



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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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.

**Experiment title:**

Probing the relationship between structure, environment, electronic and fluorescence properties of Ag clusters in Ag-exchanged zeolites

Experiment**number:**

26-01-865

Beamline: BM26A	Date of experiment: from: 11/12/2009 to: 15/12/2009	Date of report: 08/03/10
Shifts: 12	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>

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Report:

Although silver exchanged zeolites have been extensively studied since the 1970s because of their promising catalytic properties,^{1, 2} it is only very recently that highly emissive spots inside thermally (auto)reduced silver-exchange zeolite particles were pointed out at ambient conditions.³ Two different types of emitters with characteristic luminescence colours depending on the nature of the cocation, the amount of exchanged silver, and the host topology could be identified.⁴ In Zeolite A (LTA) the dominant emission bands are situated around 550 and 690 nm respectively with low and high silver content, while in X,Y (FAU) materials only a broad band around 550 nm is observed, regardless of the degree of Ag exchange. Structural information⁴ based on X-ray diffraction, ESR and modelling studies⁴ suggests that these emitters may correspond to two types of Ag clusters formed in the cages of the zeolite. Ag₆⁺ clusters with a doublet electronic ground state were associated with the appearance of the 690-nm emitter whereas the 550-nm emitter was tentatively assigned to Ag₃⁺ clusters. Although a wide agreement seems to favour the formation and stabilization of Ag₃ⁿ⁺ and Ag₆ⁿ⁺ clusters in the sodalite cages of the zeolites, the exact structure and charges of the clusters are still a matter of debate. The luminescence properties of these zeolites were also found to be very dependent on their water content that is directly controlled by heat treatment. These photostable luminescent particles offer promising perspectives for applications in lightning and intracellular imaging. However designing new materials with tailored fluorescence properties requires a full understanding of the relationship between the photoluminescence properties and the structure, charge and local environment of the Ag clusters.

To achieve this goal we have carried out a full XAFS investigation of the role of 4 key parameters on the structure, environment and electronic properties of the Ag clusters inside heat-treated silver-exchanged zeolites:

- **Zeolite type:** Ag zeolites of types A (LTA), X and Y (FAU).

• **Nature of the cocation:** Ag-Zeolite A with 3 different cocations respectively K^+ , Ag_xK-A , Na^+ , Ag_xNa-A and Ca^{2+} , Ag_xCa-A corresponding to the formula $(Ag_xM^{12-x})[Si_{12}Al_{12}O_{48}]$ ($M=Na, K$) and $(Ag_xCa^{2+}_{6-x/2})[Si_{12}Al_{12}O_{48}]$ were investigated. Ag-Zeolites X and Y were only prepared with Na^+ cocations Ag_xNa-X and Ag_xNa-Y with structural formulas $(Ag_xNa^{10.4-x})[Si_{13.6}Al_{10.4}O_{48}]$ and $(Ag_xNa^{13-x})[Si_{35}Al_{13}O_{96}]$ respectively.

• **Silver loading:** series of materials $Ag_{10}Na-A$, $Ag_{10}K-A$, $Ag_{10}Ca-A$, $Ag_{12}Na-Y$, $Ag_{11}Na-X$ corresponding to high Ag loading as well a series Ag_3Na-A , Ag_3K-A , Ag_3Ca-A , Ag_3Na-Y , Ag_3Na-Y corresponding to a low Ag stoichiometry were measured.

• **Heat treatment and water content:** each sample was measured dried after Ag exchange and after calcination. To avoid rehydration the calcined samples were directly sealed in X-ray compatible capillaries in our laboratory after treatment. In a second stage calcination of key samples Ag_3Na-A , Ag_3Na-Y and $Ag_{12}Na-Ag$ were carried out *in situ* to monitor the dynamic formation of Ag clusters as a function of temperature. Capillaries filled with dried materials were heated *in situ* with a gas blower up to 450 °C with a temperature programme including plateaux at 80, 150 and 450 °C to allow 45-min EXAFS measurements.

Self-supporting pellets or capillaries filled with Ag zeolites samples were measured in transmission mode at the Ag K edge (25514 eV). Ionization chambers were filled with Ar/He gas mixture. Data were collected with typical acquisition times of 45 min (1 to 20 s/point) up to $k = 12 \text{ \AA}^{-1}$. 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.

Phase corrected Fourier transforms (FTs) of the k^3 weighted EXAFS spectra of Ag_3NaA , Ag_3NaY and $Ag_{12}NaY$ measured *in situ* during heat treatment are presented in Figures 1, 2 and 3 respectively. All FTs show a main peak at ca. 2.2 Å corresponding to the Ag-O shell and a second peak at ca. 3.4 Å corresponding to the Ag-Ag contribution. Significant and specific local order structural changes are occurring around silver atoms during the heat treatment in both zeolite types. In the three materials the main Ag-O peak is progressively shifted to the low R values while its magnitude decreases as temperature increases. This corresponds to a shortening of the Ag-O bond distance and reduction of the O coordination number that is maximal at 450 °C. In the meantime, a sharp increase of the magnitude of the Ag-Ag peak shell coordination is observed after calcination in cooled-down zeolite Y-based Ag_3Na-Y (Figure 2) and $Ag_{12}Na-Y$ (Figure 3) samples.

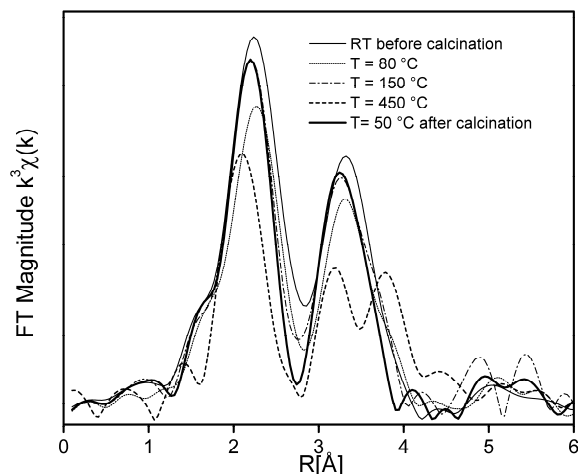


Figure 1. Phase corrected Fourier Transforms of the Ag K-edge k^3 -weighted EXAFS recorded during the *in situ* calcination of zeolite Ag_3Na-A .

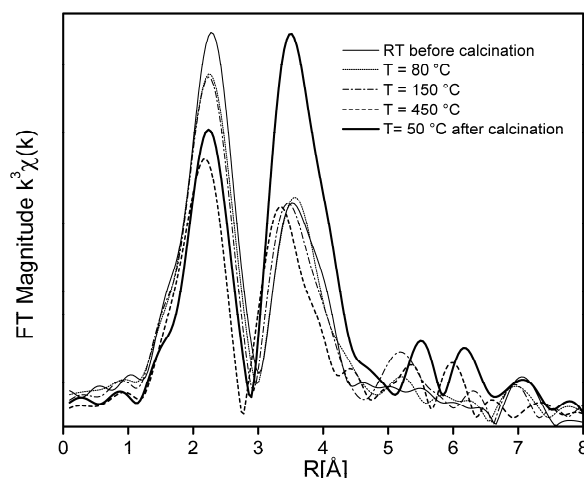


Figure 2. Phase corrected Fourier Transforms of the Ag K-edge k^3 -weighted EXAFS recorded during the *in situ* calcination of zeolite Ag_3Na-Y .

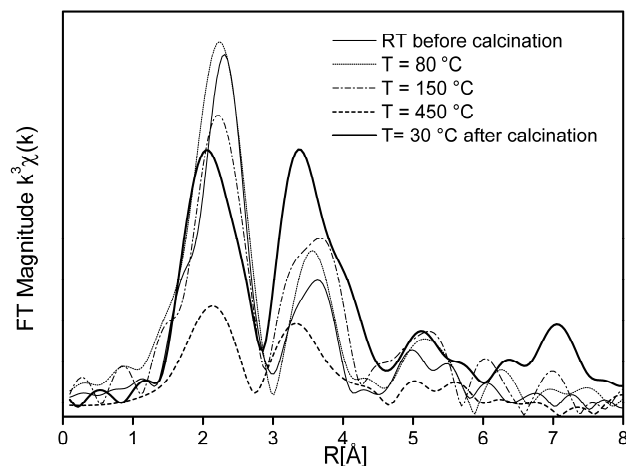


Figure 3. Phase corrected Fourier Transforms of the Ag K-edge k^3 -weighted EXAFS recorded during the in situ calcination of zeolite $Ag_{12}Na-Y$.

Preliminary EXAFS analysis shows that these changes in the FTs correspond to complex changes of the Ag atoms environment and arrangement inside the zeolites cages. A full detailed EXAFS analysis is currently underway to unravel the structural changes affecting the Ag Zeolites materials during the heat treatment and identify the different luminescent Ag clusters.

References

1. Jacobs, P. A.; Uytterhoeven, J. B., Some Unusual Properties of Activated and Reduced Agnaa Zeolites. *Journal of the Chemical Society-Faraday Transactions I* 1979, 75, 56-64.
2. Jacobs, P. A.; Uytterhoeven, J. B.; Beyer, H. K., Redox Behavior of Transition-Metal Ions in Zeolites.6. Reversibility of Reduction Reaction in Silver Zeolites. *Journal of the Chemical Society-Faraday Transactions I* 1977, 73, 1755-1762.
3. De Cremer, G.; Antoku, Y.; Roeffaers, M. B. J.; Sliwa, M.; Van Noyen, J.; Smout, S.; Hofkens, J.; De Vos, D. E.; Sels, B. F.; Vosch, T., Photoactivation of silver-exchanged zeolite A. *Angewandte Chemie-International Edition* 2008, 47, (15), 2813-2816.
4. De Cremer, G.; Coutino-Gonzalez, E.; Roeffaers, M. B. J.; Moens, B.; Ollevier, J.; Van der Auweraer, M.; Schoonheydt, R.; Jacobs, P. A.; De Schryver, F. C.; Hofkens, J.; Baruah, M.; De Vos, D. E.; Sels, B. F.; Vosch, T., Characterization of fluorescence in heat-treated silver-exchanged zeolites. *Journal of the American Chemical Society* 2009, 131, 3049-3056.