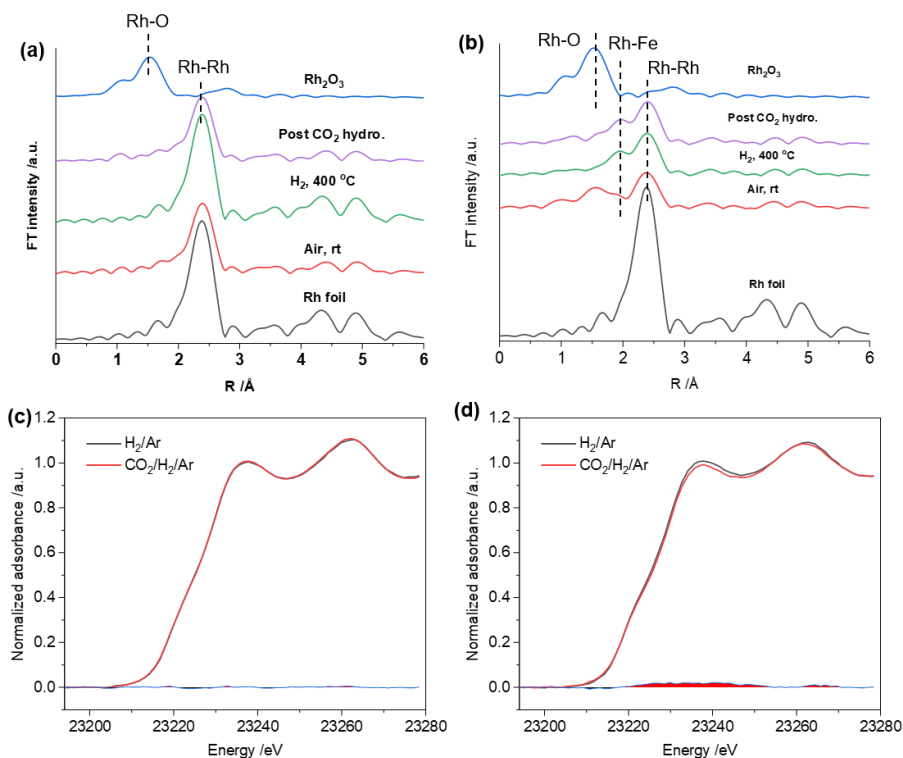


Figure 2. Representative *in situ* XAS spectra of Rh K edge for Rh@SiO<sub>2</sub> and RhFe@SiO<sub>2</sub> sample. (a) The  $k^2$ -weighted EXAFS spectra in R space, and (c) Normalized XANES spectra for Rh@SiO<sub>2</sub>; (b) The  $k^2$ -weighted EXAFS spectra in R space, and (d) Normalized XANES spectra for RhFe@SiO<sub>2</sub>. Normalization and data processing was performed on the XAS data processing software Athena

## Further work and anticipated output

The XAS data has currently been processed. The XAS data has already shown insights into the evolution of catalyst structure in the duration of H<sub>2</sub> pretreatment and CO<sub>2</sub> hydrogenation, such as the alloying and the oxidation of *M* (representing the promoter like Fe or Mn) inducing the formation of the *M*-O-Rh interface. The *in situ* IR will be further carried out to monitor the differences in the intermediates over the Rh-based catalysts in the absence and presence of promoters. Two manuscripts for the role of Mn and Fe for the Rh-based catalysts for CO<sub>2</sub> hydrogenation are expected once the complementary characterizations are at hand.