



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>

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.



	Experiment title: In operando investigation by EXAFS of ethanol steam reforming within a thermochemical loop	Experiment number: CH-4491
Beamline: BM23	Date of experiment: from: 06/11/15 to: 09/11/15	Date of report: 28/08/16
Shifts: 6	Local contact(s): Debora Meira	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Stefano Agnoli and Francesco Carraro* Laboratory Universita di Padova Dipartimento di Scienze Chimiche Via Marzolo 1 IT - 35131 PADOVA Vozniuk Olena* Laboratory Universita di Bologna Dipartimento di Chimica Industriale Viale del Risorgimento, 4 IT - 40136 BOLOGNA		

Report:

In this proposal we wanted to study in operando conditions the chemical and structural changes occurring during the steam reforming of ethanol on nanocatalysts based on ferrites with different dopants ($\text{Co}_x\text{Mn}_y\text{Fe}_2\text{O}_4$). In particular, the steam reforming is achieved using a thermochemical loop that consists in the sequential dosing of ethanol and water, which therefore determine reduction and oxidation cycles in the materials. By using QuickEXAFS on the Fe, Mn, and Co K edge, we wanted to follow the kinetics of the phase transformations induced by ethanol, during which the ferrites are transformed to more reduced oxides and eventually metal phases. Similarly, we wanted to investigate the oxidation process of the reduced form of the catalysts operated by water, with the aim of identifying the possible formation of different oxide phases, mixed oxides, and hydroxides. The in operando Quick EXAFS measurements were carried out in fluorescence mode at the Fe K, and Co K edges. The samples in powder form were diluted with boron nitride (mass ratio=1:1.2) and inserted in quartz capillaries (diameter=1.5 mm, wall thickness=0.03 mm) that were connected to a heated gas line. Ethanol and water were dosed by saturators and using nitrogen as carrier gas. The samples were heated from RT to 450°C by a hot wall furnace. Unfortunately, we had several problems with the gas dosing system of the beamline, probably due to air (?) leaks in the connections of the saturators. We passed most of the beamtime trying to figure out what was the problem, and when we solved this issue, it was too late to complete all the planned experiments: we could properly dose ethanol and water only on one sample (CoFe_2O_4). Moreover, there was a problem with the mass spectrometer (gas line obstructed?), so we could not follow the gas products of the thermochemical loop during the EXAFS measurements. After 2 hours of ethanol exposure, the material was completely reduced: both Fe (Figure 1a,c) and Co (Figure 1b,d) K edges XANES and EXAFS confirmed the formation of metallic phases. Interestingly, the Co reduced (metal?) phase was stable and the successive oxidative cycle in water did not affect significantly the material. Conversely,

in the case of Fe K-edge we could observe that after 2 hours of water dosing Fe was reoxidized, though not as much as in the starting material. Thanks to the QuickEXAFS, during the 2 hours of ethanol exposure we were able to follow carefully the kinetics of reduction. In fact, we measured a XANES spectra at the Co K-edge every 133 seconds (for sake of simplicity, in Figure 2 are not plotted all the spectra acquired, but just one in four). The Co K-edge white line started to strongly decrease its intensity after about 15 minutes and Co is completely reduced after about 100 minutes.

Unfortunately, due to the experimental problems discussed above, we couldn't exploit all the potentiality of the QuickEXAFS during this beamtime. Therefore, the data collected during this beamtime are not sufficient to understand the effect of a different dopant on the reduction/oxidation mechanism of different ferrites as planned in the proposal. Nonetheless, we were able to point out a quite different behaviour between Fe and Co, observing a quite surprising resilience of Co towards reoxidation by water. This same experiment was also attempted at the ROCK beamline at SOLEIL synchrotron. Capitalizing on the knowledge acquired at BM23, we have adopted a different experimental set up for dosing ethanol, methanol and water in the capillaries, which exploited syringe pumps. Thanks to these devices, we avoided the problems that we had with the saturators and were able to dose a higher (and more accurate) amount of the desired liquid reactant (i.e. reaching the complete reduction of CoFe_2O_4 in 20 instead of 2 hours). Therefore, we were able to exploit the potentiality of the QuickEXAFS: we investigated the reduction kinetics of different ferrites and we carefully followed the phases that are formed during the reduction and during the reoxidation cycles.

In conclusion, we regret having so many experimental problems related to the gas lines, because we are rather confident that without this issue, we could have obtained many data from this beamtime. Actually, we verify that the time resolution of the QuickEXAFS is adequate to follow the kinetic of reduction/oxidation of our catalysts in working conditions.

Moreover, the difference in the EXAFS spectra are rather obvious and quite distinctive of the different phases, therefore the use of this technique carried out in a more controlled reaction environment could have represented an ideal tool for following the oxidation and reduction phase transformation.

Figures:

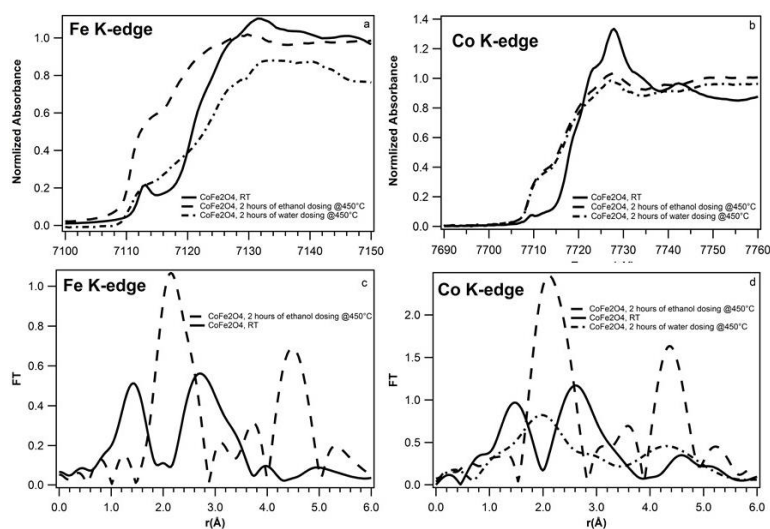


Figure 1: XANES spectra at Fe K-edge (a) and Co K-edge (b) and Fourier transforms of $k^3\chi(k)$ at Fe K-edge (c) and Co K-edge (d) of CoFe_2O_4 sample at room temperature, after 2 hours of ethanol dosing and after 2 hours of water dosing.

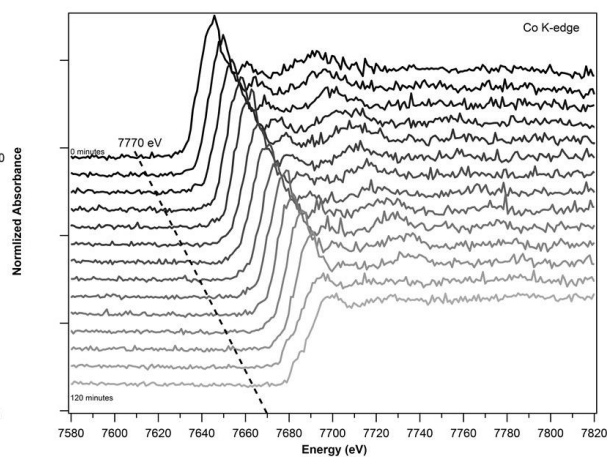


Figure 2: XANES spectra at Co K-edge of CoFe_2O_4 during the 2 hours of ethanol exposure at 450 °C.