EUROPEAN SYNCHROTRON RADIATION FACILITY
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	Experiment title: Operando coherent X-ray diffraction imaging of a single catalyst PtRh nanoparticle and surface X-ray diffraction of surface oxides	**Experiment number**: HC-4334
Beamline: ID01	**Date of experiment**: from: 09/11/2021 to: 15/11/2021	**Date of report**: 04/03/2022
Shifts: **18**	**Local contact(s)**: Tobias Schülli	*Received at ESRF:*

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Report: The aim of the proposed experiment was to track shape and strain state changes of a single PtRh alloy catalyst nanoparticle (NP) operando under catalytic reaction conditions using coherent X-ray diffraction imaging (CXDI). Furthermore, we proposed surface X-ray diffraction as sensitive technique to detect potentially forming surface or bulk oxides of the NP in a strongly oxidizing gas environment at elevated temperature. The beamline ID01 is ideally suited to analyse single NPs using operando CXDI, and to observe signals of oxide formation by surface X-ray diffraction. In this way, any detected signal of a forming surface oxide could be related to i) the NP shape and strain state as deduced from CXDI and ii) to the gas environment in the reaction chamber. The catalytic gas environment was realized by a constant total flow of 50 ml/min of a gas or gas mixture at a constant pressure, both established and controlled by a gas dosing system and a back-pressure controller in the outlet, ensuring a constant chamber pressure of 100 mbar throughout the whole experiment. In this experiment, we used inert, reducing and oxidizing atmosphere (O_2, CO in Ar carrier gas). The catalytic activity was tracked by a sensitive mass spectrometer in the outlet connected to the exhaust gas line.

Bimetallic NPs were grown by co-deposition of Pt and Rh in the MBE chamber under UHV conditions at the DESY NanoLab on a 100 oriented, Nb doped strontium titanate (STO) oxide single crystal, see, e.g. [1-3]. During the X-ray experiment at ID01, we analysed a pre-

selected and marked, fully pre-characterized single PtRh alloy NP. From SEM, a lateral diameter of 146 nm was deduced, see, e.g., Fig. 1a. AFM height and phase images are shown in Fig. 1b and 1c. During the operando experiment, we were able to collect around 20 full CXDI

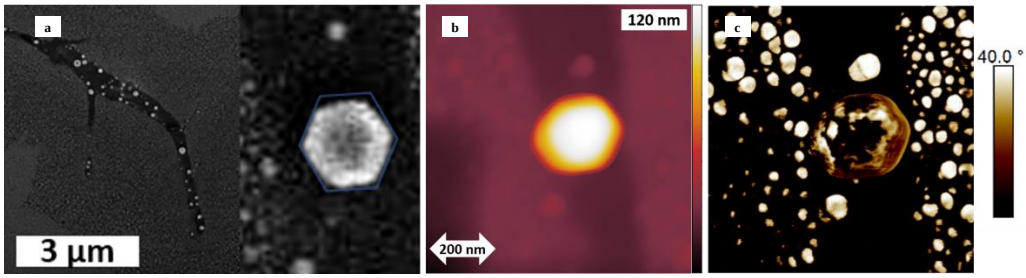

Fig. 1.: a) SEM overview and high-resolution image of the pre-selected and analysed nanoparticle, b) AFM height and c) phase image of the nanoparticle analysed during the X-ray beamtime.

datasets from this pre-selected NP at a temperature of around 700 K under various gas conditions (we used an X-ray energy of 9 keV and CRLs for focussing): The gas mixture was varied from inert (50 ml/min Ar, 0 ml/min CO, 0 ml/min O_2), over mild to strong catalytic reaction conditions (42 ml/min Ar, 4 ml/min CO, 4 ml/min O_2) to an extremely strong oxidizing atmosphere (25 ml/min Ar, 0 ml/min CO, 25 ml/min O_2). We analysed the NP by taking CXDI scans of multiple Bragg reflections, i.e., in coplanar geometry using Pt (111), see., e.g., Fig. 2a and 2b. In asymmetric geometry, we found that likely due to a twinning defect at around half the height of the NP two asymmetric reflections, Pt (102) and Pt (104) were needed to obtain CXDI signals of the full particle in these directions, see, e.g., Fig. 2c and 2d.

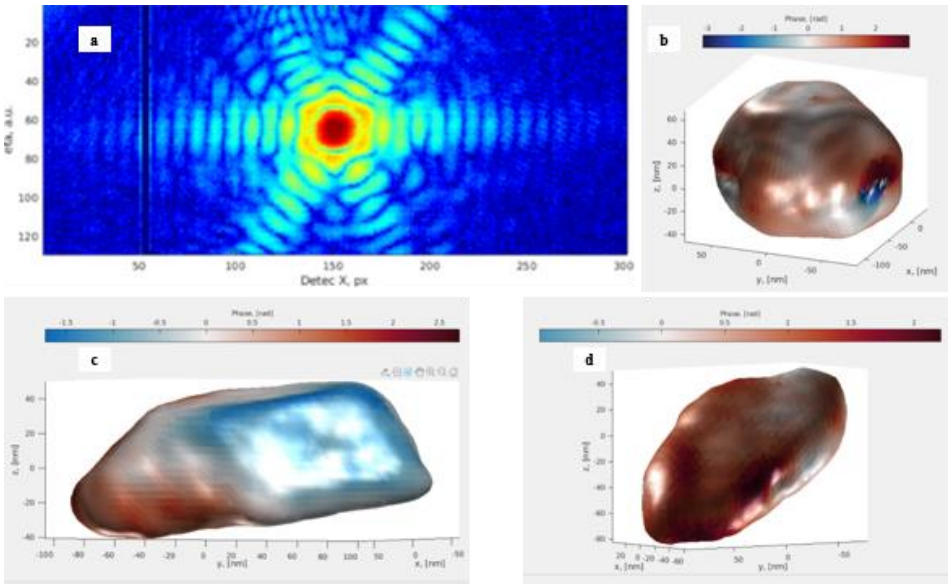

Fig. 2.: a) Image stack from a CXDI scan of the Pt 111 Bragg peak under stochiometric conditions (2 ml/min O_2, 4ml/min CO, 44mL/min Ar, at around 700 K), b) 3D reconstructed amplitude of the nanoparticle in real space obtained by a reconstruction of a CXDI scan of the Pt 111 Bragg reflection, c, d) reconstructions of the upper and lower part of the nanoparticle obtained from the Pt 102 and 104 Bragg peaks, respectively.

The AFM height image after the experiment in Fig. 3 indicates a growth of the surrounding smaller NPs due to catalytic sintering or oxidation induced volume increase – and likely of similar origin – small humps on the surface of the analysed NP. Although we could not find any evidence of crystalline oxide phases by surface X-ray diffraction, we were able to collect a comprehensive CXDI dataset of the NP that will provide important insight into the NP shape and strain state changes under such extreme oxidation conditions. The CXDI datasets are currently analysed and further complemented by *ex situ* post-analyses like Scanning Auger Microscopy to elucidate the NP surface termination.

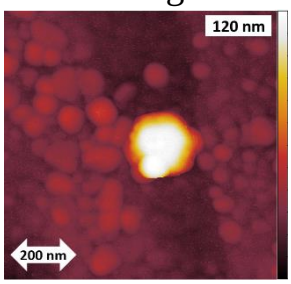

Fig. 3: AFM height image after the catalytic experiment.

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[2] T. Kawaguchi et al., "Gas-Induced Segregation in Pt-Rh Alloy Nanoparticles Observed by in Situ Bragg Coherent Diffraction Imaging," Phys. Rev. Lett. 123, (2019), https://doi.org/10.1103/PhysRevLett.123.246001.
[3] Y. Y. Kim et al., "Single alloy nanoparticle x-ray imaging during a catalytic reaction," Sci. Adv. 7, 1–9, (2021), https://doi.org/10.1126/sciadv.abh0757.