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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: Unraveling the electronic and structural properties of novel model catalysts based on series of deposited gas-phase size-selected mono and bi-metallic clusters	**Experiment number**: CH-3105
Beamline: ID 26	**Date of experiment**: from: 25/04/2010 to: 27/04/2010	**Date of report**: 25/08/2010
Shifts: 6	**Local contact(s)**: Kristina Kvashnina	*Received at ESRF:*

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Report:

Most of the catalysts used in industry nowadays consist of very small metallic particles highly dispersed on oxide supports prepared by wet chemical process. 3 key parameters that are directly influencing their performance are now well known and documented:

• **the size of the metallic particle** (molecular cluster versus larger nanoparticles)

• **the composition and structure of the mono and bimetallic particles** (alloy versus segregated core-shell)

• **the nature of the support** (non reducible SiO_2 versus reducible TiO_2)

In order to design new catalysts the specific role of each of these factors separately and in combination with the two others needs to be carefully and systematically monitored. However, due to the high heterogeneity of chemically prepared systems this task remains very difficult. Moreover very small molecule-like clusters that are expected to feature enhanced reactivity are in general very difficult to obtain with conventional chemical methods. Our interdisciplinary research project *'Clusters and Catalysis'* gathering 4 laboratories at K.U.Leuven (B) proposes to overcome these limitations by using a novel physical method to synthesize series of supported metal catalysts with a controlled and highly reproducible homogeneity. The cluster deposition setup is based on a dual-target dual-laser vaporization source optimized for the production of mono and bi-metallic clusters.[1-2] Size-selection is achieved with a quadrupole size filter and low deposition energy ensures that clusters on supports retain their original size and shape. To prevent any aggregates formation on the oxide surface, the cluster coverage is limited to 0.05-0.1 ML. We are now producing series of size-selected mono- and bi-metallic Au and Pt-based gas phase clusters (< 4.0 nm) deposited on the surface of flat SiO_2 and TiO_2 substrates on top of Si wafers. The morphology of the clusters is studied routinely by atomic force tunneling and transmission electron microscopies (AFM and TEM respectively). (Figure 1)
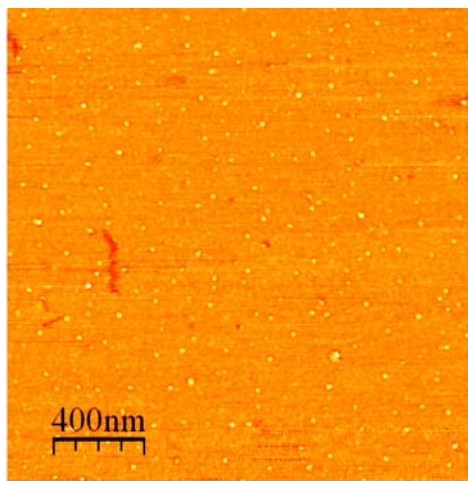
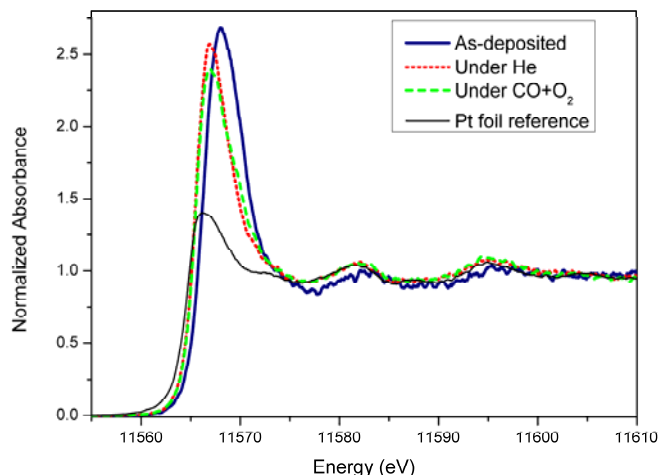Figure 1: AFM image of size-selected 2.5 nm diameter Au clusters deposited on SiO_2

Figure 2: HERFD-XANES of Pt clusters (2.5 nm) deposited (0.05 ML) on SiO_2

The main goal of this preliminary beamtime was to assess the capacity of ID26 to measure XANES of highly diluted samples (~0.05-0.1 ML) deposited on 2D surfaces (versus 3D volume as for conventional chemical process) using the high energy resolution fluorescence detection mode (HERFD).

For this purpose monometallic Au and Pt clusters samples of as well as Au0.5/Pt0.5 bimetallic clusters (3-4 nm) deposited both on SiO_2 and TiO_2 substrates have been investigated as-prepared in air. In a second stage we have implemented the in situ cell available at ID26 to measure the same samples under different gas atmospheres: pretreatment of the samples under He flow followed by a subsequent flow of CO and O_2 (CO oxidation condition). All measurements have been carried out at room temperature using the same experimental setup both at Au and Pt L_3-edges. L_β emission lines for Au and Pt (11565 eV and 11232 eV) have been measured using the same bending crystal analyser Si (844). HERFD spectra were collected using the emission spectrometer equipped with the new crystal analyser Ge (11 11 11).

Figure 2 that presents the HERFD-XANES spectra of monometallic Pt cluster (average size of 2.5 nm) on SiO_2 substrates (0.05 ML) measured as prepared and in He and CO+O_2 mixture flows demonstrates the high quality of the measurements. Preliminary analysis of the XANES spectra shows that the as-prepared Pt clusters are apparently consisting of a metal core covered by an oxide shell that is partly reduced in the He flow. Limited changes upon CO oxidation conditions can be observed with no significant re-oxidation. A detailed analysis at both Au and Pt L_3-edges is currently underway to unravel the structural changes affecting the bimetallic Pt/Au NPs and the influence of the support and composition on the electronic state and structure of the clusters.

This preliminary investigation has demonstrated the remarkable capacity of ID26 to measure XANES of extremely low loading of mass-selected deposited mono- and bi- metallic Au/Pt clusters. Moreover the high resolution XANES measured both at the Au and Pt L_3-edges under He and CO oxidation conditions (CO+O_2) has pointed out significant structural and oxidation state changes occurring in Au, Pt and Au/Pt clusters according to the gas atmosphere and the support. These very promising results confirm the validity of our project. They also show that a more detailed and systematic investigation of the activation/reduction in H_2/He as well as the adsorption processes of individual CO and O_2 gases with XANES and RIXS are needed. A more extensive ID26 beamtime will allow us to get a better understanding of the complex changes occurring in these bimetallic systems as a function of the cluster size, composition and the support type.

(1) Bouwen, W.; Thoen, P.; Vanhoutte, F.; Bouckaert, S.; Despa, F.; Weidele, H.; Silverans, R. E.; Lievens, P. *Rev. Sci. Instr.* **2000**, *71*, 54.
(2) Neukermans, S.; Wang, X.; Veldeman, N.; Janssens, E.; Silverans, R. E.; Lievens, P. *J. Mass Spectr.* **2006**, *252*, 145.