

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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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.



	Experiment title: Surface analysis of methane oxidation on Co(0001) and its linking with industrial powder catalysts	Experiment number: SI-2233
Beamline:	Date of experiment: from: 31 May 2011 to: 06 June 2011	Date of report: 29/02/2012
Shifts:	Local contact(s): Olivier Balmes	<i>Received at ESRF:</i>
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Report:

Perovskite oxide systems (ABO_3 , with B=metal) are attracting considerable interest due to their activity in the catalytic oxidation of hydrocarbons (A-site substitution controls the mobility of lattice oxygen atoms, while B-site substitution seeks to enhance the catalytic properties). They offer the structural flexibility that these catalysts require for H_2 generation. In the case of powder cobalt catalysts, the metallic elements aggregate forming particles as in the case of cobaltites. However, linking the evolution of the structure at atomic level with the variations in its catalytic activity by monitoring the production of the resulting gases at high temperatures and pressure is a difficult task due to the intrinsic polycrystalline nature of the sample that makes the identification of the basic surface mechanisms responsible of its catalytic activity. For this reason, it is necessary to follow the catalytic activity on close model systems to the real one to understand the surface mechanisms that govern these processes. For this reason we selected to study the methane oxidation process on single Co(0001) crystals at low and high temperatures.

During the experiment we first used this cobalt catalyst to study the CO-oxidation reaction process at temperatures below the hcp to fcc phase transition that takes place around $500^\circ C$. In a second part of the experiment we followed the methane oxidation reaction process between $550^\circ C$ and $850^\circ C$ using in all cases 5% diluted reagent gases in Ar, i.e. CO, CH₄ and O₂.

Previous to the methane oxidation experiment, the cobalt crystal was pre-treated in the reaction chamber by oxidation (0.2 mbar O₂ at 520 K) and annealing at 575 K cycles until removing the residual carbon and oxygen from the surface. The same cleaning procedure was already applied in a previous LEED and STM experiment in our home UHV lab.

The methane oxidation reaction experiment was divided in three parts:

- i) A series of ramp temperatures were measured at different constant CH₄:O₂ partial pressure ratios to determine the lower activation temperature of the reaction as shown in figure 1, where the CH₄:O₂ ratio was of two.

- ii) Measurements performed at constant temperature (600 to 850°C) and CH₄ partial pressure while increasing/decreasing O₂ partial pressure in constant steps and vice versa.
- iii) Measurements performed at constant temperature (600 to 850°C) while increasing/decreasing the CH₄ and O₂ partial pressures at constant CH₄:O₂ ratio.

These measurements were performed to get the activation energy of the partial oxidation reaction of methane and to explore the selectivity of the methane oxidation since it depends on different parameters as temperature, partial pressures of reactive gases and total flux rate of the gas mixture. The ratios between the gas partial pressures from the reaction, H₂:CO₂ or H₂:CO, will help to discriminate the type of reaction process takes place. Moreover, it could also happen that the oxygen concentration in the cobalt sample (surface oxide and bulk oxide formation) could modify the selectivity of the methane oxidation.

For this reason, apart to follow the evolution of the surface oxide and bulk oxide single crystal peaks, we also followed the evolution of identical phases but in polycrystalline form that were formed on the crystal. For this reason a series of two-theta scans at fixed grazing incidence angle were also measured. From the partial analysis of these scans three different phases were identified from the diffraction pattern (cobalt fcc, cobalt oxide: CoO and bulk oxide: Co₃O₄). These patterns show an evolution that depends on both the temperature and partial pressure of the reagent gases and the history of the applied condition measurement. The analysis of the data still is not completely finished due to the extra measurements we are doing in our lab on polycrystalline cobalt samples to reproduce the same behavior than that observed in the present experiment. However, this procedure we are doing in our lab is not completely identical to that followed in ID03 since our reacting chamber is not coupled to any diffractometer, so, the diffraction measurements can only be done ex-situ.

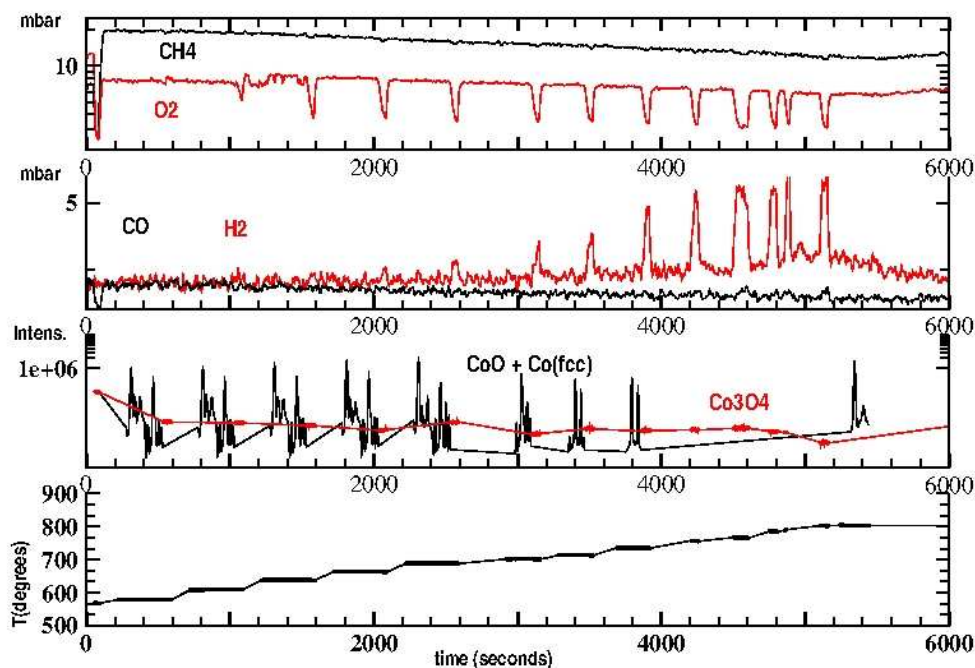


Fig. 1. Evolution of the partial pressures of the reagent CH₄ and O₂ gases and products of the reaction. The peaks are due to the fact that measurements were done in batch mode (gas flow interrupted). Intensity measurements were done in flow mode measuring some directional scans to follow the evolution of metallic cobalt, surface oxide (CoO) and bulk oxide (Co₃O₄) with temperature. It is clearly observed that methane oxidation increases with temperature being even observable in flow mode as a modulation of the background curve. At this particular (CH₄:O₂) partial pressure ratio, the CO as well as the H₂O formation is still small.