

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.



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| | Experiment title: Investigation of an active site structure of CoMo/Y-Al ₂ O ₃ hydrosulfurization catalysts containing phosphates and glycols. | Experiment number: 01-01-273 |
| Beamline: BM01B | Date of experiment: from: 7/11/2001 to: 12/11/2001 | Date of report: 5/02/2003 |
| Shifts: 15 | Local contact(s): Wouter VAN BEEK | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Daniele Nicosia*, Viviane Schwartz*, Prof. Roel PRINS | | |

Report:

Cobalt-Molybdenum sulfide catalysts are used in the petroleum industry to remove sulfur atoms from molecules in oil fractions. Usually they are prepared by pore volume impregnation of a γ -alumina support with a solution containing cobalt and molybdenum salts. To activate the dried powder a further sulfiding step is required. This is done by means of flowing an 10% H₂S/H₂ mixture over the catalyst precursor. Recently it has been proved that significant improvements of the catalytic activity are obtained when glycosidic compounds and phosphate are added during the preparation of the catalyst. It is very important to understand how these compounds interact with the active sites.

In this study we performed Mo and Co-K edge EXAFS measurements of catalyst supported on γ -alumina and prepared in absence and presence of triethylene glycol (TEG). The sample containing TEG will be called CoMoPTEG/Al and the one not containing TEG will be called CoMoP/Al. All the measurements were carried out in transmission. The temperature was 77 K in order to diminish the Debye-Waller effect. Each spectrum was averaged over 3 scans in order to increase the signal-to-noise ratio.

Results

Figure 1 shows the Mo K edge EXAFS spectra of the oxidic alumina-supported catalyst. Both spectra are typical for polymolybdate clusters. These experiments show that when glycol is present in the catalyst, the structure of the Mo clusters changes dramatically. The signal at ca. 1.7 Å (phase not corrected), due to the nearest oxygen shell, broadens; the amplitude of the signal at 3.5 Å (phase not corrected) due to Mo-Mo second coordination, increases. This might be due to the fact that glycol affects the interaction between the

Fig.1: Mo K-edge of CoMoP Alumina supported: The TEG effect

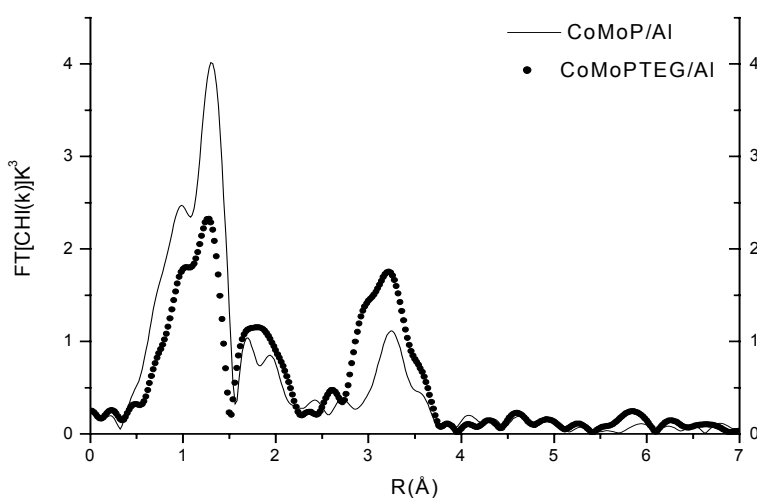
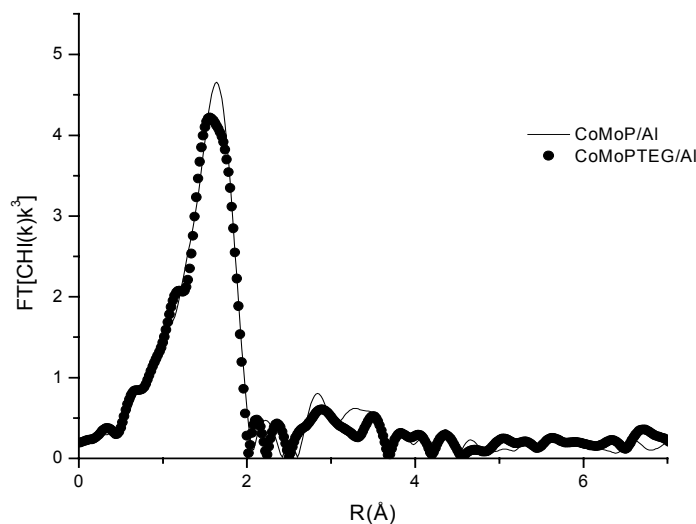


Fig.2: Co K-edge of CoMoP Alumina supported: The TEG effect



molybdenum precursor species and the alumina support leading to larger molybdenum clusters in which the Mo atoms are surrounded by a much more distorted octahedral shell of oxygen atoms. Figure 2 shows the Co-K edge of the same samples. As we can see, the glycol does not affect the Co local structure. Thus we conclude that the main role of glycol is to prevent a strong interaction between molybdenum precursors and alumina support. According to Topsøe et al. such a system can be better sulfided and leads to the most active “Co-Mo-S” type II structure. .