

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: Mn-doping on Co-based Fischer-Tropsch Catalysts	Experiment number: 31-01 158
Beamline: SNBL-BM31	Date of experiment: from:14.09.21 to:21.09.21	Date of report: 20/12/2021
Shifts: 21	Local contact(s): Dr. Wouter van Beek, Dr. Dragos Stoian	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Xiaoyu Zhou*, Scott Docherty*, Christian Ehinger*, Dr. Wei Zhou* Laboratorium für Anorganische Chemie, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland		

Report:

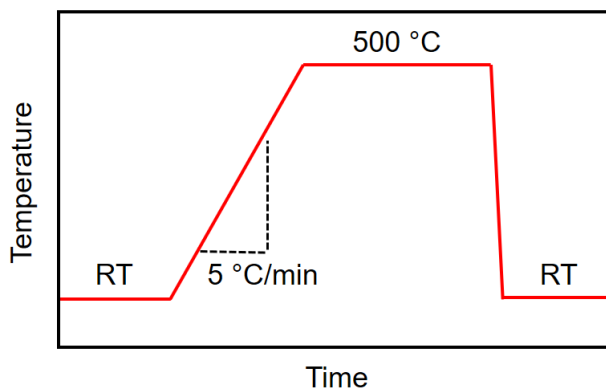
Overview:

The presence of Mn on Co-based Fischer-Tropsch (FT) catalysts has been recently shown to significantly shift the product selectivity from classical FT products towards long chain olefins and alcohols, opening a direct path towards long-chain olefins and oxygenates from syngas mixtures (CO+H₂). Via surface organometallic chemistry (SOMC), an approach shown to be effective for the synthesis of model catalysts for an array of reactions, we have synthesized highly dispersed Mn-doped Co nanoparticles (NP) on SiO₂ (CoMn@SiO₂) with tailored surfaces and interfaces to study the origin of this Mn effect. By conducting *ex situ* as well as *in situ* x-ray absorption spectroscopy experiments, we hope to elucidate the interplay between Co and Mn. Specifically, the speciation of the Mn within such materials and the consequences for catalytic activity, stability and selectivity. Pairing *in situ* XAS with other spectroscopic (IR, EPR, XPS), microscopic (TEM, STEM-HAADF, EDX) and physico-chemical characterization (Chemisorption, TPR) techniques on these materials, as well as finding the link to catalytic data represents a promising approach to contribute to the understanding of the Mn promotional effect. With rising interest towards Mn as a promoter to various catalytic systems, the outcomes of this study are potentially interesting to a broader audience in heterogeneous catalysis.

Data obtained and experimental parameters

In situ X-ray absorption spectra data were collected on powdered samples of Co@SiO₂ and CoMn@SiO₂ in their non-reduced form, using quartz capillaries (o.d. 1mm, i.d. 0.9mm). All samples were supported on Degussa AEROSIL-200 (200 m² g⁻¹). Data were collected at beam energies ranging from 6.4 – 7.6 keV for the Mn K edge and from 7.65 – 8.6 keV for the Co K edge. Flow rates (He, H₂) were controlled using mass-flow controllers (Bronkhorst), and pressure was retained using a back pressure regulator (Bronkhorst, EL-PRESS). Temperatures

for temperature-programmed reduction (TPR) were maintained using a nitrogen gas blower. Temperature calibration was performed using a K-type thermocouple mounted inside a sample cell in prior to measurements. Outlet gas composition was monitored using a mass spectrometer (MS, Pfeiffer vacuum) mounted after the back-pressure regulator.



- 1: Pristine EXAFS: He, 1 bar, 10 sccm
- 2: Reduction XANES: H₂, 1 bar, 10 sccm, 5 °C min⁻¹
- 3: Post-TPR EXAFS: He, 1 bar, 10 sccm

Figure 1. Schematic representation of the temperature profile for a typical TPR experiment.

In a typical experiment, EXAFS spectra were acquired right after the sample was mounted and still under inert / pristine conditions at ambient temperature. Subsequently, the gas composition was changed to hydrogen and the temperature was ramped to 500 °C with a gradient of 5 °C per minute, while continuously collecting XANES spectra. Depending on monometallic or bimetallic samples, the time resolution would change from 34 seconds per spectrum in a monometallic sample to 1 minute in a bimetallic sample, where to edge jumps had to be acquired. After reaching 500 °C, the quartz capillary was allowed to cool to ambient temperature for the acquisition of post-TPR EXAFS spectra.

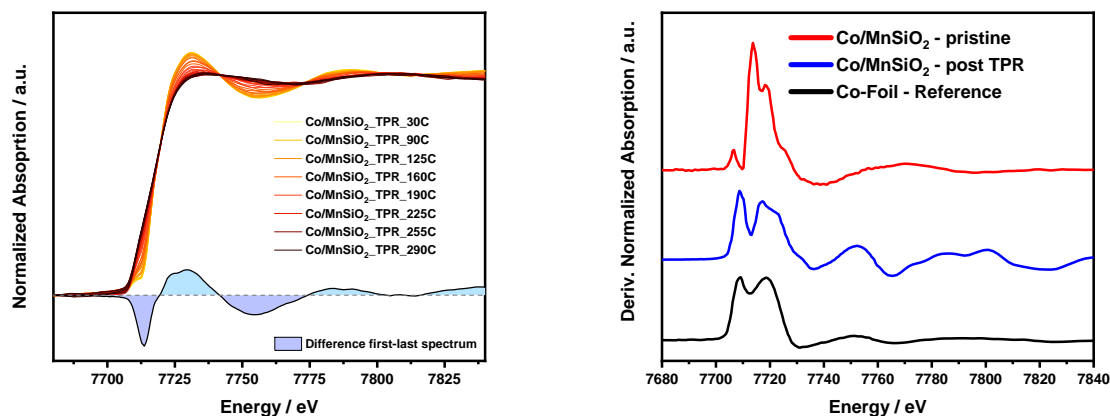


Figure 2. Representative XAS spectra for the *in situ* reduction (left spectra) of a SiO₂-supported cobalt molecular species. Comparison of the 1st derivative spectra indicate the metallic state of the supported cobalt after reductive treatment (right spectra). Normalization and data processing was performed on the XAS data processing software Athena.

Further work and anticipated output:

Currently, the data is being further processed. Especially the EXAFS part of the data will be promising in giving further insights into the state of the material after reductive treatment in presence/absence of cobalt and in dependence of various molecular precursors. Multivariate curve resolution, linear combination fitting as well as EXAFS fit are currently applied to extract further information from the obtained spectra. The data has already given intriguing insights into the reductive behaviour of different molecular precursors as well as the implication

of alloying. Rigorous catalytic testing will be performed to understand the consequences of structural features we found in the XAS data and link them to reactivity. A manuscript for the monometallic species is expected once catalytic data as well as complementary data from further studies are at hand.