



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: Boosting the ethanol synthesis from CO ₂ hydrogenation over Rh-based catalyst generated via SOMC	Experiment number: A31-1-197
Beamline: SNBL-BM31	Date of experiment: from: 28.04.2023 to: 02.05.2023	Date of report: 04.09.2023
Shifts: 12	Local contact(s): Dr. Wouter van Beek, Dr. Dragos Stoian	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Wei Zhou*, Colin Hansen*, Xiaoyu Zhou*, Christian Ehinger* Laboratorium für Anorganische Chemie, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland		

Report:

Overview

Gallium (Ga) has emerged as a promising promoter in several systems (M/support), from the classical Cu-based catalysts to Ni-based and Pd-based systems. Thanks to tailored made materials prepared using Surface Organometallic Chemistry, that enable to better control composition and interfaces, this change of reactivity has been ascribed to the (reversible) formation of MGa alloy and M/GaO_x or MGa/GaO_x interfaces. Such promotional effect is particularly noteworthy for Ni- and Pd- since both of these metals are not known to promote CO₂ hydrogenation to methanol, but rather methanation (Ni) or be prone to poisoning by CO (Pd). We thus further explore a series of Ga-promoted bimetallic catalysts (MGa@SiO₂, M = Ru, Os, Rh, and Ir) prepared via an SOMC approach and show that in all cases the presence of Ga promote the selective hydrogenation of CO₂ hydrogenation towards methanol/DME with selectivity > 50%, in contrast to the mono-metallic cases (M@SiO₂ catalysts) that always favor methanation reaction (CH₄ > 97%). By conducting *ex situ* as well as *in situ* x-ray absorption spectroscopy experiments to identify the speciation of these monometallic and bimetallic catalysts especially under working state, we hope to elucidate the interplay between structure and catalytic performance for Ga-promoted catalysts. 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 universally promotional effect of Ga and the associated reaction mechanism. The outcomes of this proposal will enable to rationally design the next generation of catalysts for CO₂ hydrogenation, which would have an important impact on decarbonizing our economy.

Data obtained and experimental parameters

In situ X-ray adsorption spectra data were collected on powered sample of monometallic M@SiO₂ and Ga-promoted bimetallic MGa@SiO₂ catalysts (M = Ru, Rh and Ir) packed into the quartz capillaries (1.5 mm with 0.02 mm wall thickness). Data were collected at beam energies range from 22-23.1 keV for the Ru K, from

23.21-24.21 keV for the Rh K, from 11.12-12.22 keV for the Ir L₃ and 10.27-11.37 keV for Ga K. Flow rates (Ar, H₂, CO₂) 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 H₂ reduction (400 °C) and CO₂ hydrogenation (230 °C) were maintained using a SiC heating element. Outlet gas was detected using a mass spectrometer (MS, Pfeiffer vacuum) mounted after the back-pressure regulator.

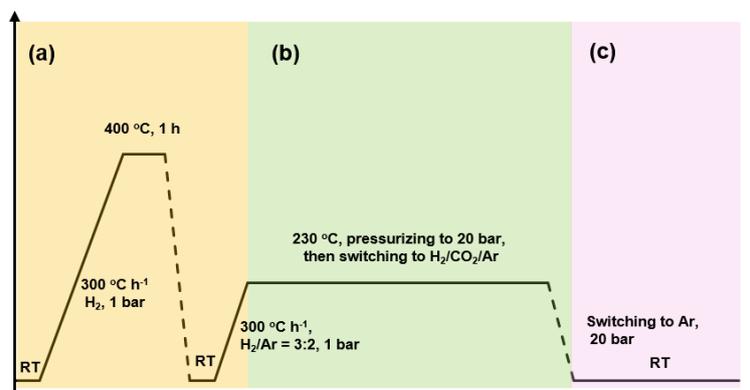


Figure 1. Scheme for the temperature profile for a typical experiment.

In a typical experiment, EXAFS spectra were first collected after the sample was mounted and exposed to air. Subsequently, H₂ pretreatment was carried out under 10 mL/min of H₂ for 1 h at 400 °C (300 °C h⁻¹ 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 H₂/Ar mixture (300 °C h⁻¹ ramp), followed pressurizing to 20 bar and keeping 20 min. Subsequently, switching to CO₂/H₂/Ar mixture for CO₂ hydrogenation 2 h, then, the XANES spectra were collected during the CO₂ hydrogenation. After CO₂ hydrogenation, the gas was switched to Ar and the temperature was cooled to room temperature for the post-CO₂-hydrogenation EXAFS spectra.

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 H₂ pretreatment and CO₂ hydrogenation, such as the MGa ($M = \text{Ru, Rh, Ir}$) alloying detected after H₂ reduction and CO₂ hydrogenation. The *in situ* DRIFTS will be further carried out to monitor the differences in the intermediates over the monometallic catalysts Ga-promoted catalysts bimetallic catalysts. Two manuscripts for the universal role of Ga on the transition metal for CO₂ hydrogenation to methanol are expected once the complementary characterizations are at hand.

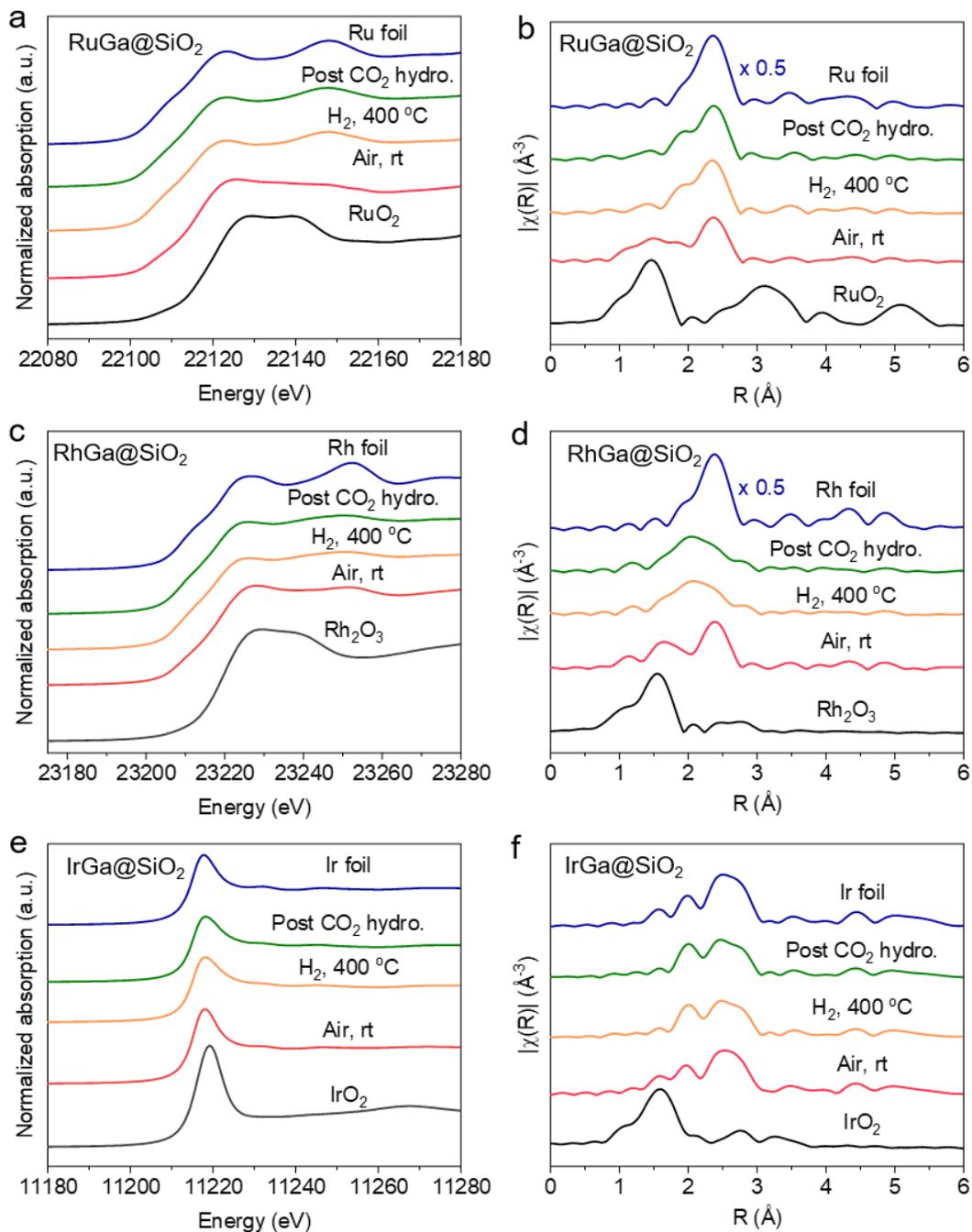


Figure 2. Representative XANES spectra and the k^2 -weighted Fourier transforms of EXAFS spectra under different conditions for RhGa@SiO₂ at Rh K-edge (a) and (b); RuGa@SiO₂ at Ru K-edge (c) and (d); IrGa@SiO₂, and Ir L₃-edge (e) and (f) respectively. Normalization and data processing was performed on the XAS data processing software Athena