EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.

ESRF	**Experiment title:** ASAXS study of the influence of the critical steps of the catalyst synthesis on oxide precursor phase and sulfide slabs multiscale Mo organization	**Experiment number**: 02-01-901
Beamline: BM02	**Date of experiment**: from:13/07/2021 to: 16/07/2021	**Date of report**: 09/09/21
Shifts: 9	**Local contact(s)**: DE GEUSER Frederic	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Objectif & expected results:

The aim of this study, which was an integral part of C. Cottrez's thesis, was to lead to a detailed description of the multi-scale structure of hydrotreatment catalysts, based on molybdenum sulfide supported on alumina, and synthesized by incipient wetness impregnation. First, these results should help to evaluate the role of synthesis steps as ageing, drying or either additivation, onto the arrangement of the sulfides slabs. These knowledges should then allow to elucidate the genesis of Mo aggregates and establish a relationship between the sulfide phase multi-scale repartition, its accessibility, and the intrinsic activity.

Results and preliminary conclusions of the study:

36 catalysts were analyzed, varying: the loading of molybdenum oxide (from 18 to 30% wt), the presence of organic additives (with/without), the presence of an ageing step (with/without), and the drying parameters.

ASAXS experimentations were recorded slightly below the Mo K-edge, at 5 different energies: 19700, 19860, 19940, 19975, 19990 eV. As we wanted the largest q-domain as possible (typically between 10^{-2} and 1 A^{-1}), two detector/sample distances were used (3m and 35cm). As a first step, the curves of intensity measured for the 5 energies were subtracted two by two in order to obtain the intensity scattered by the sulfide slabs and to eliminate the contribution of the porous support [1,2].

Information obtained from the ASAXS data can be divided into two parts through the q-scale: (i) the large q that are related to the scale of the slabs: the intensity depends on the size of the slabs and on their stacking, (ii) the low q that are related to the cluster/aggregate of the slabs. The comparison of the ASAXS curves already give qualitative information but preliminary data exploitations have also been done for the last three months, but this work is underway and must continue. Few examples are presented below.

First results

- Effect of ageing step:

Three different catalysts are compared to assess as a first sight the effect of the ageing step:

- A 26%Mo-catalyst subjected to an 8h-ageing, then dried
- A 26%Mo-catalyst with no ageing step, followed by a necessary freeze-drying step
- A 26%Mo-catalyst subjected to an 8h-ageing and then freeze-dried

The ASAXS curves obtained on the three catalysts are reported on figure 1. Significant differences can be observed for both isolated slabs and clusters of sulfide slabs. At smaller scale, the ageing step leads to taller slabs (2.7 nm versus 1.8 nm). At larger scale, the ageing step might tend to obtain larger aggregates (9 nm versus 7.7 nm). To rule out the effect of the freeze-drying step, the aged catalysts dried and freeze-dried can also be compared. It appears that the shape of both curves is very similar and differences in terms of slabs length and aggregates size are much smaller. Therefore, we might affirm that the ageing effect is predominant on the Mo organization compared to the freeze-drying effect.

- Influence of %Mo aggregated onto the intrinsic activity:

As a first approach, the intrinsic activity was faced to the amount of molybdenum involved into aggregates (figure 2), since this relationship had been observed in a previous work [3]. It seems that this relationship is indeed verified for many catalysts that have undergone post-additivation, freeze-drying (with or without an ageing step). However, these results remain preliminary and need to be consolidated.

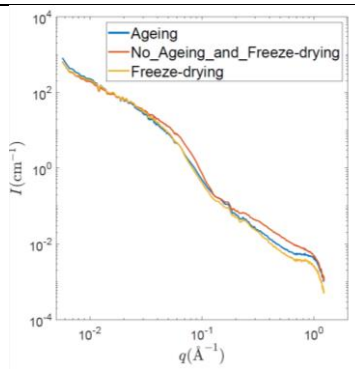

Figure 1. ASAXS curves (I_{19940}-I_{19990}) of catalysts at 26% wt MoO_3 about the effect of ageing step

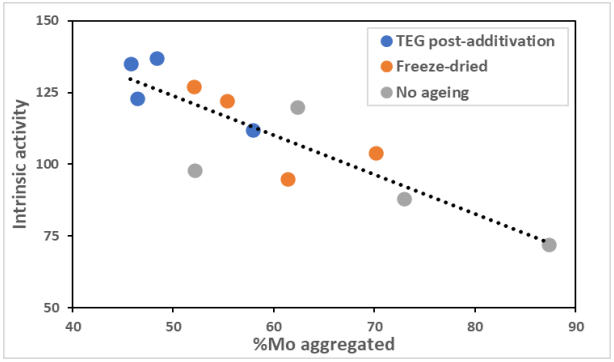

Figure 2. Influence of %Mo aggregated onto the intrinsic activity

Pesrpectives

Exploitation of the data needs to be continued and finalized. ASAXS technique is totally suitable to characterize the sulfide active phase of this kind of catalyst as it gives crucial information on the size of the slabs and aggregates. It is crucial for C. Cottrez's thesis project as it allows studying the influence of each synthesis step on the catalyst active phase arrangement. Furthermore, it is now necessary to study the influence of the impregnation step through different impregnation modes (incipient wetness with successive impregnation steps or with different solution viscosity, impregnation by equilibrium adsorption, or impregnation by melt infiltration). This additional investigation will complete the study of the complete chain of the catalyst synthesis.

Justification and comments about the use of beam time:

The 1st session (2 shifts) was used to set up the beamline and the acquisition conditions at long detector/sample distance. The 2nd session was used to record the data. The 3rd session consisted in changing manually the distance (2 shifts). The fourth session has consisted in recording the data at this short distance. This global beamtime was necessary to success recording good data as the anomalous experiments with 5 different energies is not trivial.

Publication(s):

These valuable results will undoubtedly be the subject of a future publication.

References:

[1] H.-G. Haubold, et al., Journal of Applied Crystallography 30 (1997) 653–658.
[2] T. Binninger, et al., Phys. Rev. Applied 3 (2015).
[3] S. Humbert, et al., Journal of Catalysis 395 (2021) 412–424.