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	**Particle Size Effect in Cobalt-Based CO_2 Hydrogenation – Tailoring Selectivity to Methanation or rWGS activity**	**CH 6465**

Beamline: BM-31	**Date of experiment**: from: 02.11.22 to: 07.11.22	**Date of report**: 03.02.2023
Shifts: 15	**Local contact(s)**: Dr. Wouter Van Beek, Dr. Dragos Stoian	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Xiaoyu Zhou*, Scott Docherty*, Christian Ehinger*, Kazutaka Sakamoto*.

Laboratory for Inorganic Chemistry (LAC), Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland.

Report:

Overview:

The effect of particle size on the reactivity of cobalt nanoparticles in Fischer-Tropsch chemistry is well established, but less is known about the impact on cobalt-based CO2 hydrogenation. To study this, we used Surface Organometallic Chemistry (SOMC) to synthesize well-defined cobalt nanoparticles (Co-NPs) on SiO_2, varying particle size by adjusting treatment temperature: Using $Co(Alkyl)_2$tmeda as molecular precursor, yielded highly dispersed Co-NPs on SiO_2. Characterization of the SOMC-derived materials was carried out using microscopy and spectroscopy to assess surface cleanliness and particle formation. The catalytic behavior of the materials was studied in CO_2 hydrogenation and found to change with particle size. The objective of the experiment at BM31 was to obtain *in situ* XAS data under CO_2 hydrogenation conditions, which would allow us to link the fundamental shift in reactivity to the state of catalyst under working conditions.

Data obtained and experimental parameters:

X-ray absorption spectra data was collected on powdered samples of Co@SiO2 that were reductively treated with hydrogen flow at different temperatures to vary particle size. The samples were supported on Degussa AEROSIL-200 and data was collected using a quartz capillary with an outer diameter of 1.0 mm and inner diameter of 0.9mm, which were mounted on stainless steel-frames equipped with swagelok 3-way valves allowing to bypass the sample prior to the experiment. Beam energies ranged from 7.65 to 8.6 keV to capture the Co K edge. The flow rates of He and H_2 were controlled using mass-flow controllers and pressure was maintained using a back-pressure regulator. The temperature was maintained for for all stages of the experiment using a nitrogen gas blower and was calibrated prior to measurements using a K-type thermocouple inside the sample cell. The outlet gas composition was monitored using a mass spectrometer mounted after the back-pressure regulator.

A typical experiment for *in situ* CO_2 hydrogenation was performed as follows:

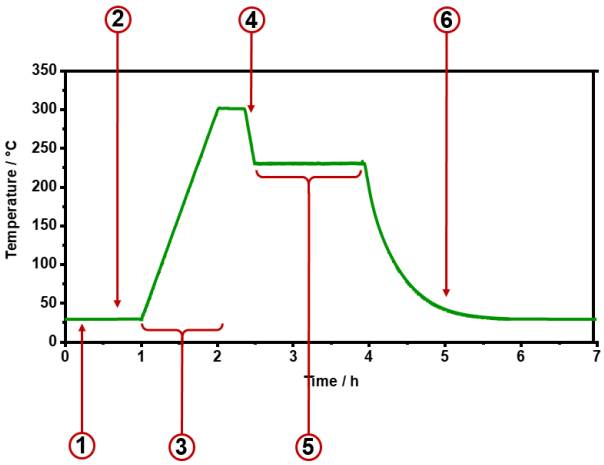

Figure 1. Schematic representation of the temperature profile and acqiusition modes for a typical CO_2 hydrogenation experiment.

1: **Pristine EXAFS:** Ar, 1 bar. 10 sccm

2: Pressure test to 20 bar in Ar

3: **Continous XANES:** Pretreatment, H_2, 10 sccm, to 300 °C (5 °C min^{-1}), hold for 1h

4: *Cool to 230 °C (reaction temperature)*

5: **Continous XANES:** Pressurize to 20 bar, switch to 10 sccm reaction gas (H_2:CO_2:Ar = 3:1:1)

6: **EXAFS:** Cooling to rt., depressurize, acquire spectra

This procedure allowed us to follow the catalyst changes under reaction conditions while having maximum control over the system (complete air/ moisture-free environtment from synthesis at home institution until end of experiment), revealing a sharp change in catalyst state as the cobalt nanoparticles become smaller than 2 nm. (see Fig. 2)

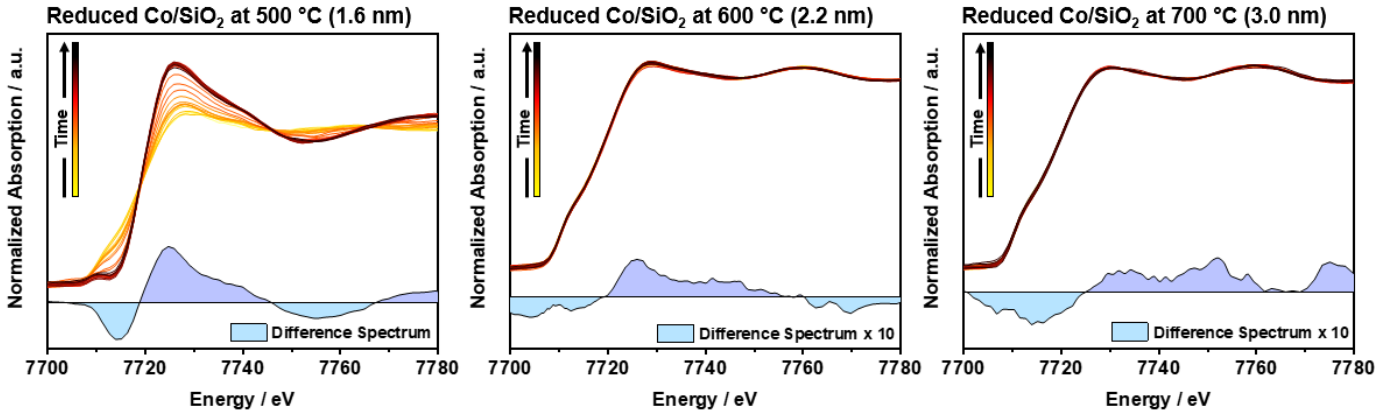

Figure 2. In situ XANES of SOMC-derived cobalt nanoparticles with different particle sizes, showing a sharp change in oxidizability under CO_2 hydrogenation conditions.

Further work and anticipated output:

Currently, the data is being further processed, especially in regards to the EXAFS data analytical part, to obtain a deeper understanding of what is happening under reaction conditions. The obtained XANES data are already intriguing and are among the missing pieces of this particle-size project. A manuscript including the *in situ* XAS data is being drafted and planned to be submitted later this year.