

## 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.



	<b>Experiment title:</b> In situ XAFS study of the supporting CoMo catalytic precursors on $\gamma$ -alumina. Effect of phosphorus and glycol on the crystallites catalytic sites	<b>Experiment number:</b> 01-01-608
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 5/10/2002 to: 8/10/2002	<b>Date of report:</b> 08/08/2003
<b>Shifts:</b> 9	<b>Local contact(s):</b> Hermann EMERICH	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Nicosia Daniele*, Jeroen Van Bokhoven*, Virginie Zuzaniuk*, Eveline Bus*, Prof. Roel Prins Institute for Chemical- and Bioengineering ETH Zürich Wolfgang Pauli Strasse 10 8093 Switzerland		

## Report:

Cobalt-molybdenum catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are extensively used in the refinery industries to remove sulfur from oil feedstock. Recently, improvements in the catalytic activity have been achieved using glycol and phosphate during the preparation of the catalyst [1]. The first step in the preparation of this catalyst is the dissolution at 80°C of cobalt carbonate and molybdenum trioxide in a solution containing phosphoric acid. Phosphoric acid and molybdenum trioxide form phosphomolybdate species in the impregnating solution [2]. When the solution becomes clear, a certain amount of glycol like triethylene glycol (TEG) is added. The catalyst precursor is prepared by pore volume impregnation of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. This method consists in pouring an amount of impregnating solution that corresponds to the pore volume of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> drop-wise over this material. A subsequent drying step at 120°C causes the precipitation of the catalytic precursors in the pores of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Normally phosphomolybdate species are unstable on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Such species react with the coordinative unsaturated (C.U.) alumina sites and decompose into AlPO<sub>4</sub> and aluminum molybdate [3]. The TEG may also react with the alumina C.U. sites in order to prevent the decomposition of the phosphomolybdate. As a weak reducing agent, TEG can reduce the molybdenum in the phosphometalate cluster [4]. This reaction can occur during the drying step of the impregnated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. The aim of our experiment was to investigate what happens with the electronic state of molybdenum during the drying step. We performed in-situ Mo-K edge XANES experiments of two samples: CoMoPTEG/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, containing

TEG, and CoMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> without TEG. In the ESRF chemistry laboratory we did a pore volume impregnation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The wet powder was fixed in the sample holder by means of two layers of kapton tape and then the sample holder was mounted in the EXAFS cell. The in-situ XANES experiments (energy range 19800-20100 eV) were performed while heating from room temperature to 150°C at 5°C/min. The results are shown below.

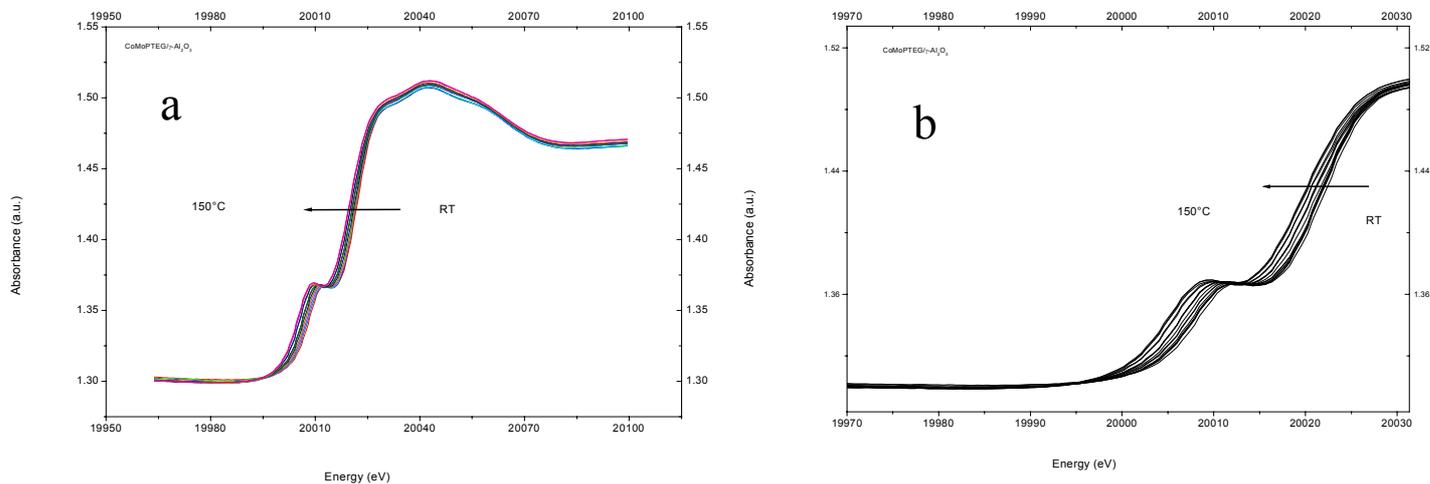


Figure 1: In-situ XANES of CoMoPTEG/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> – a) overall view, b) closer view

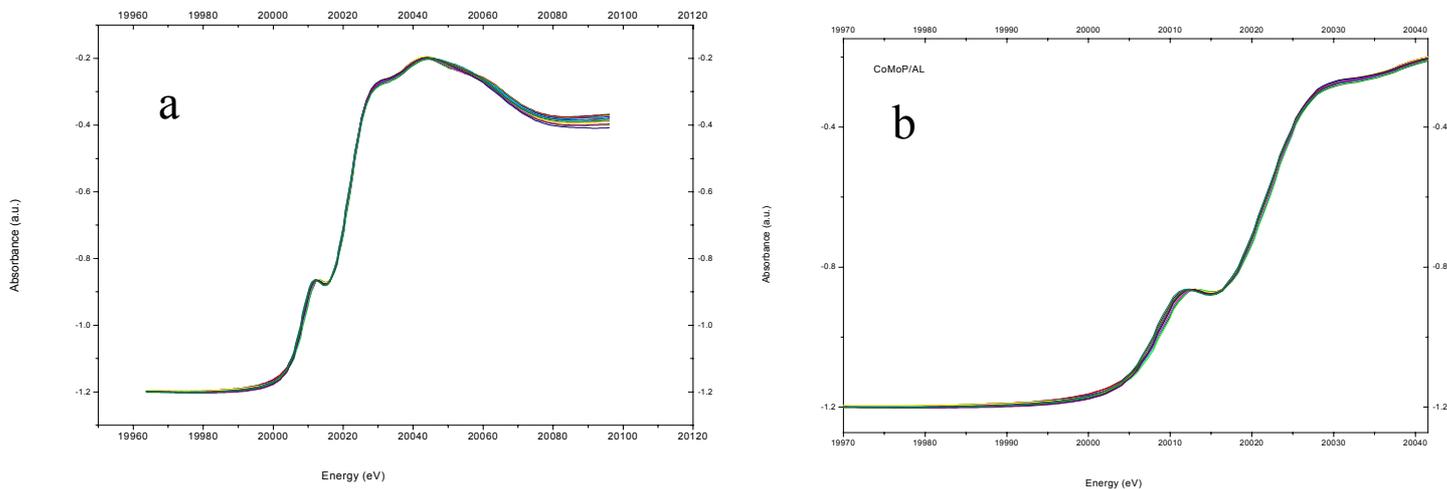


Figure 2: In-situ XANES of CoMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> – a) overall view, b) closer view

Figures 1 and 2 show the in-situ Mo-K edge XANES of CoMoPTEG/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively. Figure 1 shows that during the heating the Mo-K energy edge is moving to lower energy (from 20023 to 20019 eV), meaning that the oxidation state of Mo is decreasing. Figure 2 shows that during the experiment the energy edge stays almost constant. Since the only difference between the two samples is the TEG, we can state that during the drying step TEG is reducing the molybdenum in the phosphomolybdate.

## Referencies

- [1] Euro Patent EP 0601722 B1
- [2] Petterson L. *Acta Chem. Scand.* **25**, 1959-1974 (1971)
- [3] Cheng W-C, Luthra N. P. *J. Catal.* **109**, 163-169 (1988)
- [4] Bandwar R.P., Rao C.P. *Carbohydrates Res.* **277**, 197-207 (1995)