ESRF	**Experiment title:** Operando Study of PtPd Nanoparticles on Al2O3 During Methane Oxidation	**Experiment number**: CH6401
Beamline: ID 31	**Date of experiment**: from: 31.01.23 to: 06.02.23	**Date of report**: 07.03.2023
Shifts: 18	**Local contact(s)**: Andrea Sartori	*Received at ESRF:*

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Report:

Seven samples were brought to the beamline, five of which we were able to investigate. One sample consisting of Pd NPs supported by $Al_2O_3(0001)$ and 4 samples consisting of PdPt alloy particles, supported on a CeO_2 thin film on a YSZ(001) substrate with Pd:Pt ratios of 1:0, 1:1, 3:1, and 9:1, respectively. Sample preparation and and pre-charcterization for all samples were conducted at the DESY NanoLab. The alloy particles as well as the CeO_2 thin film were grown by MBE. For the particles supported by Al_2O_3, the pre-characterization consisted of AFM, XRR, and GIXRD after particle growth. For the Ceria samples, AFM, XRR, and GIXRD were measured at 3 different steps during sample preparation: After CeO_2 growth in MBE, after annealing the film in air, and after particle growth. Additionally, all samples were precharacterized by SEM after particle growth.

All particles and film showed a clear epitaxial relationship to the substrate. PdPt particles on Al_2O_3 were [1,1,1]-oriented ([1,1,1] PdPt alloy crystal axis || sample normal), with the [1,1,0] directions lying in the high-symmetry planes of Al_2O_3 ([1,0,-1,0], [1,-2,1,0]). The Ceria thin film supported on YSZ exhibits a cube on cube-epitaxy. The alloy particles supported by the Ceria thin film grow in two different configurations: Firstly, in a cube-on-cube epitaxy with the in-plane principle axes rotated by 45° relative to the Ceria film, secondly with the [1,1,1] axis along the sample normal with the [110] axis lying in the high-symmetry planes of Ceria ([1,0,0],[1,1,0]). The coverage of the samples with nanoparticels was homogeneous over the whole single crystal surface and of the order of 50 to 60%. Particle height was about 5nm, particle diameter about 10nm. For the Al_2O_3 samples the diameter was slightly higher at around 13nm.

For best comparability, the total pressure (0.1bar) and total flow (100mL/min), as well as the reaction gas mixture (2mL/min CH_4, 20mL/min O2), reducing gas mixture (3mL/min H_2 and 97mL/min Ar), and neutral gas mixture (100mL/min Ar) was chosen for all samples. During the beamtime we fully characterized the sample before the onset of methane oxidation and after degassing at 150°C in pure Ar by rocking scans covering 100° sample rotation for YSZ samples and 70° for Al_2O_3 covering covering all unique planes in reciprocal space of particles and thin films.

During the operando part of the experiment, we were slowly ramping the sample to ~600°C in reaction gas mixture using our operando mini chamber equipped with a gas mixing system and in-line spectroscopy. During the ramp to 600°C we did quick re-alignment steps every ~50°C while taking images throughout the ramp in order to maintain alignment and record high qualitz HEGIXRD data throughout the full light-off.
At 600°C we waited for an equilibrium to establish, thoroughly checked alignment of the sample and characterized it by rocking scans as described above.
For part of the samples we also included a reduction step, probing the reducibility of the different alloy compositions. For this purpose the sample was heated to ~400°C in the reducing gas mixture defined before.
Throughout the experiment we record gas flows into the chamber, as well as the exhaust gas composition using our gas mixing system and the in-line mass spectrometer, allowing us to determine the particles activity towards methane oxidation. The diffraction data was recorded using the Pilatus 3M at a beam energy of 75keV with beamstops covering thin-film and substrate Bragg peaks, as well as parts of the Be powder rings originating from the Be dome of the operando mini chamber. Covering high intensity signal allowed us to observe subtle changes in the shape of the PdPt alloy diffraction signal, and the Ceria CTRs. We also observed the formation of different oxide phases some of which are preferentially oriented. Figure 1 shows examplary diffraction data of the pure palladium nanoparticle on CeO_2 sample. The Pd Bragg peaks smear out into verz narrow rings, indicating strong sintering and loss of epitaxial relationship to substrate. In Figure 1 B, palladium oxide Debye-Scherrer rings were observed (i.e. at the x-axis between 750 and 1000 pixels).
We rate the experiment a success. We were able to investigate all priority samples and were able to record high-quality diffraction data for all. Beamline support, especially the work of Florian Russello and Andrea Sartori was exceptional. All major components of the beamtime worked reliably.

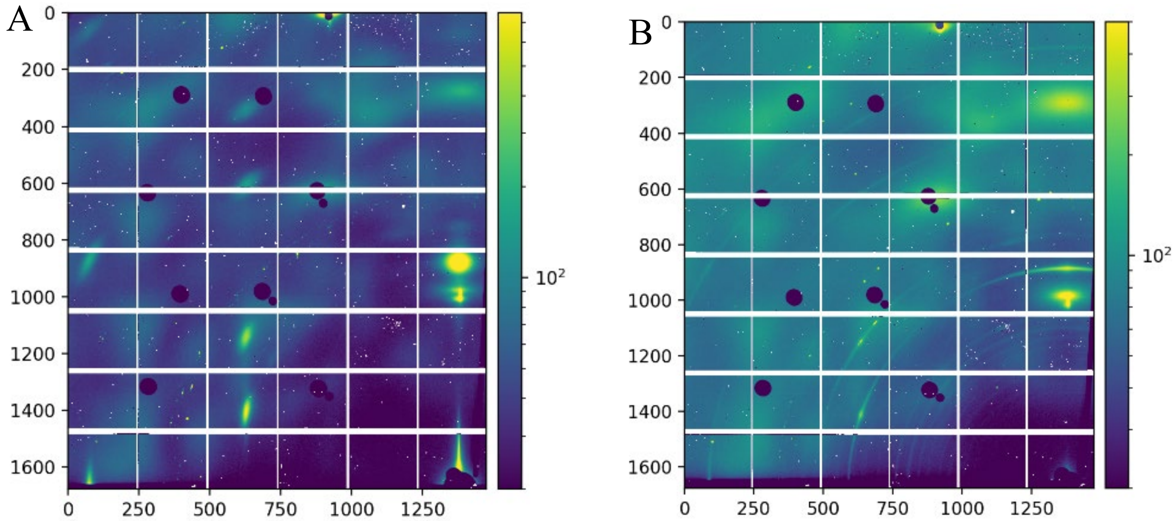

Figure 1: A) High symmetry plane of Pd particles on CeO2/YSZ at 150°C in 100mL/min Ar at 100mbar. B) High symmetry plane of Pd particles on CeO2/YSZ, recorded at 600°C in 2mL/min methane, 20mL/min O2, and 78mL/min Ar at 100mbar, revealing extreme sintering, partial loss of epitaxial relation to substrate, and oxide formation.