EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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	**Experiment title:**	**Experiment number**: CH-4149
Beamline: ID15	**Date of experiment**: from: 21 Oct 2014 to: 27 Oct 2014	**Date of report**: 21-03-2015
Shifts:	**Local contact(s)**: Marco Di Michiel	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): Andrew M. Beale (UCL), Pierre Senecal (UCL), Simon Jacques (Manchester University) – all*		

Report:

The objective of this study is to describe a Cobalt-based Fisher-Tropsch catalyst, to showcase the potential of using XRD-CT to study and understand the effect of different reduction protocols on these types of catalysts. For each experiment, three trilobe pellets (Ø 1.5 mm, h = 3 mm) of the catalyst were mounted on top of each other in a capillary. Five different reductions were carried out on the sample and are presented in Table 1.

Table 1: Description of the reduction parameters

Exp.#	Gas (H_2)	GHSV (h^{-1})	Temperature programme
1	100%	5000	RT to 300°C at 1°C/min. Hold at 300°C for 4h
2	25%	5000	RT to 300°C at 1°C/min. Hold at 300°C for 4h
3	25%	2000	RT to 300°C at 1°C/min. Hold at 300°C for 4h
4	4%	2000	RT to 300°C at 1°C/min. Hold at 300°C for 4h
5	4%	5000	RT to 300°C at 1°C/min. Hold at 300°C for 4h

A difference in reduction over the three extrudates placed in a single capillary have been observed. Even in such small amounts of catalysts, Figure 1 shows this difference on the experiment at 4% and 100% of H_2 at the space velocity of 5000 h^{-1}.

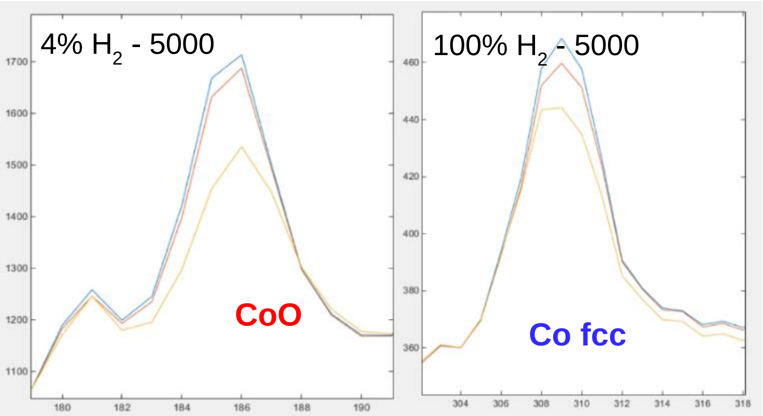

Figure 1: Diffractograms after the experiment at 4% and 100% of H_2 at the space velocity of 5000 h^{-1} of three extrudates mounted in capillaries.

An important difference is also observed when we compare those two experiments. The fresh catalyst presents the Bragg reflections of the Co_3O_4 phase while the experiment at 4% of H_2 shows CoO and the experiment at 100% of H_2 shows Co fcc (Figure 2).

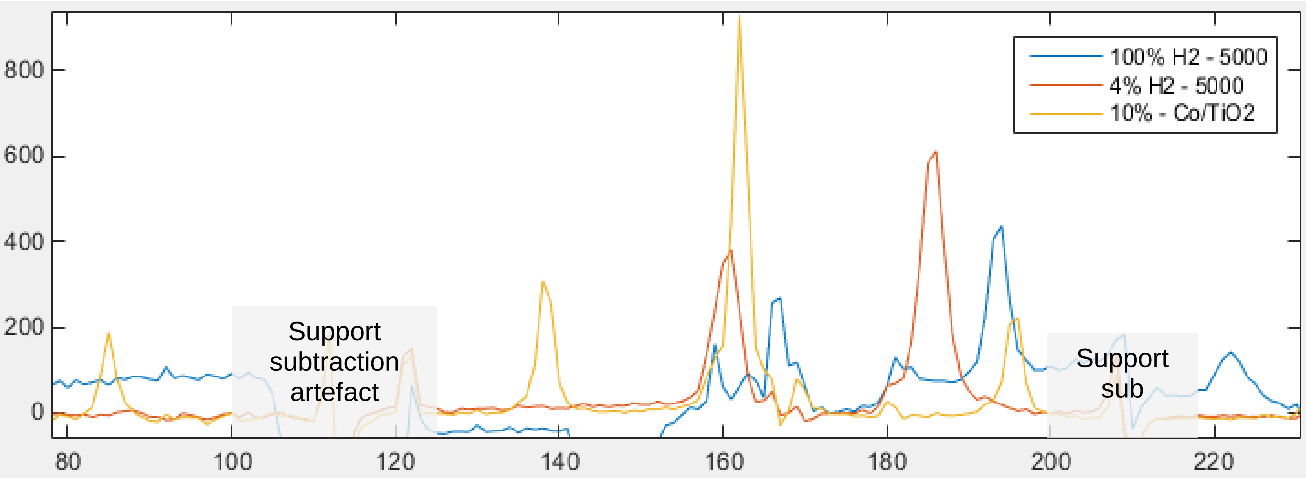

Figure 2: Diffractograms after the experiment at 4% and 100% of H_2 at the space velocity of 5000 h^{-1} of the first extrudates.

The experiment was designed to obtain 2 dimensional information on the formation of cobalt phases within a catalyst body during reduction. This necessitated mounting the catalyst body in a quartz cell with a gas delivery connector. The reduction experiments were carried out offline in the ID15 chemical laboratory at the ESRF on a setup containing two heat guns and a gas delivery system. At the end of each experiment, the reactor cells were sealed, fixed to a goniometer and then attached to a rotation stage for XRD-CT analysis.

This experiment was carried out at station ID15A using a high energy monochromatic, 50 µm square section pencil beam. For each sample, diffraction was recorded at 70 translations spaced 50 µm across the body each with 60 rotations of 3°, corresponding to 4200 projections. Each diffraction pattern was recorded for 500 ms. Powder ring data were obtained and these were radially integrated for each diffraction "projection". For each observed intensity in these radially integrated patterns, a sinogram was constructed and then back-projected to a 66 x 66 pixel image. The Figure 3 shows examples of reconstructed images for the fresh sample Co_3O_4 phase [220] and experiment #5 CoO [200] and experiment #1 Co fcc [111].

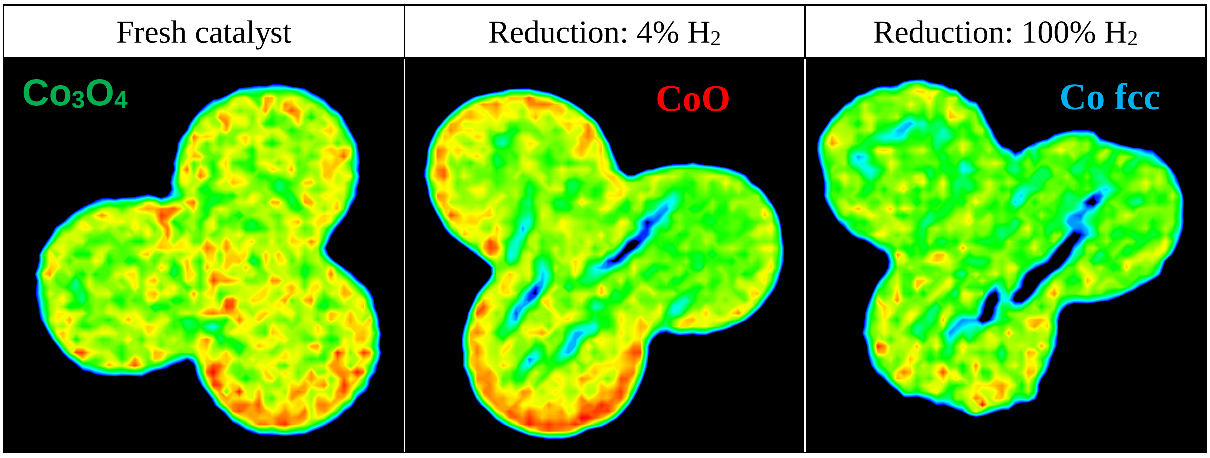

Figure 3: Reconstructed images of Cobalt phases of the catalyst before and after reduction at 4% and 100% of H_2 at the space velocity of 5000 h^{-1}.

Two cobalt phases are observable depending on the reduction parameters:

- at low H_2 concentration (4%), only the oxide CoO is observable
- at 100% H_2, the active phase for the Fischer-Tropsch synthesis, Co fcc, appears.

The reconstructed images show that the cobalt is well distributed inside the pellet but with a slightly higher intensity in the outer circumference probably due to impregnation conditions.