

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: Characterization of innovative Rhodium based catalysts for hydrogen production from natural gas	Experiment number: MA 1287
Beamline: ID21	Date of experiment: from: 08/07/2011 to: 12/07/2011	Date of report: 14/02/2012
Shifts: 12	Local contact(s): Murielle Salome	<i>Received at ESRF:</i>

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Report:

Introduction:

The goal of this experiment was to determine the speciation of rhodium in rhodium based catalysts. These are being used for the production of H₂ from methane by catalytic partial oxidation and coat a FeCrAl metallic foam that has a very high porosity and heat capacity. The catalysts are obtained by calcination of hydrotalcite-type (HT) compounds electrosynthesized on the surface of the foam. Previous characterization revealed that deposition of the catalytic materials by means of this new electrochemical process, yields a thin and stable catalyst layer coating the foams [1]. An overview of the lifecycle of these rhodium catalysts, from "bare metallic foam" to "used catalyst" is given in fig. 1. The catalysts produced under different experimental conditions were examined in three states: A, B and C. The different samples were embedded in polymethylmethacrylate, these resins were then cut and polished in a way that cross sections of different struts were free at the surface of the resin. Before any XANES measurements was done, XRF maps were taken of areas of interest. By setting a ROI of interest around the Rh-L α fluorescence line these maps could then be used to localize Rh rich areas, of which XANES spectra could be taken.

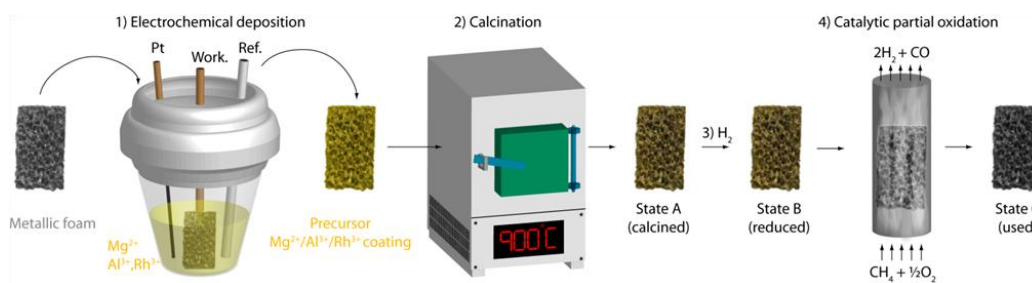


Figure 1: Different stages in the lifecycle of a structured rhodium catalyst based on a FeCrAl metallic foam. (1) Electrochemical deposition of Rh^{3+} , Al^{3+} and Mg^{2+} cations with formation of hydrotalcite-type compounds (2) Calcination of the precursor at $900^{\circ}C$: state A. (3) Reduction under hydrogen flow: state B. (4) Use in a catalytic partial oxidation reactor: state C.

Quality of measurement/data:

The flux (10^{10} ph/s, for the measured samples using the zone plate focussing optics) made it possible to measure noise free XANES spectra in less than 20 minutes. The 0.22 by 0.85 microns beamsizes allowed us to examine the thin Rh layer, which is not a lot thicker than 5 microns. A 0.5 micron step size could then be used for the XRF maps. On the downside the beam moved during the XANES energy scan, which made it difficult to acquire good XANES spectra of the heterogeneous Rh layer. Since the movement resulted in scanning regions with different Rh concentration and thus a higher or lower fluorescence intensity.

Status and progress of evaluation:

For both the XRF mapping and the XANES measurements the PyMCA software package was used for the fitting of the XRF spectra, as is visualised in figure 2.

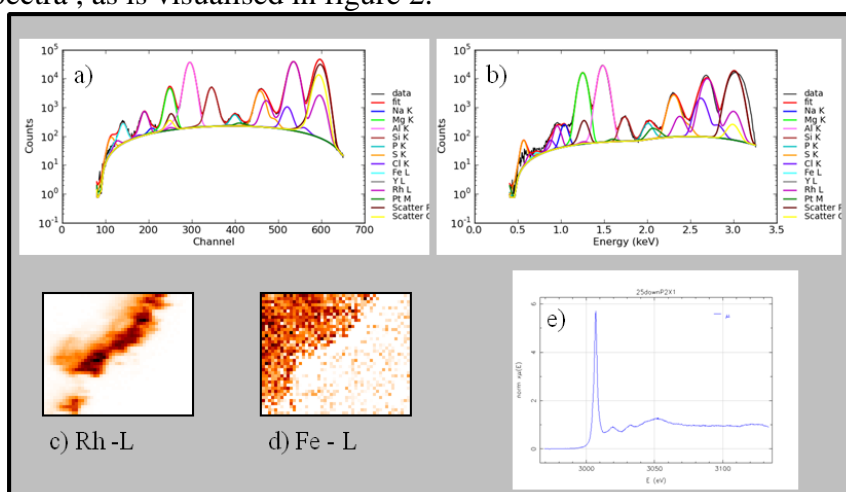


Figure 2: After scanning the surface of the resins with the focused x-ray beam, the X-ray fluorescence spectra of the Si drift diode array (a) are fitted with PyMCA and the resulting elemental maps can be calculated from the fitted intensity (c: Rh-L and d: Fe-L). For the XANES measurement a point of interest is scanned with a X-ray beam varying in energy and for each energy a XRF spectrum (b: spectrum with excitation energy 3005 eV) is recorded. After fitting these spectra the intensities of the Rh-L lines are given as a function of the excitation energy resulting in a XANES spectrum (e).

Several points were measured on each sample, distributed over the entire sample area. The XANES spectra were then fitted with measured reference compounds, by means of linear combination fitting using the ATHENA software package. The reference compounds included several $Rh_xMg_yAl_z$ HTs, calcined $Rh_xMg_yAl_z$ compounds, Rh_2O_3 oxide and Rh metal.

Results:

The different states in combination with different synthesis conditions that have been analyzed, are summarized in table 1.

Atomic ratio's	Precursor (HT)	State A (900°C)	State B (750°C)	State C
Rh ₁₁ Mg ₇₀ Al ₁₉	20	4, 22	23	24, 25
Rh ₅ Mg ₇₀ Al ₂₅		28		
Rh ₂ Mg ₇₀ Al ₂₈		34		
Rh ₅ Ni ₁₅ Mg ₅₅ Al ₂₅		38		
Rh ₁₁ Al ₈₉		44		

Table 1: Catalyst production states and experimental conditions.

The experiment clearly revealed that after calcination and before reduction Rh is mainly present as a Rh spinel compound, as is shown in figure 3 for example. After reduction Rh is found also as Rh⁰ in the measured samples in a relative concentration range of 21.37% - 53.4% in relation to the spinel compound. Meaning that reduction is apparently not complete. After catalytic tests there is a relative decrease of Rh⁰ (range 10.1% - 38.7%) in respect to Rh in the spinel form. This indicates that the Rh is being partially oxidized during usage; however, the oxidation of the Rh by exposure to the atmosphere could not be discarded.

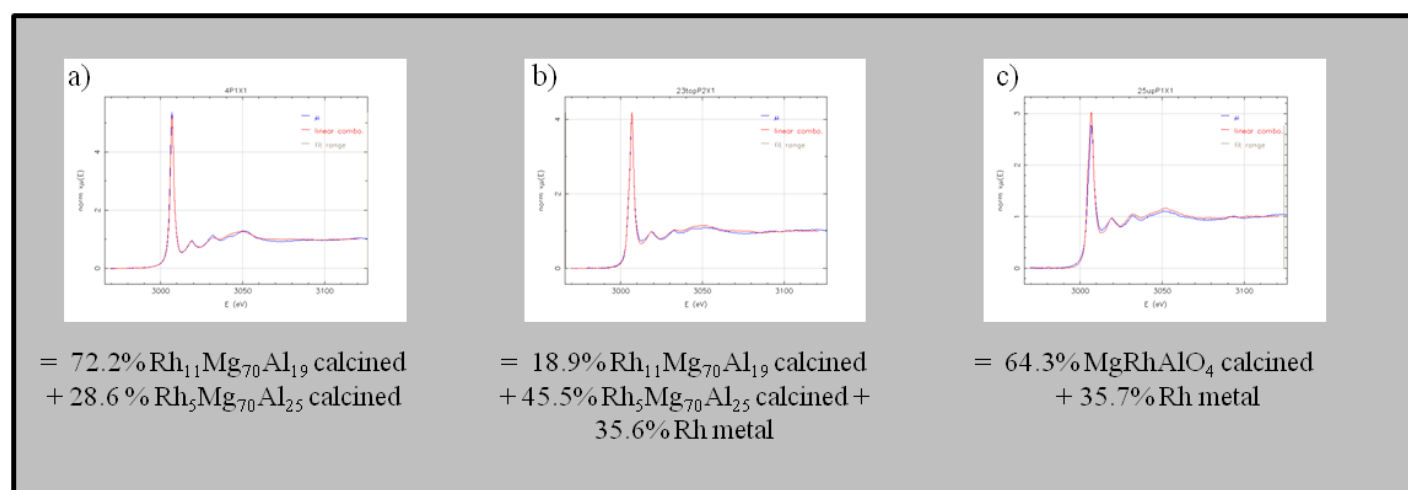


Figure 3: LCF of a XANES spectrum of a point from the sample in three different stages. A) calcined at 900°C, b) reduced at 750°C and C) used.

References

1. Basile, F., et al., *Combined Use of Synchrotron-Radiation-Based Imaging Techniques for the Characterization of Structured Catalysts*. *Advanced Functional Materials*, 2010. 20(23): p. 4117-4126.