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Experiment Report Form

ESRF	**Experiment title:** Electrochemical Promotion of Catalyzed Surface Reactions	**Experiment number**: SI-2331
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Report: Electrochemical Promotion of Catalyzed Surface Reactions

This beamtime aimed at the atomic scale elucidation of the so-called NEMCA effect, which allows activity control of a particular surface reaction by simply applying a polarisation voltage. We chose the model CO oxidation reaction over single crystalline model electrodes Pt(111)/YSZ(111). Preliminary experiments during the beamtime SI-2134 indicated little changes in the oxidation behaviour of the Pt(111) film when polarizing the electrode (see report of SI-2134). However, these changes were in comparison to the produced noise from the detector too small to be convincing. Therefore we applied for an additional beamtime (as a continuation of beamtime SI-2134) which was finally approved (SI-2331).

Beamtime SI-2331 could not confirm the polarization dependent modifications of the Pt(111)/YSZ(111) model electrode. We did not see any variation of the structure of the Pt(111) film due to electrochemical polarization over a wide range of reaction conditions. After three days we decided to concentrate on the CO oxidation reaction over Pt(111) and how the surface structure is affected by the reaction conditions rather than by external electrochemical polarization.

In a series of CO oxidation reaction experiments, we performed a comparative study of the reactivity of the Pt oxide-precovered surface and the clean Pt(111) surface. A typical experiment of this series was started by exposing the clean Pt(111) film to 18.9 mbar oxygen at 600 K, the resulting surface oxide being identified by the full development of the reflex at $H = 0.89$ (data not shown). The CO oxidation reaction over this surface Pt-oxide layer was studied at typically much lower reaction temperatures, for which the sample was cooled and thermally stabilized at 430 K in oxygen. The quality of the surface Pt oxide layer did not diminish in the process, as seen in H-scans taken afterwards.

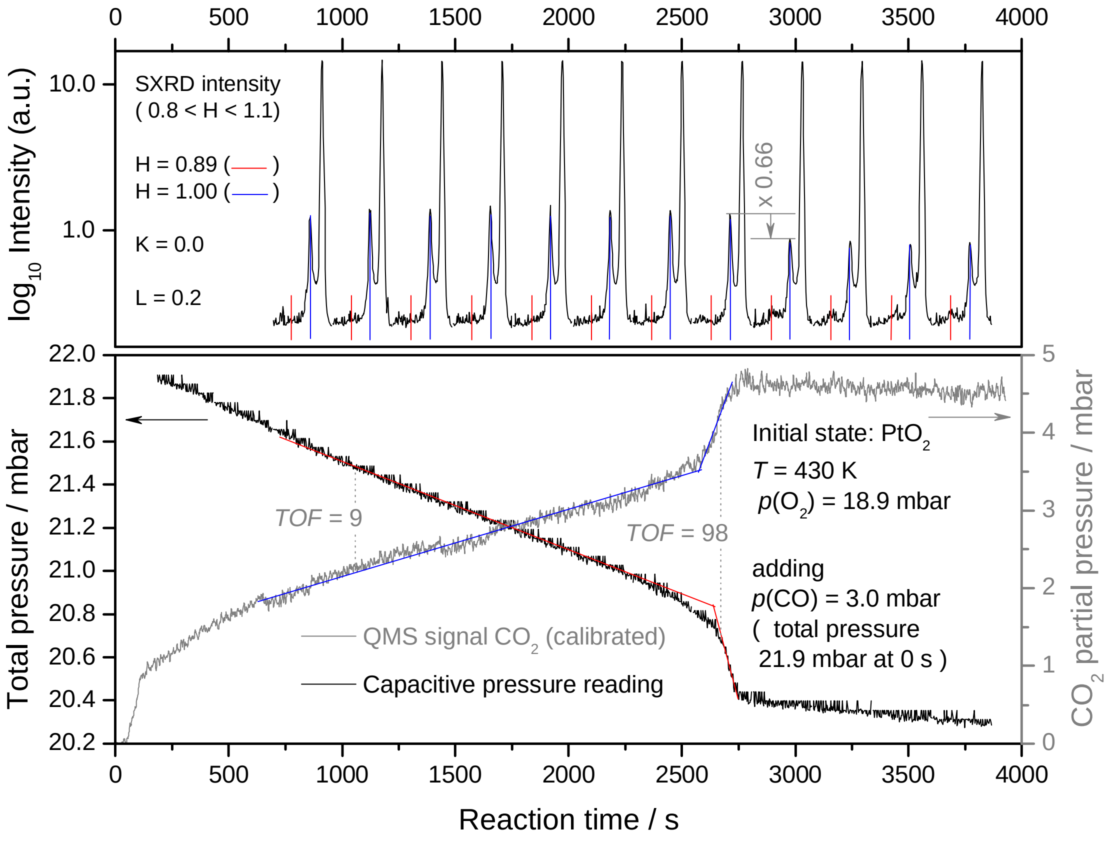

Figure: In-situ SXRD plots showing the evolution of a Pt-oxide layer on the Pt(111) film (upper panel) and the reaction kinetics (lower panel) during CO oxidation. The clean Pt(111) film has been prepared by exposure to 18.9 mbar O_2 at the reaction temperature 430 K. The entire CO quantity in the reaction vessel has been oxidized in the 0-2750 s interval, as proved by the stoichiometrically correct total pressure drop of 0.5 p(CO) (lower panel). The reaction kinetics display a slow (0-2650 s, *TOF*~10/site/s) and a highly active phase (2650-2750 s, *TOF*~100/site/s). At 430 K the reaction takes 46 minutes to complete, after which the Pt-oxide layer instantaneously emerges, as shown by the SXRD signal, which decreases at H=1.00 due to a roughening of the Pt(111) surface, and increases at H=0.89 due to the formation of a single layer thick surface oxide.

After introducing p(CO) = 3.0 mbar into the O_2 gas atmosphere the surface oxide disappeared "instantaneously" within one H-scan (260 s) and the intensity of H=1.00 reflex increased to its value characteristic of the clean Pt(111) film (cf. **Figure** upper panel). We should note that the reaction mixture is strongly oxidizing. The surface oxide does not reappear during the reaction (0-2750 s), as concluded from the absence of the diffraction peak at H=0.89. Monitoring of the simultaneous evolution of the total gas pressure and of the partial pressure of the product CO_2 (**Figure** lower panel) has been carried out by registering on-line the signal from a capacitive pressure gauge and from a quadrupole mass spectrometer (MKS).

From the linear rate of the decrease in the total pressure, as well as from the partial pressure increase of the product CO_2, the turn over frequency (*TOF* or number of product molecules generated/site/s) of the CO oxidation reaction can be derived (cf. lower panel of **Figure**). During the first reaction phase (0-2650 s), when the catalyst surface is not covered with a Pt oxide layer, the activity is approximately constant with *TOF*~10 /s. The composition of the reaction mixture changes steadily during the reaction, in a way that the excess of oxygen increases. For the short time interval 2650-2750 s the activity increased steeply by one order of magnitude (*TOF*~100/site/s) until the entire CO quantity in the batch reactor was consumed.

The simultaneous monitoring of the surface structure by SXRD (**Figure** upper panel) indicates that we can rigorously exclude the emergence of a Pt oxide layer (intensity increase at H=0.89) as well as a roughening of the surface for the short period of highly active phase (2650-2750 s). The structure of the slow and the highly active phase are therefore identical in SXRD. Only when the entire CO quantity in the batch reactor has been consumed (2750 s) and the reaction is ended, the Pt oxide layer emerges again, within the following scan. The growth of this post-reaction Pt oxide layer is evidenced by the emerging peak at H=0.89. A corresponding paper is now under preparation.