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:** Elucidating the Structural Similarities between Fe-Mo Sulfide Clusters Encapsulated in the Micropores of NaY Zeolite and the FeMo-cofactor of Nitrogenase Enzyme	**Experiment number**: CH 6033
Beamline: ID26	**Date of experiment**: from: 14 Sep 2021 to: 21 Sep 2021	**Date of report**: 16.11.2022
Shifts: 18	**Local contact(s)**: Dr. Pieter Glatzel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Abstract

Preparation of catalytically active and stable mixed transition metal sulfide (TMS) clusters that mimic the active site in nitrogenase enzyme is an exciting concept for the development of new classes of functionalized and/or catalytically active materials. Following this concept, we have synthesized a novel material consisting of well-defined transition metal sulfide clusters encapsulated in the micropores of NaY zeolite. These materials are catalytically active for ethylene hydrogenation and show excellent stability for this reaction. The key to an advanced understanding of the properties and the functionality of these materials are the structural and electronic properties Mo, which was studied via Kα Kβ valence-to-core (VtC) XES.

Results and Discussion

We measured Mo Kβ valance-to-core X-ray emission spectra (VtC XES) on mixed transition metal sulfide cluster encapsulated in the micropores of NaY zeolites. The zeolite precursors were loaded into quartz capillary inside the glove box. The capillary was glued to a stainless steel capillary holder using epoxy based adhesives and the capillary holder was isolated usint shut-off valves, before being moved out of the glove box. The capillary was placed on a gas-dosing and treatment setup. The capillary was heated from below using a hot-air gas-blower. The catalyts were first sulfided in H2S at 673 K. The catalysts were then measured at low temperature (maintained using liquid nitrogen cryostream) in different gas-compositions: (i) helium, (ii) hydrogen, (iii) ethene, (iv) hydrogen + ethene, and (v) carbon monoxide. The measurements were performed on five different mixed metal sulfide catalytsts:

1. Mo_xS_y/NaY
2. Mo_xS_y/NiNaY
3. Mo_xS_y/CoNaY
4. $Co_xMo_yS_z$/NaY
5. $Fe_xMo_yS_z$/NaY

For data analysis, the XES spectra were normalized and background subtracted. The data will be further complemented with density functional theory calculations and EXAFS measurements performed at DESY.

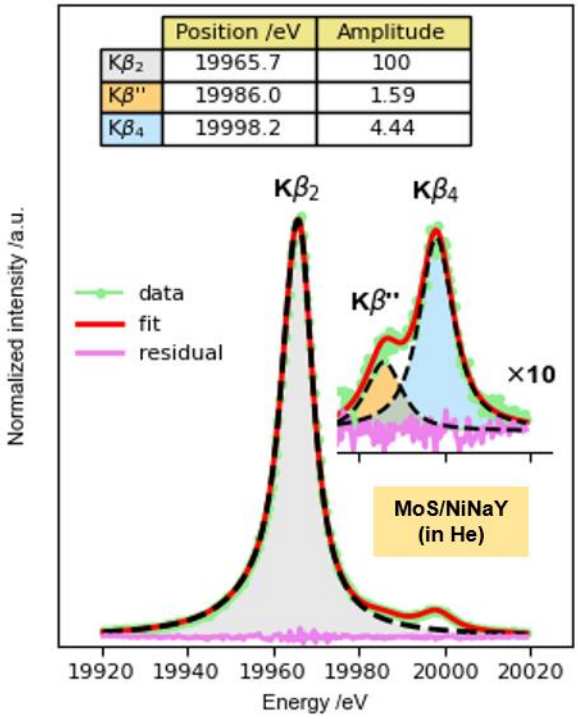

Figure 1. Mo Kβ VtC XES spectra of Mo_xS_y/NiNaY catalyst in Helium

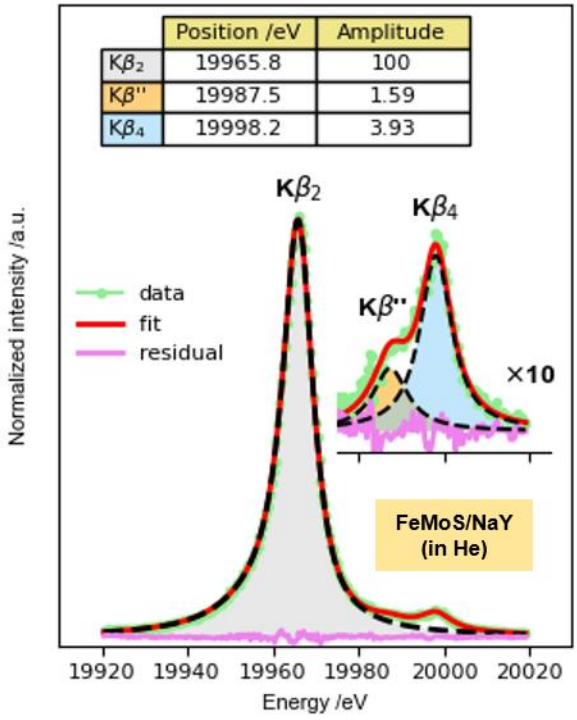

Figure 2. Mo Kβ VtC XES spectra of $Fe_xMo_yS_z$/NaY catalyst in Helium