ESRF	**Experiment title:** Combinatorial study of the structure and shape of Pt-Rh nanoparticles during CO Oxidation	**Experiment number**: SI2260
Beamline: ID15A	**Date of experiment**: from: 8.6.2011 to: 14.6.2011	**Date of report**: 25.8.2011
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Report:

Pt, Rh and bimetallic Pt-Rh nanoparticles are widely used as catalyst materials in exhaust control, gas sensors and low temperature fuel cells. The shape, structure, morphology and alloying of the particles may influence catalytic activity, selectivity and catalyst lifetime. Thus, a more profound understanding of the particle behaviour during catalytic reactions is important for future catalyst improvements.

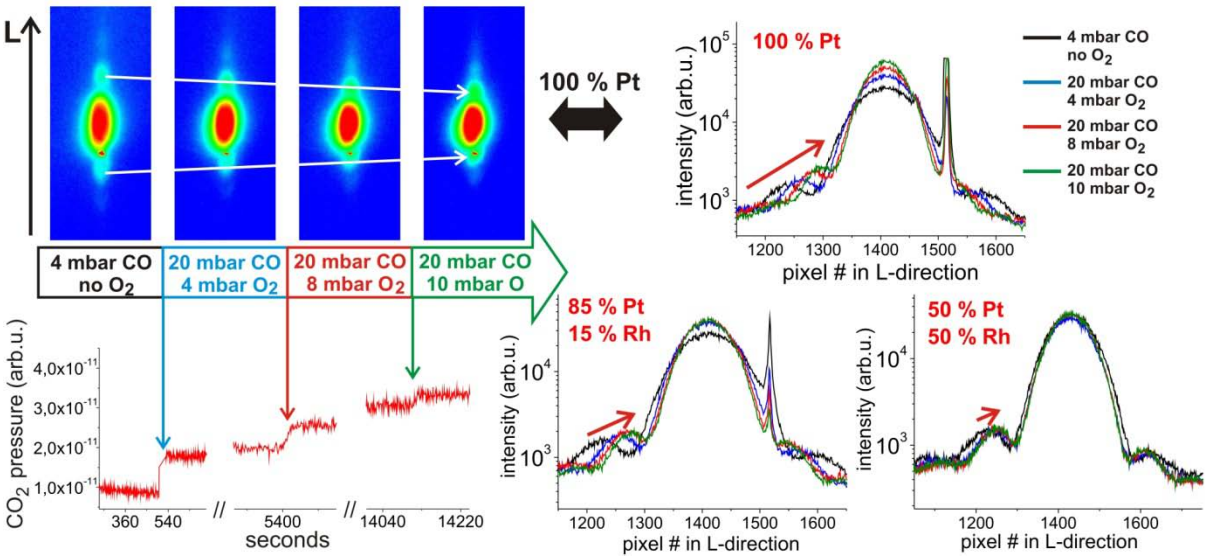
The aim of the present experiment was to study the particle shape, structure and size change during in-situ CO oxidation reactions in dependence of the Pt/Rh content. The use of 78.7 keV as x-ray energy, which is slightly above the Pt K edge at 78.395 keV, allowed to map large areas in reciprocal space and to observe during the in-situ experiment signals from various particle domains simultaneously. In the course of the beamtime two combinatory samples were studied which had been prepared in the home lab in Siegen by means of simultaneous physical vapour deposition of Pt and Rh on top of a UHV-clean 10x10 mm^2 (0001)-oriented Al_2O_3 substrate. Both samples contained seven parallel stripes with nanoparticles. Most of them were made up of 2 nm high particles with constant concentration, varying from pure Pt to pure Rh. One sample also contained Rh stripes with different particle height varying from 1.5 to 2.8 nm. With the incident x-ray beam parallel to the stripes particles with different concentrations and / or size could be measured under the same conditions by translating the sample perpendicular to the beam. On the two samples the parallel stripes were oriented along two different azimuthal substrate orientations. This allowed to investigate two different planes in reciprocal space and thus to obtain complementary information on particles of a certain Pt/Rh concentration.

For the in-situ investigation the ID03 catalysis chamber was employed for which the z-stage and the x- and y-stages of the HEMD diffractometer on which it was mounted had to be changed. Apart from the FRELON#38-KODAK-TAPER 2D camera used for imaging reciprocal space maps we employed the CYBERSTAR scinitallation counter for complementary reflectivity measurements.

At least one day of beamtime was lost due to complications generated by the general ESRF power cut on the morning of June 8th, 2011. Prior to the reaction experiment both samples were annealed at 250 – 300 °C under $2 \cdot 10^{-5}$ mbar H_2 in order to reduce the natural oxide on the particles. After that the as-prepared particles were investigated under slightly reducing conditions at a constant flow of 4 mbar CO and 196 mbar Ar. The total pressure of 200 mbar was kept constant during the whole experiment only changing the pressure of the gas components CO, O_2 and Ar. In the main reaction experiment which we performed on both samples we increased the O_2 pressure step by step while keeping a constant temperature of 280°C and a constant CO pressure of 20 mbar. At various important steps all stripes were characterized by reflectivity measurements and by taking images with the 2D detector. During the whole experiment the reactivity was studied by monitoring the CO_2 production rate with the mass spectrometer which increased with higher O_2 pressure. In

this way we increased the O_2 pressure up to 14 mbar and 16 in case of the first and the second sample, respectively.

For the as-prepared samples we found that Laue oscillations occurred in L-direction on the particle Bragg peaks. They were the more pronounced the higher the percental Pt content of the particles indicating a higher internal structural perfectness for particles with a higher Pt content. Furthermore, we observed that the fringes of the Laue oscillations moved closer towards the particle Bragg peaks with increasing O_2 pressure and increasing CO_2 production rate implying that the particles grow higher during high reactivity conditions. This was backed by our reflectivity measurements. Also here we found a concentration-dependent behaviour: the higher the Pt percentage the higher the particle size change indicating that the presence of Rh suppresses the sintering process.



Top left: 2D maps showing the $(13\text{-}1)_{bulk}$ Bragg peak of the 100 % Pt stripe. With increasing CO_2 production the fringes move closer towards the peak as indicated by the white arrows. **Bottom left:** CO_2 production rate in dependence of the O_2 pressure. **Right side:** line-scans in L-direction through the $(13\text{-}1)_{bulk}$ particle Bragg peak for various Pt/Rh concentrations. The higher the Pt content the more move the fringes with increasing CO_2 production towards the Bragg peak.

On one sample we performed the same type of experiment at a constant temperature of 400 °C increasing the O_2 pressure even to 50 mbar. However, we found the changes of the Laue oscillations in dependence of the O_2 pressure to be more pronounced at 280 °C.

In conclusion we can say that we succeeded in meeting our goals: we were able to obtain consistent information from both our samples at 280 °C; for the first sample we even measured a whole data set for the CO oxidation experiment at 400 °C. The data are currently being analyzed and will give important insight into shape, size and structural changes of Rh, Pt, and bimetallic Pt-Rh nanoparticles during CO oxidation reactions in dependence of the Pt/Rh content. The data will also reveal information which is of paramount interest for a better understanding of nanoparticle sintering processes during catalysis.