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

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:** Stability of ordered arrays of tiny supported platinum clusters exposed to gases	**Experiment number:** **MA-4736**
Beamline: BM32	**Date of experiment:** from: June 1, 2021 to: June 9, 2021	**Date of report:** June 28, 2021
Shifts: 21	**Local contact(s):** Maurizio De Santis, Lucio Martinelli	*Received at ESRF:*

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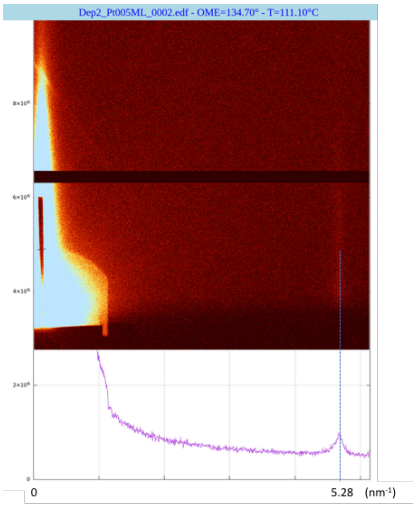
1/ Aim of the experiment and summary

This experiment aimed at exploring the stability of ordered arrays of supported tiny Pt clusters under pre-catalytic conditions (i.e. exposed to low pressures of O_2, CO, CO+O_2 and increasing temperature). We previously showed that Pt clusters organize on a template consisting of a thin alumina film on $Ni_3Al(111)$ with a density 3 or 9 times higher than palladium, depending on the growth conditions. These tailored ordered arrays open the way to explore the emerging topic of single-atom catalysis by using surface science techniques in order to understand the link between atomic-scale properties and catalytic performance. In this experimental session, we performed GISAXS to *in situ* monitor the Pt clusters' growth and their stability. We explored various conditions of substrate's temperature and gas atmosphere (mainly CO). We were able to i) estimate the stability of very tiny Pt clusters with respect to temperature, CO (or CO + O_2) pressure, ii) establish the growth conditions to stabilize the Pt clusters on the dot structure (organization only observed for Pd clusters) and iii) study the Pt diffusion process as a function of the experimental conditions.

2/ Experimental results

The lattice mismatch between the Al_2O_3 ultra-thin film and the $Ni_3Al(111)$ substrate yields two surface superstructures designated as *dot* (lattice parameter of 4.1 nm) and *network* structures (2.4 nm lattice parameter, rotated by 30° regarding the dot structure). Palladium atoms self-organize on the dot structure forming nice and almost perfect two-dimensional hexagonal cluster arrays with a narrow size distribution, whereas vanadium atoms self-organize on the network structure. The possibility of growing such ordered arrays with various metals is important for fields such as magnetism and catalysis in order to better understand the macroscopic properties. But the organization is usually poor, except when Pd is used as seeds on the dot structure.

In a previous experiment (Experiment 20160416; results published in Sitja *et al.*, J. Phys. Chem. C 123 (2019) 24487−24494; DOI: 10.1021/acs.jpcc.9b05109), we showed that, at room temperature, very small Pt deposits are organized on a new superstructure, 9 times denser than the dot structure.



In a first part of this experiment, we mainly focused on very small Pt deposits of 0.05 equivalent monolayer (eq. ML). The organization on the new dense sub-structure is highlighted by the presence of only one sharp scattering rod at Q// = 5.28 nm^{-1} (Figure 1). Such deposits were heated up to 200 °C (and even 400 °C for some of them). We observed that the organization is fairly good up to ~ 180-190 °C and that a low oxygen pressure (5.10^{-8} mbar) does not have a strong effect on the organization quality (images not shown).

Figure 1 – GISAXS image recorded for a 0.05 ML Pt deposit (done at 110 °C). The observed signal at Q// = 5.28 nm^{-1} corresponds to an organization on the dense superstructure, of which surface lattice parameter is 3 times smaller than the one of the dot structure.

We also manage to organize the Pt clusters on the dot structure. As said, this was previously achieved only by seeding the surface with Pd atoms, prior to Pt deposition. Here, by playing with substrate's temperature and CO pressure, we were able to obtain a very good spatial organization, highlighted by the presence of four rods of diffraction corresponding to the (10), (11), (20) and (30) reflections of the hexagonal dot structure (Figure 2).

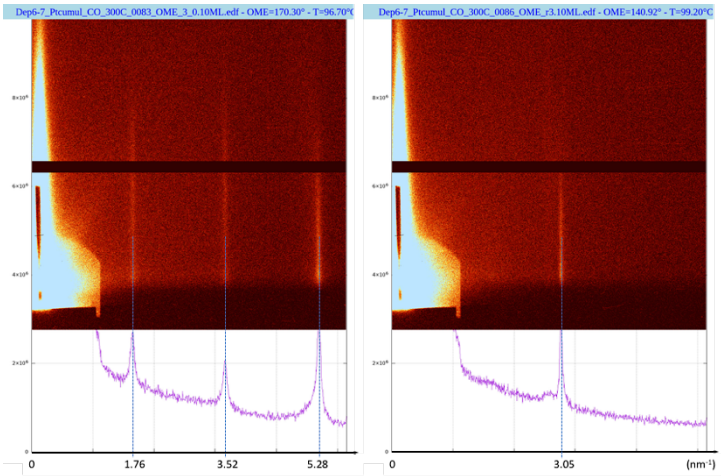


Figure 2 – GISAXS images obtained for a 0.1 ML Pt deposit (done in presence of CO). (10), (20) and (30) diffraction rods arising from clusters organized on the dot structure (left) and (11) diffraction rod (right).

Lastly, thicker Pt deposits done at higher temperature (300 – 400 °C) were also studied (Figure 3). After deposition, the (11) rod appears to be much more intense than the (30) one, pointing to an organization on the network structure (or on the dense one, with a modulation of atoms position along the z direction; simulations needed). The diffuse scattering around the (10) position is intensified after heating up to 300 °C, indicating a clear cluster coalescence.

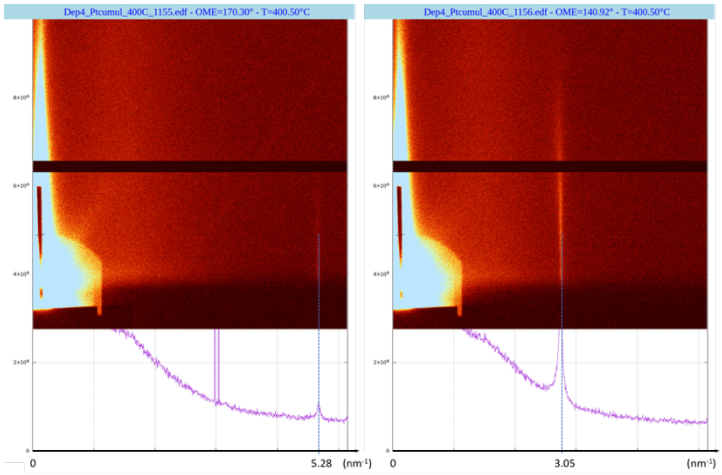


Figure 3 – GISAXS images of a 0.2 ML Pt deposit (done at 400 °C), heated up to 400 °C and exposed to CO + O_2.

We finally showed that the Pt adatom surface diffusion is strongly altered when the surface is kept for several hours in UHV before Pt deposition (images not shown).

These partial results and initial conclusions are very encouraging. They must be confirmed by simulations and will be published as soon as possible.