EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

Reports supporting requests for additional beam time

Reports can 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.

ESRF	**Experiment title:** ASAXS Characterization of Ni/MoS_2 hydrotreating catalysts: impact of the synthesis conditions on the organization of the sulfide slabs.	**Experiment number**: 02-01-859
Beamline: BM02	**Date of experiment**: from: 23/04/2015 to: 27/04/2015	**Date of report**: 13/10/2015
Shifts: 12	**Local contact(s)**: Frederic De Geuser	*Received at ESRF:*

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Objective & expected results

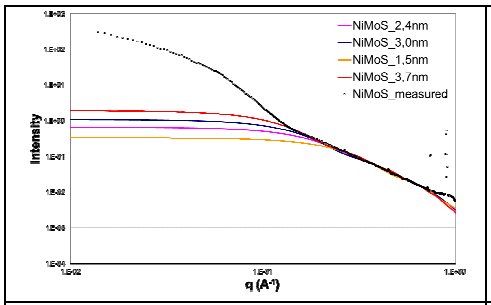
Hydrotreating catalysts consist of molybdenum sulfide slabs promoted by nickel (or cobalt) and supported on an oxide (alumina, silica-alumina, etc.).
The aim of this study was to lead to a detailed description of the multi-scale structure of MoS_2 sulfide catalysts thanks to ASAXS measurements. These results should help us to understand the role of various parameters such as the surface and textural characteristics of the support, but also of the synthesis and sulfidation conditions, on the arrangement of the sulfide slabs.
Using the ASAXS technique close to the Mo K-edge should help us to characterize the length of the sulfide slabs but also their organization (stacking, aggregation, dispersion) inside the porosity of the alumina support. The data analysis is supported by various simulation of scattered intensity performed on molecular models and by complementary techniques such as HR-STEM that allows visualizing the geometry of the MoS_2 slabs. Thanks to these characterizations, issues of interest will be addressed such as: i) the impact of the alumina properties (surface chemistry, crystallite size, pore distribution) on the sulfide slabs (size, stacking, aggregation and spatial repartition) ii) the effect of the organic additive and the amount of molybdenum (suspected to be antagonist) on the aggregation, iii) the differences generated between a gas and a liquid sulfidation, iv) the possible synergy between these synthesis conditions.

Results and the conclusions of the study (main part):

16 catalysts and 2 alumina supports were analyzed varying the support (γ/ δ-alumina), the sulfidation environment (gas/ liquid), the presence of organic additives (with/without) and the amount of molybdenum oxide (8%/22% wt).

ASAXS experimentations were recorded slightly below the Mo K-edge, at 6 different energies: 19700, 19860, 19940, 19975, 19990 and 19999 eV. As we wanted the largest q-domain as possible (typically between 10^{-2} and 1 A^{-1}), two detector/sample distances were used (1m and 30cm). The samples, in powder form, were analyzed in capillaries, using the sample changer.
As a first step, the curves of intensity measured for the 6 energies were substracted two by two in order to obtain the intensity scattered by the sulfide slabs and to minimize the contribution of the porous support [1, 2].

Information obtained from the ASAXS data.
First, we have shown that ASAXS is totally suitable to characterize the sulfide active phase of this kind of catalyst as it gives information on the size of the slabs and the size of their stacks and aggregates. The exploitation of the ASAXS data was successfully helped by the simulation of scattered intensity performed with an home-made software [3] and from molecular models obtained by DFT calculations (see figures 1, 2 and 3).



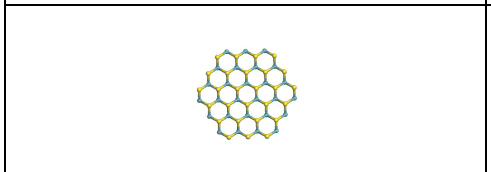
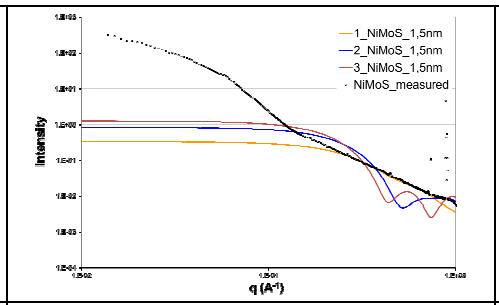


Figure 1. Simulated curves obtained from models of hexagonal slabs of different sizes.



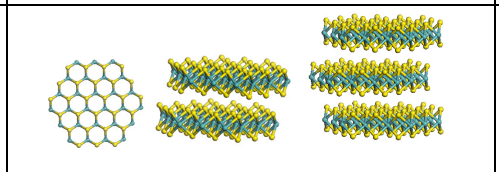
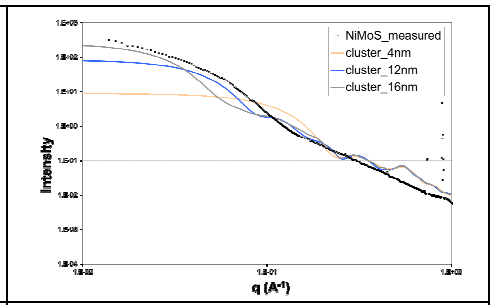


Figure 2. Simulated curves obtained from models of different stack of slabs.



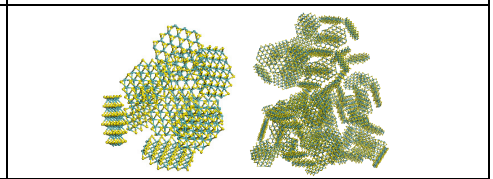


Figure 3. Simulated curves obtained from models of cluster of slabs with different sizes.

The q-scale can be divided into two parts: (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.

Main results

The quantity of information is significant so the main results are presented on figures 4 and 5.

- Effect of the organic additive:

At low amount of molybdenum (8% wt of MoO_3) and for a gas sulfidation, on gamma alumina, it is observed (figure 4, curves n°3 and 4) that the slabs are significantly smaller in the absence of organic additive. This is not so obvious when performing a liquid sulfidation on the same sample (figure 5, curves n°5 and 6).

At large scale and so at smaller q, it seems that the shape and the size of the aggregates of slabs are not impacted by the presence of organic additive.

At high amount of molybdenum (22% wt of MoO_3), for both kind of sulfidation, it seems that the organic additive does not affect the size of the slabs (figure 3, curves n° 13 and 14 and figure 4, curves n°11 and 12). However, some changes are observed on the aggregates scale for the gas sulfidation, but not for the liquid sulfidation: the aggregates or clusters of the sulfide slabs seem to be bigger when using an organic addtive.

To resume, it appears that the effect of the organic additive is not trivial : it depends on the sulfidation conditions, but also on the amount of molybdenum. The size of the slabs is higher in the presence of additive, and the size of the aggregates seems to be also higer when performing a liquid sulfidation.

These results are in good agreement with characterization performed by high resolution scanning transmission electron micrsocopy (HR-STEM).

- Effect of the amount of molybdenum:

The effect of the amount of molybdenum is also not very obvious and depends on the other parameters :

After a gas sulfidation (see figure 4), in the absence of organic additive, increasing the amount of Mo allows to increase the size of the slabs and to keep constant the size of the aggregates. On the contrary, the size and/or shape of the aggregates seeems to be changed in the presence of addtive.

After a liquid sulfidation (see figure 5), whatever the presence or absence of additive, the increase of amount of Mo does not modify the size of the slabs but does impact their aggregation.

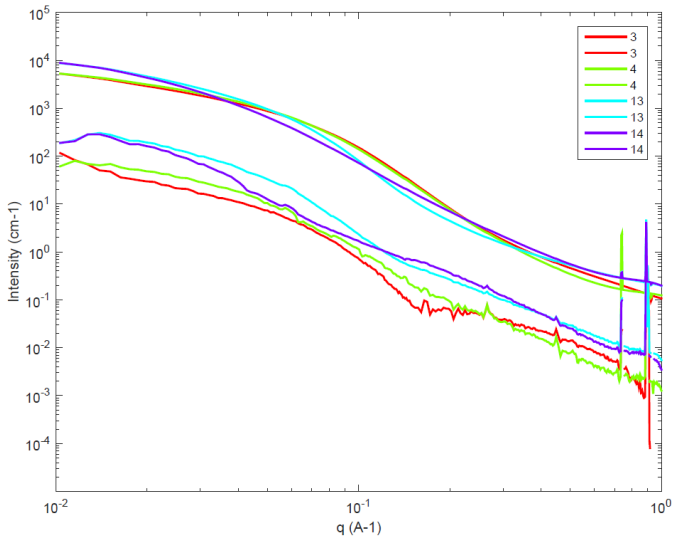


Figure 4. ASAXS curves (I_{19700}-I_{19975}) for samples with a γ-alumina support, obtained after a gas sulfidation: 3 and 4) 8% wt of MoO3, 13 and 14) 22% wt of MoO3, 3 and 13) without organic additive and 4 and 14) with an organic additive.

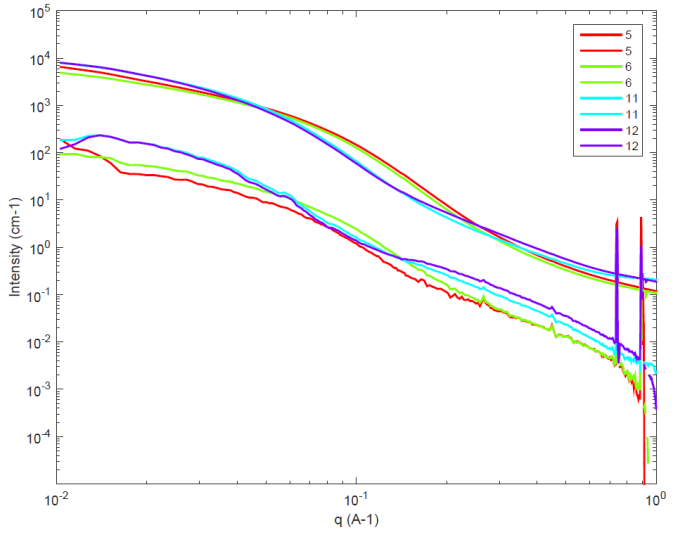


Figure 5. ASAXS curves (I_{19700}-I_{19975}) for samples with a γ-alumina support, obtained after a liquid sulfidation: 5 and 6) 8% wt of MoO3, 11 and 12) 22% wt of MoO3, 5 and 11) without organic additive and 6 and 12) with an organic additive.

- Effect of the sulfidation conditions:

At first sight, the influence of the sulfidation conditions (gas or liquid) is not significant on gamma alumina as the curves are not very different, whatever the amount of Mo or the presence of additive.

Perspectives

For instance, these observations are only qualitatives. Consequently, the exploitation of the data should be performed basing on the scattering theory. The slabs will be modelled by discs or thin ellipsoids and the aggregates could be, at first approximation, modelled by ellipsoids. The results will be compared with the ones obtained by electron microscopy.

Let's precise that the results are very interesting and allow to imagine lot of perspectives as the ASAXS technique, that nowadays is not used on these kinds of samples, is very complementary to the electron microscopy but can also go further in the characterization, bringing information on the aggregation of the slabs, which is suspected to affect significantly the catalytic properties of the catalysts.

Justification and comments about the use of beam time (5 lines max.):

The allocated shifts were divided into three sessions : the first session of 2 shifts was used to validate and to set up the experiment: optimisation of the acquisition conditions, choise of the energies, creation of the macros that control the sample changer. The second session was used to record the data at the first detector/sample distances. And finnally, after the manual change of distance and so the set up of the beamline, the third 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 6 different energies is not trivial.

Publication(s):

- Publication under progress.
- The results have been proposed for a presentation at the international congress MACS7 "7th International Symposium on Molecular Aspects of Catalysis by Sulfides".

References :

[1] H.G. Haubold, X.H. Wang, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 97 (1995).
[2] H.G. Haubold, et al., *Journal of Applied Crystallography*, 30 (1997).
[3] D. Espinat, et al., *Journal of Applied Crystallography*, 26 (1993).