EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY
INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Photon-in/Photon-out study of reduction process of supported rhodium-nanoparticles**	**Experiment number**: CH 3754
Beamline:ID26	**Date of experiment**: from:12/06/2013 to: 18/06/2013	**Date of report**: 16/01/2014
Shifts:18	**Local contact(s)**:Erik Gallo	*Received at ESRF:*

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Report (written by E. Gallo and G. Agostini):

We have investigated the electronic structure of Rh-nanoparticles (~ 1 nm) supported on carbon and allumina. The aim of experiment is to observe the modifications of the electronic structure of rhodium nanoparticles owing to the nanoparticle-substrate interaction and to hydrogenation of toluene.

All sample treatments and measurements were performed using the "Toyota in-situ cell" developed at E.S.R.F. by the sample environment pool. The nanoparticles were reduced fluxing 5% H_2/He at 500K and vapor of toluene were contacted with nanoparticles fluxing 5% H_2/He by bubbler.

It is well established that metal nanoparticles weakly interact with carbon. This general view has been confirmed in the present study. We have observed that the electronic structure of Rh oxide nanoparticles on carbon (Rhox/C) present the same electronic structure as Rh oxide (Rhox/bulk) using the chemical sensitivity of the $K\beta_2$ X-ray emission line (~23170 eV).

This emission energy is one of the most high in energy ever measured at ESRF. It was recorded using the 11th reflection of Ge(111) Bragg analyzer crystals.
We observed that within the uncertainty of the points (determined using a level of confidence of the 95%) the two sample are equivalent.
The $K\beta_2$ X-ray emission line of Rh nanoparticle supported on allumina (Rhox/Al_2O_3) varies respect to Rhox/C: it increases in intensity and blueshift of 0.6 eV, see Figure 1. This effect is a clear indication of the electronic interaction of the nanoparticles with the alumina support. The support can be seen as an electronic "resevour" of electrons for the Rh on the surface of the nanoparticles. Quantum mechanics calculations can also be used for the identification of the chemical origin of such behaviour.
The second step of the investigation was to observe the variation of the electronic structure between Rhox/Al_2O_3 nanoparticles and Rh metal nanoparticles (Rh/Al_2O_3). We observed that the X-ray emission spectrum of Rh/Al_2O_3 presents more features than Rhox/Al_2O_3 . The new features appear at high energy close to the elastic. This effect mirrors the metallic character of the reduced sample, i.e. the Fermi level shifts within an occupied electronic band
The last step of this investigation pointed towards the investigation of the chemical reactivity of Rh/Al_2O_3 using a prototype reaction: hydrogenation of toluene to metil cyclo-hexane.
We observe that a small feature appears at high energy above the $K\beta_2$ X-ray emission line. This feature can be linked to the coordination of toluene on the surface of the Rh/Al_2O_3.
This finding can be corroborated using other table-top techniques as well as EXAFS spectroscopy.

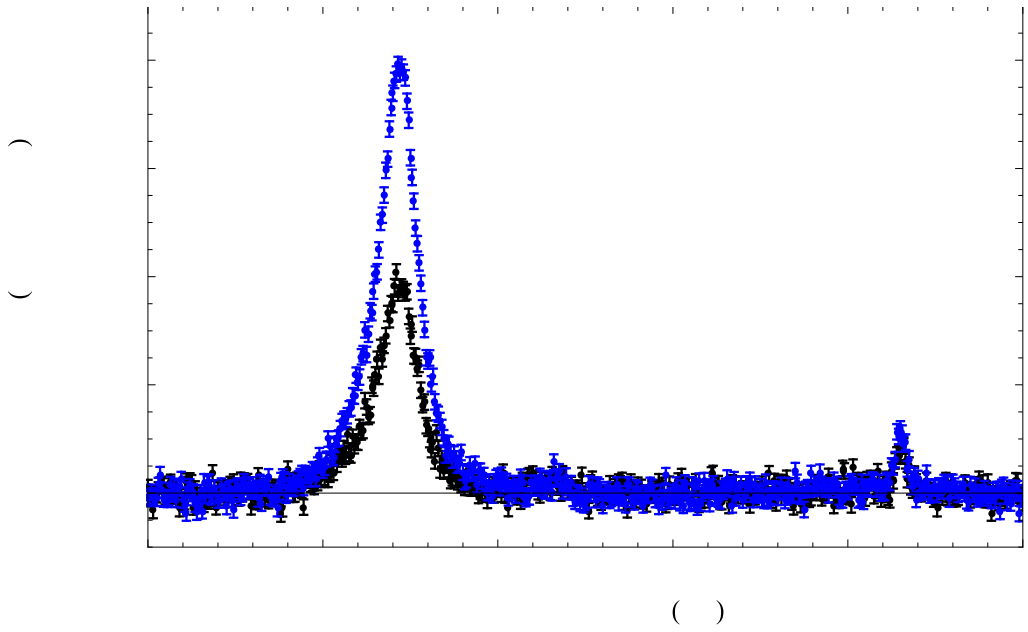

Figure 1. Comparison of the Kβ2 X-ray emission line of Rhox/Al2O3 (blue) and Rhox/C (black). The feature at high energy is the elastic peak.

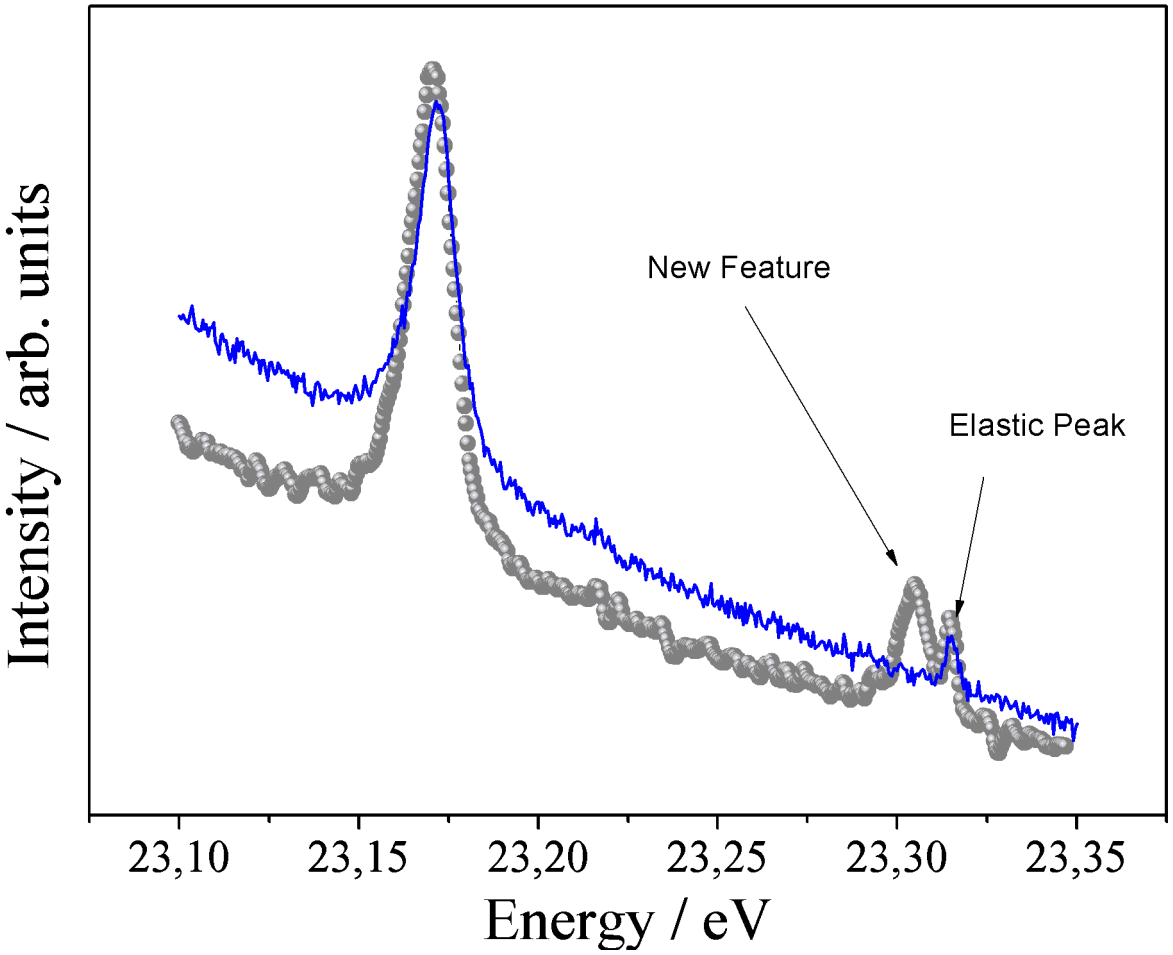

Figure 2 Comparison of Rhox/Al2O3 (blue) and Rh/Al2O3 (gray). The new feature at high energy is indicated.