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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: In situ XAFS investigation of bimetallic clusters Ag-Au and Ag-Pt formed in LTA zeolite as a function of reduction temperature	Experiment number: 26-01-908
Beamline: BM-26A	**Date of experiment**: from: 09 June 2011 to: 14 June 2011	**Date of report**: 15 March, 2012
Shifts: 15	**Local contact(s)**: Miguel Silveira & Sergey Nikitenko	*Received at ESRF:*

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Report:

Two different types emitters (550 and 690 nm) have been identified in thermally (auto)reduced silver exchange LTA zeolites with promising perspectives for various applications such as biocompatible labels for intracellular imaging. Structural information suggested that Ag_6^+ clusters with a doublet electronic ground state are associated with the appearance of the 690-nm emitter whereas the 550-nm emitter was tentatively assigned to Ag_3^+ clusters. In parallel current investigations of the catalytic properties of these Ag LTA-zeolites have shown that these materials reduced at high temperature featured promising performances in catalyzing CO oxidation at room temperature. In both applications the extent of the reduction process appears to be a crucial parameter in controlling the structure, charge and properties of the Ag clusters and the luminescence properties can be controlled by a precise treatment of the zeolites with H_2 or O_2 at various temperatures. More recently we have prepared series of bimetallic Ag/Au, Ag/Pd and Ag/Pt exchanged LTA zeolites that are expected to feature new luminescence properties with possibly different emission bands as well as improved performances and better stability over time.

Our previous in situ EXAFS investigation of Ag exchanged LTA zeolite carried out at Dubble beamline *(see experimental report 26-01-865)* showed that significant dynamic local structural changes were occurring around silver atoms during a simple heat treatment in air up to 450 ºC as shown in the Fourier transforms of Ag3Na-LTA zeolite. According to the reduction temperature two cationic Ag clusters possessing a complex structure presenting an Ag core with unusually short Ag-Ag distances have been identified. The smaller cluster, likely formed inside the sodalite cages, emits light at 550-nm while the larger one produces a 690-nm luminescence. However the detailed EXAFS analysis has revealed that a significant level of beam damage has been caused to some of the clusters.

This has led us, in addition to the bimetallic samples, to measured a second time a series of pure Ag LTA materials under different conditions to take into account the beam effect. XAFS data have been collected in transmission mode at Ag K-edge (25514 eV) and up to k= 14 Å^{-2} with typical acquisition times of 45 min (1 to 20 s/point) corresponding to a very good signal to noise ratio. Ionization chambers were filled with Ar/He gas mixture. Due to limitations of the Si (111) monochromator, the energy resolution at Ag K-edge did not exceed ca. 1.5 eV in the XANES regions. Except for the in situ measurements, 4 spectra were averaged to improve the signal to noise ratio to an optimal level.

A set of samples have been measured as-prepared as self-supported pellets whereas 3 samples have been measured in situ in capillaries under various gas flows and temperatures. We have used the integrated gas rig system recently installed at Dubble to mimic the laboratory treatment of the zeolites at different temperatures and under H_2 and O_2 gas flows. The temperature provided with a N_2 heater gun has been raised up to 550ºC at a rate of 5 ºC / with 4 plateaus at RT, 150, 450 and 550 ºC programmed for combined XANES and EXAFS measurements. Dubble gas rig has proved to be very efficient and flexible to use although a faulty mass flow controller and a leaking gas pipe have prevented us from completing our last planned in situ measurements.

Figure 1 presenting the XANES spectra of Ag-based bimetallic Na-LTA zeolites shows the energy shift of the Ag K-edge pointing out significant changes of silver oxidation state according to the nature of the second metal and the sample treatment (Ag/Au).

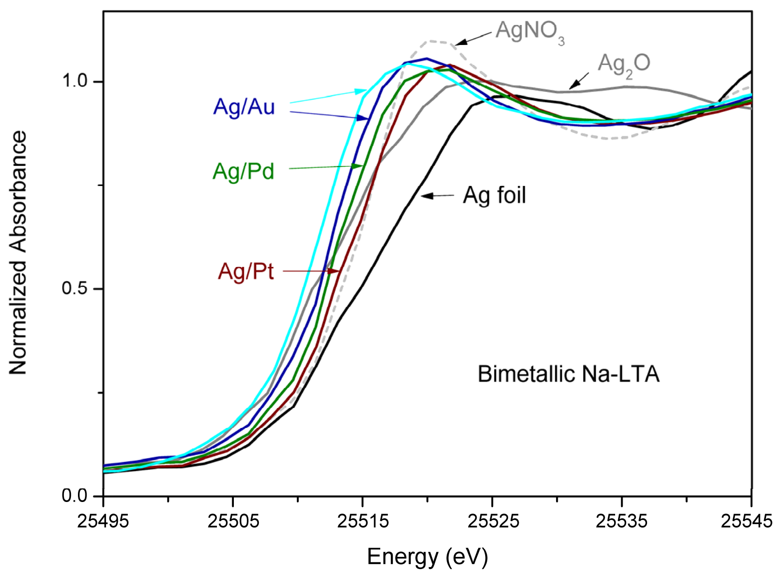

Figure 1: Normalized Ag K-edge XANES of different Ag-based bimetallic Na-LTA zeolites

The EXAFS and XANES data have now been analyzed and the structural results are being correlated with detailed luminescence and absorption measurements as well as DFT theoretical modeling that is currently underway.