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 impregnation modes on multiscale Mo organization (quantitatively and spatially resolved)	**Experiment number**: A02-1-905
Beamline: BM02	**Date of experiment**: from: 06/15/2022 to: 06/20/2022	**Date of report**: 19/01/2023
Shifts: 15	**Local contact(s)**: DE GEUSER Frédéric	*Received at ESRF:*

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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 (IWI). These results will complete the ones obtained during the previous A02-01-901 experiment about the influence of the synthesis parameters onto the multiscale sulfide slabs arrangement and currently going under publication [1]. Here, the impact of the support or metallic precursors, or the number of successive impregnations have been investigated. Also, the influence of the support heterogeneities has been investigated by ASAXS spatially resolved as it could lead to different Mo organization.

Results and preliminary conclusions of the study:

62 oxide or sulfide catalysts were analyzed, varying: the loading of molybdenum oxide (from 18 to 30% wt), the textural properties of the support (A, B and C), the nature of oxidic precursors, or the number of successive IWI. ASAXS experimentations were recorded slightly below the Mo K-edge, at 5 different energies E_i, respectively: 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 (3579 and 332 cm). Also, 6 catalysts sections (around 100µm thick) from the previous A02-01-901 experiment have been characterized by ASAXS spatially resolved with pixel resolution of 40 µm x 40 µm. ASAXS experimentations were recorded only for E_1, E_3 and E_5 for a unique and optimized detector/sample distance at 811 mm.

Information obtained from the ASAXS data can be divided into two parts through the q-scale [1,2]: (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 slabs aggregates. The comparison of the ASAXS curves already give qualitative information but preliminary data exploitations have also been done for the last months, however this work is underway and must continue. Few examples are presented below.

- **Effect of support:**

Series of catalysts have been prepared using three different supports with mono (A and B) or bi-populated (C) populations of interconnected pores. The ASAXS curves obtained for the 26 %wt MoO_3 catalysts are reported on Figure 1a. It appears that porosity has a direct impact on the slabs aggregates morphologies as the catalyst prepared on support C has a curve totally different from the two others at the smaller q values. Moreover, the aggregate content has been estimated from the modelling of the curves, which allowed to underline (see Figure 1b) the influence of the support on the aggregation state, and thus on the catalytic activity.

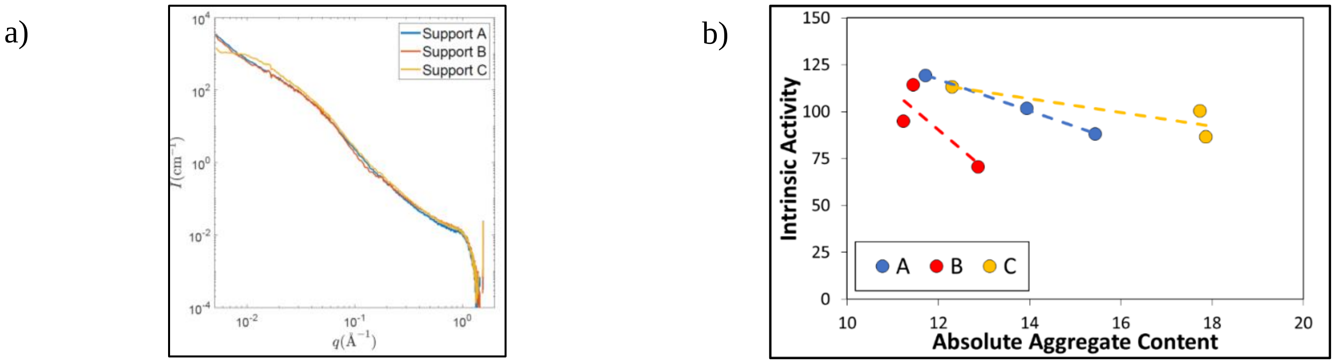

Figure 1 a) ASAXS curves (I_{19940}-I_{19990}) of catalysts at 26% wt MoO_3 about the support effect, b) Influence of the Absolute Aggregate content onto the intrinsic activity depending on the support used (A, B and C).

- **Effect of the support heterogeneities:**

Positions of areas of interest of a 26 %wt MoO_3/A catalyst aged and dried have been surveyed upstream by MEB as shown in Figure 2a. Thus, SAXS spatially resolved has been carried out and shows qualitative differences within the extrudates. Four areas of interests have been raised by MEB: the center and edges of extrudates, and the matrix and macroscopic grains of the support. ASAXS curves extracted from four pixels from these areas demonstrates that there are less Mo aggregates at the edges than in the center, and a completely different Mo arrangement in the macroscopic grains.

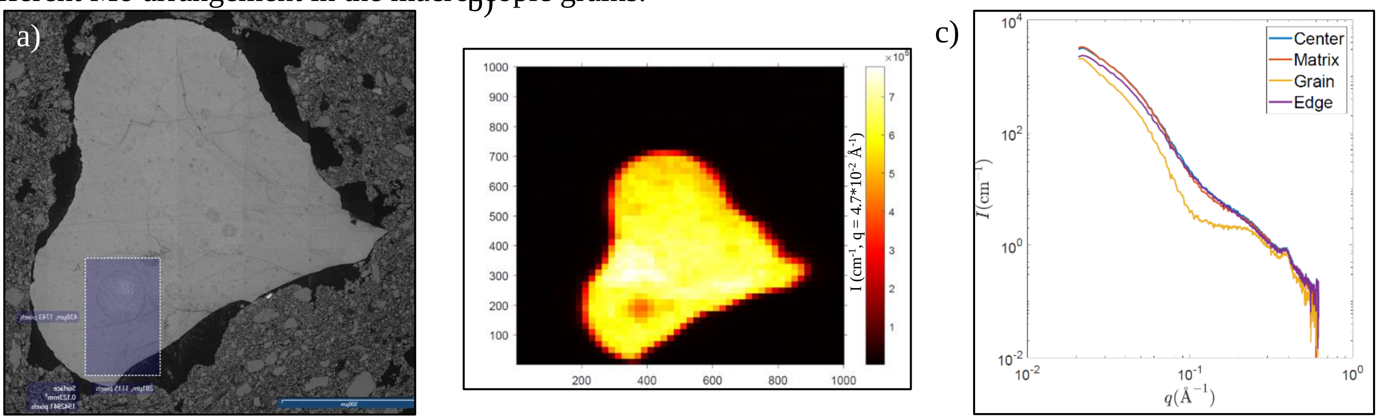

Figure 2 a) MEB image, b) SAXS spatially resolved, c) ASAXS curves extracted from pixels of the the center and edges of extrudates, and the matrix and macroscopic grains of the support of a 26 %wt MoO_3 aged and dried catalyst.

Justification and comments about the use of beam time:

For the capillary measurements, 2 shifts were dedicated to the setup of the beamline, one at each detector/sample distance, and 2 shifts for each distance were necessary to record the data (6 shifts in total). For the last session, 9 shifts were finally used, to set up the beamline, the acquisition conditions and to perform the spatially resolved measurements.

Publication(s):

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

References:

[1] C. Cottrez *et al.*, submitted ChemCatChem, under revision.
[2] S. Humbert *et al.*, Journal of Catalysis 395 (2021) 412–424.