EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Structure of supported Keggin heteropolyacid under dark and irradiated conditions	**Experiment number**: 25-01-1035
Beamline:	**Date of experiment**: from: 25.11.2017 to: 28.11.2017	**Date of report**:
Shifts:	**Local contact(s)**: Aida Serrano	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The present research aimed to shed a light on the structural deformations of HPA structure, while it is supported on the oxide surface, which determine the material's catalytic and photocatalytic activity by modifying the composite's acidity. It was supposed that the establishing of such HPA rearrangements would help to elaborate and improve the existing preparation procedures of this important catalyst. The proposed XAS investigations in-situ under catalytic and photocatalytic conditions gave invaluable information about the contribution of oxidation state and structural changes under light irradiation or thermal treatment to the activity of the material, thus providing a deeper understanding of the fundamental processes underlying the HPA catalytic performance. XAS study of pristine Keggin and HPA supported on various metal oxides, earlier tested in catalytic propene hydration (E.I. García-López, G. Marcì, F.R. Pomilla, L.F. Liotta, B. Megna, M.C. Paganini, C. Gionco, E. Giamello, L. Palmisano, Eur. J. Inorg. Chem., 2017, **2017**, 1900), reveals that the deposition of HPA on SiO_2 does not provoke significant distortions in $PW_{12}O_{40}$ cluster structure due to poor silica basicity, hence weak interaction (Fig. 1). More basic supports such as TiO_2 and ZrO_2 provide stronger HPA-metal oxide interactions deforming the immobilized HPA and significantly affecting first coordination shell of W (Fig. 2, 3). Noteworthy, the in-situ hydrothermal preparation of TiO_2 and ZrO_2 with HPA leads to the destruction of HPA structure (Fig. 2, 3) due to its reaction with the products of metal alkoxides hydrolysis, as the result the catalytic activity of such materials is low (G. Marcì, E.I. García-López, V. Vaiano, G. Sarno, D. Sannino, L. Palmisano,

Catal. Today, 2017, **281**, 60).

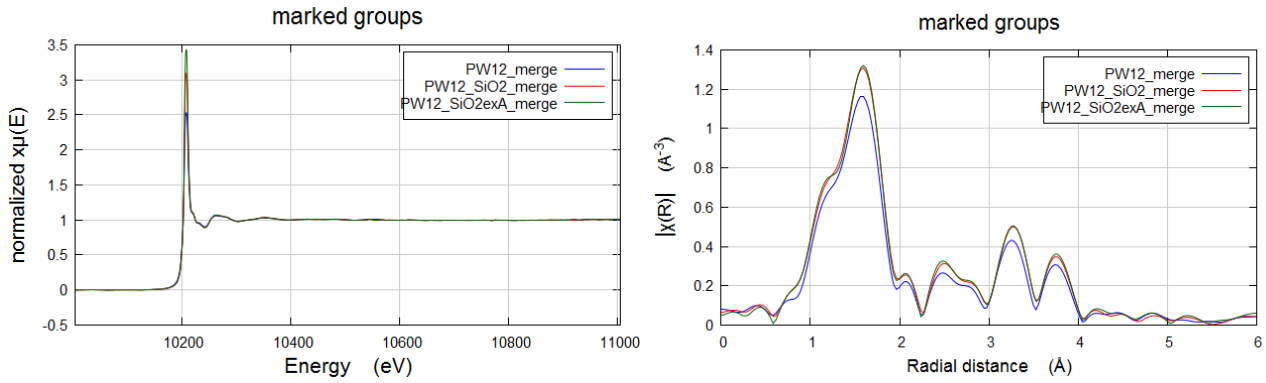

Figure 1. XAS data for Keggin HPA supported on SiO_2 via deposition (PW12_SiO2) and hydrothermal approaches (PW12_SiO2exA)

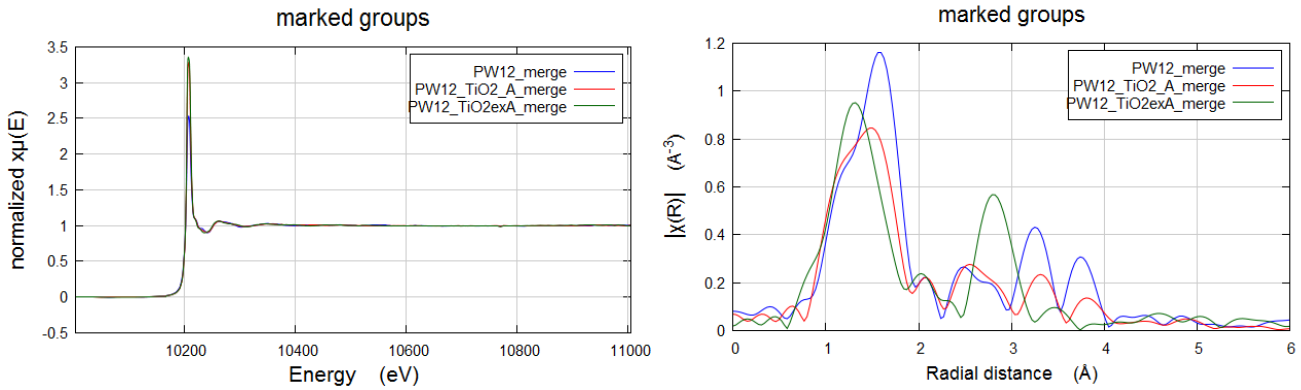

Figure 2. XAS data for Keggin HPA supported on TiO_2 via deposition (PW12_TiO2) and hydrothermal approaches (PW12_TiO2exA)

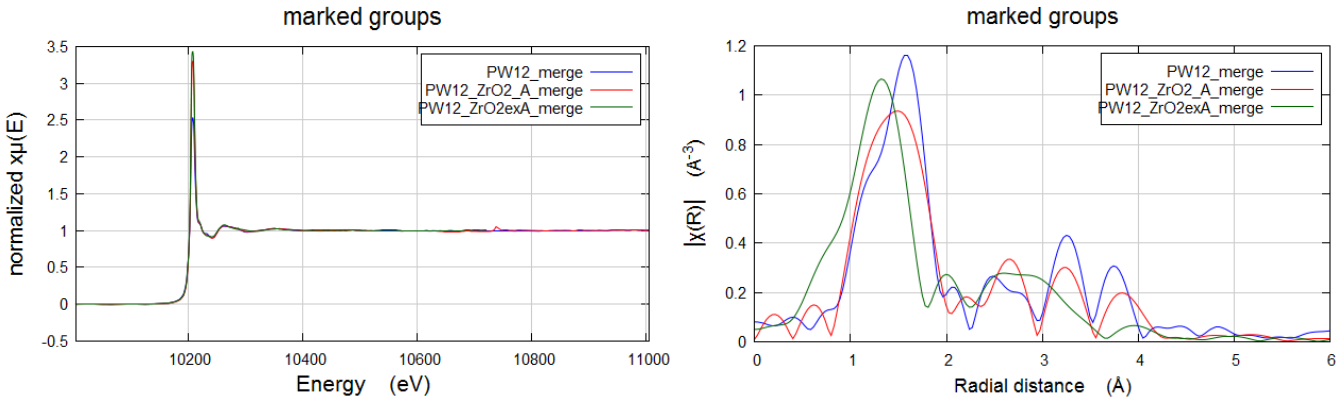

Figure 3. XAS data for Keggin HPA supported on SiO_2 via deposition (PW12_ZrO2) and hydrothermal approaches (PW12_ZrO2exA)

The carried out XAS study of the supported HPA has allowed to explain the differences in their performance in catalytic propene hydration and 2-propanol dehydration. The in-situ part of the research, which is currently under analysis, will provide us with additional information about the behaviour of HPA deposited on various oxide supports under the reaction conditions.