FYSN21 - Manual for research project

Catalytic methane oxidation over clean and oxidized Pd(111)

Aim

The aim of the project is to determine if there is a dependence in the catalytic activity for methane oxidation over Pd(111) on the structure and thickness of a PdO film on the surface. The hypothesis is that the metallic surface is highly active, but not stable under oxidation conditions, a single layer oxide (which is not detectable with GIXRD) is low-active, a thin but at least two layer thick oxide film is highly active, and a too thick (the limit is unknown) oxide is low-active [1-3]. We want to test the hypothesis growing oxides of different thickness and, if relevant, find the point where the oxide becomes too thick.

Experimental setup

The experiment is performed using the surface X-ray diffraction (SXRD) setup in the X-ray lab of the division of Synchrotron Radiation Research in the basement of the Astronomy building, which is (not completely) described in Ref. 4. This setup is designed for surface diffraction, with a Mo based microfocus X-ray source (Xenox), a diffractometer (Huber) allowing for an accurate alignment of the surface relative to the beam and a medium sized 2D detector (Dectris, Pilatus 300k). The X-ray intensity is a bit weak for proper SXRD, analysing the structure of single atomic layers, but enough for grazing incidence X-ray diffraction (GIXRD), analyzing the near-surface 3D structure. We might also be able to use X-ray reflectivity (XRR), for the analysis of the thickness of thin films on the surface.

The sample will be mounted in a vacuum chamber/catalysis reactor with a Be cylinder allowing the X-rays to pass through. The sample can be exposed to gases (O2, Ar and 5%CH4 in Ar), heated using a boralectric heater and cleaned through Ar sputtering.

The gases inside the reactor can be analysed by a mass spectrometer (MS). At elevated pressures (above 5x10-6 mbar) the part of the chamber where the MS is situated is closed off and 5x10-6 mbar gas is leaked from the reactor through a leak valve.

The sample temperature is estimated by a calibration curve of the heating current vs temperature.

Experimental procedure

The Pd(111) sample is cleaned by Ar sputtering (bombardment with Ar ions) at an argon pressure of 2x10-4 mbar, 10 mA emission current and 2 kV acceleration. After this the surface will be very rough, and is flattened out by annealing (heating) at about 800°C for 5 min. This will be done before you arrive.

To perform GIXRD and XRR, it is important that the sample surface is properly aligned with the beam. How to do this will be described in the lab. After the alignment, the incidence angle, mu, is set to 0.2° for GIXRD. For XRR the incidence angle and measured outgoing angle (detector position) are scanned from 0° to 2° in 200 steps with an exposure time of 5 s. (If not too time consuming.)

Task 1 Align the sample with the beam.

The sample is oxidized by adding 10 mbar O2 at room temperature, followed by heating to about 500°C (1.4 A) in 140 s (same as for the oxidation). Anneal (keep this temperature) for a desired amount of time and ramp down the heating to 0 A in 130 s. During the annealing step, we will follow the PdO(011) diffraction spot of a PdO film oriented with the PdO(101) planes parallel to the Pd(111) planes of the substrate (the Pd(111) crystal). If you want more info on how to identify three different PdO orientations (for a (111) oriented Pd3Au thin film on saphire) this is shown in Ref 5.

Task 2 Test the catalytic activity of the oxidized surface.

The catalytic activity will be tested by filling the reactor with 1 mbar O2 and 1 mbar 5%CH4/Ar at room temperature, where no reaction is expected to take place, followed by a rapid increase of the temperature to about 500°C (to 1.4 A heating current in 140 s) to initiate the reaction and keep this temperature throughout the reaction. The transformation of CH4 into CO2 will be followed by mass spectrometry, while any appearance/disappearance/change in the oxide structured is followed by GIXRD, similar as during the oxidation.

To remove any remaining oxide, flash (heat and cool immediately) the sample to 800°C (3 A).

Repeat task 1 and 2 for several oxidation times

The above points have already been performed for oxidation times of 5, 10, 20, 40 and 80 min. The data will be summarized and provided as close to raw data. You need to analyse it and create nice figures.

Task 3 Extend the project with one more experiment during your visit to the lab.

While you are writing the first version of the paper, think about any lack of information that you may fill with an extra experiment. You can discuss this within your project group, for instance via Canvas, where I think you will find a discussion forum function connected to your group.

References

1. . Hellman et al., The Active Phase of Palladium during Methane Oxidation, J. Phys. Chem. Lett. 3 (2012) 678-682 (doi: 10.1021/jz300069s)

2. N.M. Martin et al., Intrinsic Ligand Effect Governing the Catalytic Activity of Pd Oxide Thin Films, ACS Catalysis 4 (2014) 3330 (DOI: 10.1021/cs5010163)

3. J. Gustafson et al., The role of oxides in CO oxidation over Rh and Pd, ACS Catal. 2018, 8, 4438−4445 (DOI: 10.1021/acscatal.8b00498).

4. K. von Allmen et al., A new lab diffractometer for surface X-ray diffraction (SXRD), unpublished. Draft available on Canvas under the research project module.

5. J. Gustafson et al., Orientation of Oxide on $Pd_{15}Au_{05}$, unpublished.
Slide available on Canvas under the research project module.