

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: Deactivation of Co-based single particle Fischer-Tropsch Catalyst	Experiment number: CH-4021
	Beamline: ID15	Date of experiment: from: 03 April 2014 to: 08 April 2014
	Shifts: 15	Date of report: 26-09-2014 <i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Andrew M. Beale (UCL), Antony Vamvakeros (UCL), Simon Jacques (Manchester University) – all*		

Report:

The objective of this study is to describe a well-known system, a Co/Al₂O₃ catalyst, to showcase the potential of using XRD-CT to study cobalt-based Fischer-Tropsch catalysts.

A 3 mm cylindrical pellet of a 10 wt. % Co/Al₂O₃ catalyst prepared by the impregnation of a γ -Al₂O₃ support with a cobalt solution followed by drying and calcination at 300 °C for 4h (ref C1414501). Reduction was performed under 39 ml/min of H₂ from room temperature to 450 °C with a ramp of 2°C/min with steps of 60 min at 150 °C, 310 °C, 350 °C and 420 °C. Fisher-Tropsch synthesis (FTS) was performed at 250 °C under CO (5 %, 20 ml/min), H₂ (100 %, 2 ml/min) and He (100 %, 19 ml/min). The experiment was designed to obtain 2 dimensional information on the formation of cobalt phases within a catalyst body during reduction and FTS. This necessitated mounting the catalyst body in a quartz cell with a gas delivery connector. The latter was fixed to a goniometer attached to a rotation stage. This entire setup itself was mounted upon a translation stage, onto which were also mounted two heat guns.

This experiment was carried out at station ID15A using a high energy monochromatic, 50 μ m square section pencil beam. For each time slice, diffraction was recorded at 70 translations spaced 50 μ m 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.

Through the reduction and FTS on the Co/Al₂O₃ catalyst, three cobalt phases are observable: Co₃O₄, CoO and Co fcc. Figure 1 shows two diffractograms of the cobalt species at the beginning of the reduction at 150 °C

(slide #002) and at the end of the experiment (slide #032) with the three cobalt species clearly observable. Figure 2 shows the reconstructed images of those cobalt phases at four steps of the experiment.

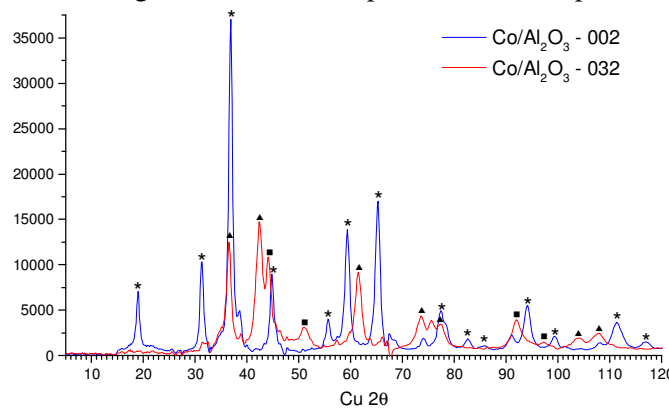


Figure 1: Sum of all the diffractogram of the slides #002 in blue (beginning of the reduction at 150 °C) and #032 in red (end of the experiment) after subtraction of the quartz and the γ - Al_2O_3 patterns; Co_3O_4 (*), CoO (▲) and Co fcc (■)

At the beginning of the reduction process (150 °C), the catalyst presents two cobalt phases. Some CoO is visible at the outer part of the pellet while Co_3O_4 , the predominant phase, is present throughout the catalyst with two rings of higher intensity (on the outer circumference and within the pellet). At 350 °C, the intensity of the Co_3O_4 Bragg reflections is highly reduced. CoO has now spread through all of the pellet in place of the Co_3O_4 and Co fcc is starting to appear. At the end of the reduction step (450 °C), the metallic cobalt is now the predominant phase. However, not all of the cobalt oxide is reduced as the Co_3O_4 phase didn't change and the CoO phase is still present. Finally, during FTS, the cobalt inside the pellet isn't greatly altered, but the outer circumference undergoes a major re-oxidation (CoO and Co_3O_4) which have been reported as a potential effect of the presence of water [2]. This significantly reduces the metallic Co fcc in this area.

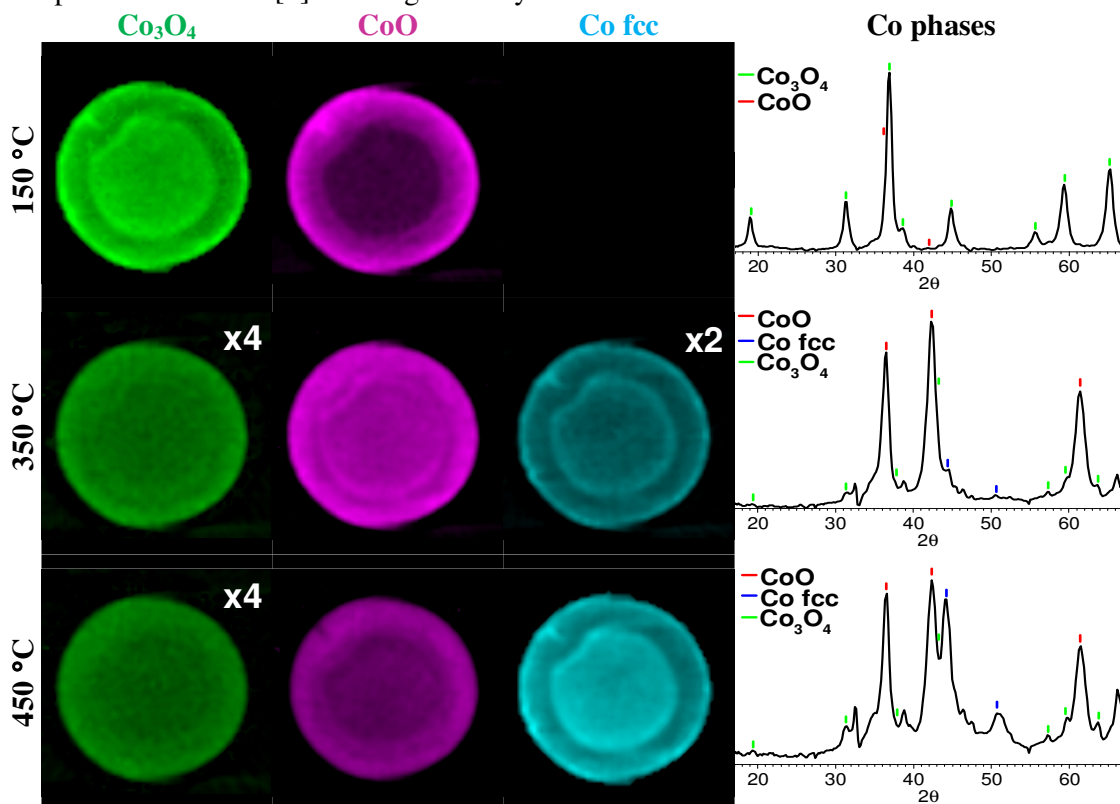


Figure 2: Reconstructed images and diffractograms (after suppression of the quartz and the γ - Al_2O_3 patterns) of cobalt phases observed at 150 °C, 350 °C and 450 °C under reduction and during FTS (250 °C) of a γ - Al_2O_3 supported Co catalyst precursor.