

## 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> Relationship between glycol and phosphomolybdate structure in the CoMo hydrodesulfurization catalys	<b>Experiment number:</b> 01-01-280
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 05 July 2002 to: 11 July 2002	<b>Date of report:</b>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Wouter VAN BEEK	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Daniele Nicosia*, Virginie Zuzaniuk*, Gerhard Pirngruber*, Prof. Roel Prins		

## Report:

Cobalt-Molybdenum sulfides catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are extensively used in the refinery industries to remove sulfur from oil feedstocks. Recently, improvements in the catalytic activity have been achieved using glycols and phosphate during the preparation of the catalysts. The catalyst is prepared by pore volume impregnation of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support with a solution containing phosphoric acid, cobalt carbonate, molybdenum trioxide, and a glycol like triethylene glycol (TEG). Phosphoric acid and the molybdenum precursor form a phosphomolybdates species in solution, whereas the structural role of the glycol is not known yet. Phosphomolybdates are unstable over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. They may react with the coordinative unsaturated Al sites (C.U.S.) forming AlPO<sub>4</sub> and heptamolybdate. Our previous Mo-K edge EXAFS experiments proved that triethylene glycol affects the structure of the molybdenum precursors over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support as shown in figure1 (not phase-corrected). Now we report the proof that the effect of TEG is to suppress the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> C.U. sites preventing the decomposition of the phosphomolybdate. Figure 2 shows a comparison between the Mo-K edge EXAFS (not phase-corrected) of a silica-supported CoMoP catalyst and a CoMoP catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> impregnated with TEG. The silica support does not have C.U. sites thus the silica-supported CoMoP catalyst and the CoMoP supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TEG, show a similar EXAFS.

Fig. 1

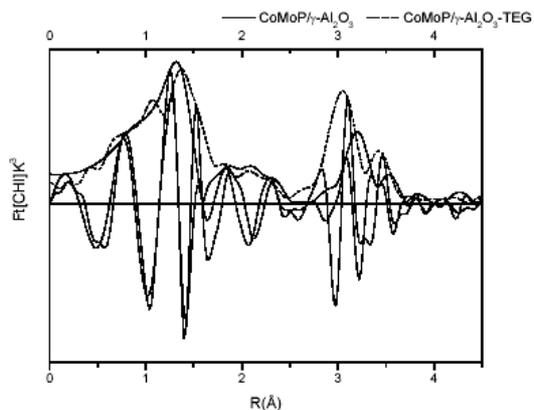
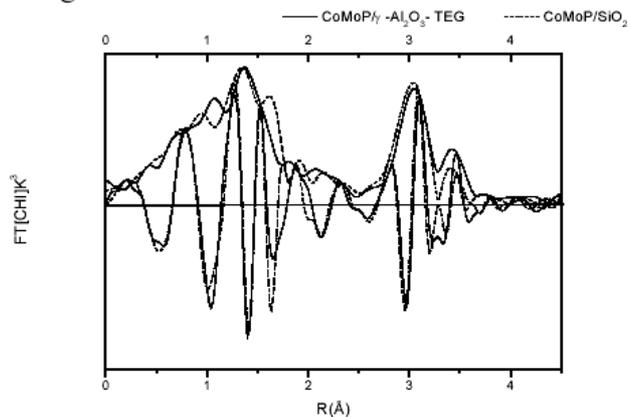


Fig. 2



According to our preparation method and to IR measurements, the CoMoP/SiO<sub>2</sub> sample might contain the cobalt diphosphopentamolybdate species (Co<sub>3</sub>P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>). So we did a data-fit (Fig. 3, not phase -corrected) based on the crystallographic data of Na<sub>5</sub>HP<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>. Table 1 show the result of the fits. The region between 1 and 2 Å (not phase-corrected) in all the spectra, shows a typical distorted octahedral O shell. The results of the fit in the CoMoP/SiO<sub>2</sub> sample in the region between 2 and 4 Å confirm that the cobalt and molybdenum precursors crystallize as Co<sub>3</sub>P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub> on the SiO<sub>2</sub> support.

Table 1: Mo-K EXAFS: CoMoP/SiO<sub>2</sub> Fit-data  $\Delta k = 16.0$ ,  $\Delta R = 2$

Shell	$N_{\text{fitted}}^a$	$N_{\text{th.}}$	$\Delta\sigma^2 * 10^{-3}$	$R(\text{\AA})_{\text{fitted}}^b$	$R(\text{\AA})_{\text{th.}}^c$	$\Delta E^\circ$
Mo-Mo	2.17	2	2.94	3.40	3.37	6.13
Mo-P	1.87	2	0.25	3.55	3.46	4.0
Mo-Co	1	1	6.0	3.65	3.71	-8.54

<sup>a</sup>:  $\pm 10\%$ , <sup>b</sup>:  $\pm 1\%$ , <sup>c</sup>: average values

FitGoodness: 0.04      Variances: Im part / ABS part: 2.45 / 1.03

The fit of CoMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TEG (Fig. 4 and Table 2) shows that the structure of Co<sub>3</sub>P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub> is retained although TEG causes an increase of the Debye-Waller factors of the Mo-P and Mo-Co shells. This can be explained by the fact that TEG suppressed C.U.S of alumina and prevented the decomposition of the phosphomolybdate species. We observed the same behaviour when bare SiO<sub>2</sub> is used as support.

**Table 2: Mo-K EXAFS: CoMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TEG Fit-data  $\Delta k = 15.1$ ,  $\Delta R = 2$**

Shell	N <sub>fitted</sub> <sup>a</sup>	N <sub>th.</sub>	$\Delta\sigma^2 * 10^{-3}$	R(Å) <sub>fitted</sub> <sup>b</sup>	R(Å) <sub>th.</sub> <sup>c</sup>	$\Delta E^\circ$
Mo-Mo	1.88	2	3.48	3.42	3.37	5.07
Mo-P	1.77	2	1.11	3.56	3.46	6.5
Mo-Co	0.87	1	2.75	3.64	3.71	-7.06

<sup>a</sup>:  $\pm 10\%$ , <sup>b</sup>:  $\pm 1\%$ , <sup>c</sup>: average values

FitGoodness: 0.0033 Variances: Im part / ABS part: 2.27 / 1.36

Fig. 3

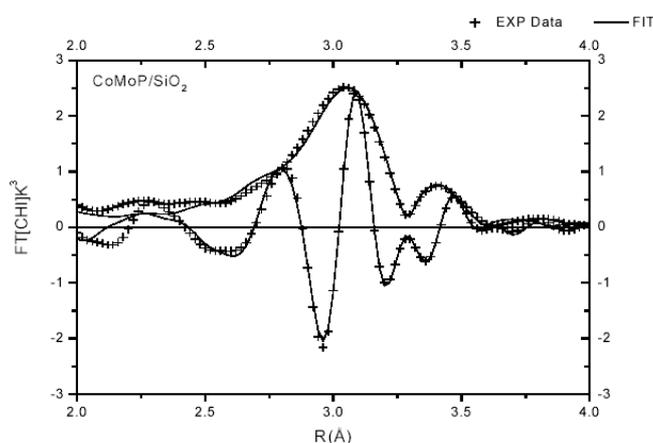
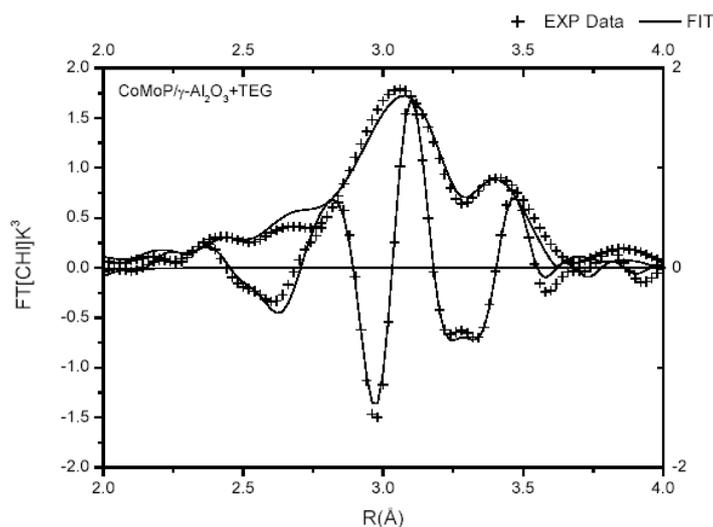


Fig. 4



Thus, the results prove that the main role of glycol is to retain the structure of the phosphomolybdate structure over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Phosphomolybdate may be responsible for the increase of the catalytic activity in the CoMo hydrodesulfurization catalysts.