

**Experiment title:**

Dynamic surface response of three-way catalysts studied by synchrotron X-ray methods

**Experiment number:**  
CH-3542**Beamline:**

ID15B

**Date of experiment:**

from: 23.1.2013 to: 29.1.2013

**Date of report:**

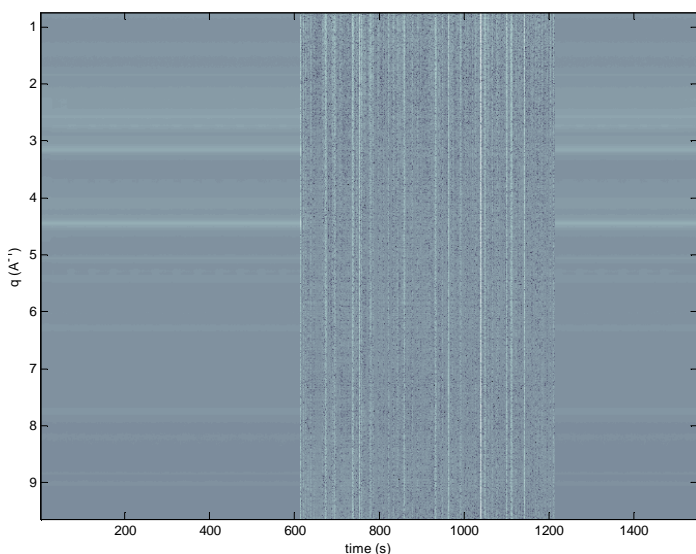
19.9.2013

**Shifts: 15****Local contact(s):** M. Di Michiel*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):****Dr. D. Ferri,\* PSI, CH-5232 Villigen PSI, Switzerland****Dr. M.A. Newton, ESRF, 38043-Grenoble, France****Report:**

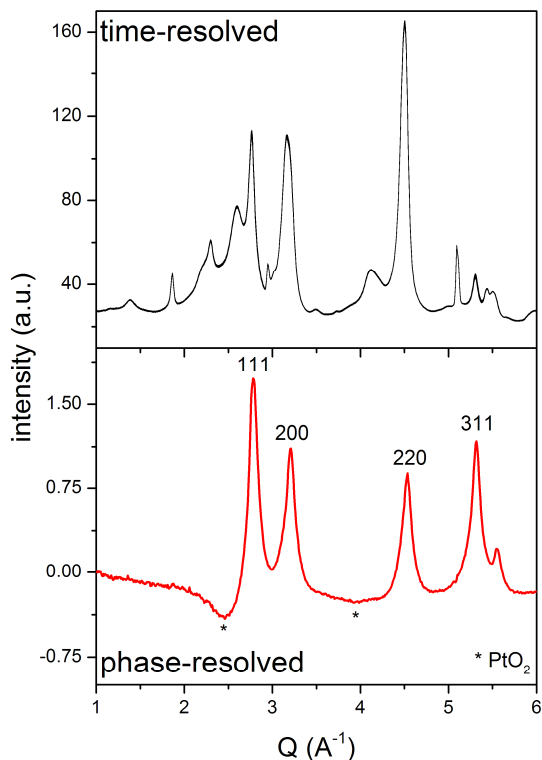
Equipment set up and correct alignment of the beamline lasted over 2 days. From Friday morning (8-9 a.m., Jan. 25<sup>th</sup>) to Monday morning (8 a.m., Jan. 28<sup>th</sup>) the beamline operation and therefore data acquisition was massively disturbed. The position of the X-ray beam was lost at intervals of minutes. This is shown in Figure 1 in a 2D visualization (Q vs. time) of a typical experiment. Since the modulation experiments for the requested beamtime consist of pulses of few seconds repeated over 40-50 min the success of the experiments depended on this. Repetition is crucial for averaging. Since the problem persisted for long time, modulation experiments were chopped in smaller experiments with the hope to be able to accumulate enough periods, which otherwise would make analysis considerably more demanding. During the week end it was possible to temporarily stabilize the position of the beam by changing the beamline control software.

Despite this issue, several samples were measured for pulse sequences of different composition and duration. A description of a typical experiment performed within the allocated beam time is provided here. Data were collected during concentration modulation experiments consisting in the periodic switch between two gas flows, i.e. CO and O<sub>2</sub> pulses (both gases 1 vol% in He) at given temperatures. The two gases were admitted to the cell for an equal time (25 sec each pulse).

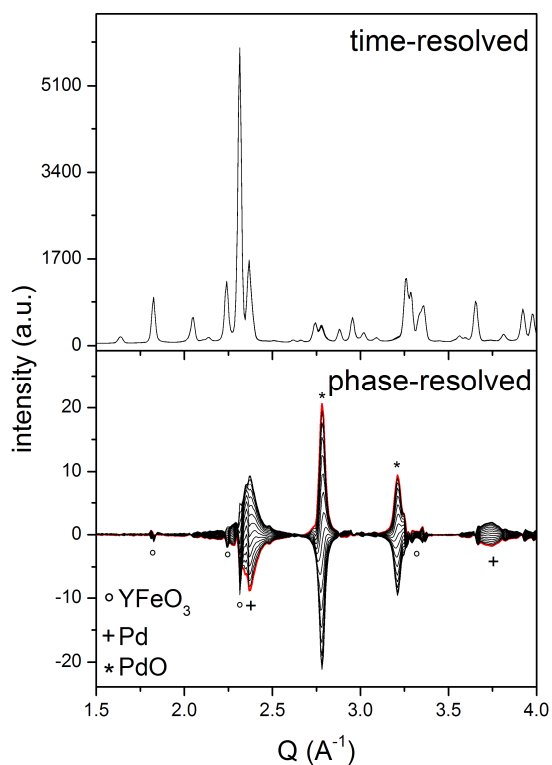
During pulsing, time-resolved high energy XRD data have been continuously collected. A full modulation period is defined as the time required to conclude a full O<sub>2</sub> vs CO sequence. A homemade cell equipped with graphite windows was used as the reactor. The exhaust of the cell was additionally monitored online using a MS (not shown here). The full sets of time-resolved XRD (100 patterns/period, 0.5 sec/pattern) can be independently processed into sets of phase-resolved XRD by phase sensitive detection (PSD).<sup>1</sup> PSD generates diffractograms free from contributions responding with a frequency different from that of the stimulation. Therefore, only the changes biased by the external stimulus, i.e. the concentration variation, are emphasized; all static signals (including noise) are filtered out and do not appear in the phase-resolved data. Figure 2 shows that the cell, which is used for IR spectroscopy at the home



**Figure 1.** 2D time resolved high energy XRD data during CO vs. O<sub>2</sub> modulation experiment at 300°C on 1.6% Pd/CeZrO<sub>2</sub>. Q values are on the Y-axis, time on X-axis. Vertical lines demonstrate beam loss.



**Figure 2.** Time- and phase-resolved high energy XRD data obtained during a CO vs. O<sub>2</sub> modulation experiment at 300°C on 2 wt% Pt/Al<sub>2</sub>O<sub>3</sub>.



**Figure 3.** Time- and phase-resolved high energy XRD data obtained a CO vs. O<sub>2</sub> modulation experiment on 2 wt% Pd/YFeO<sub>3</sub> at 400°C.

institution with CaF<sub>2</sub> windows and has been used at SLS for quickEXAFS acquisition on the same sample is suitable for use with XRD. The phase-resolved data obtained on Pt/Al<sub>2</sub>O<sub>3</sub> show the changes associated with the oxidation-reduction of Pt. A contribution from Pt-O can also be isolated. The very broad features corresponding to the Pt oxide like phase are likely due to the formation of a thin oxidic layer on the reduced Pt particles.

A similar experiment is shown in Figure 3 for an aged 2 wt% Pd/YFeO<sub>3</sub> (900°C). The catalyst is characterized by metallic Pd particles of ca. 20 nm diameter (electron microscopy). The metallic Pd phase ( $Q = 2.78 \text{ \AA}^{-1}$ ) is already visible in the time-resolved XRD data. However, the time-resolved data collected at 400°C hardly display any tangible change during the modulation experiment. Additionally, the XRD data show a complex feature that is given by the crystalline orthorhombic YFeO<sub>3</sub> structure obtained at this temperature. The reflections of Pd containing phases (PdO and metallic Pd) overlap with this phase. Structural changes are massively highlighted by PSD. The phase-resolved data exhibit narrow reflections of metallic Pd and broad reflection of a PdO-like phase. Additionally, the YFeO<sub>3</sub> phase is also responding to the CO-O<sub>2</sub> modulation. YFeO<sub>3</sub> serves as oxygen storage material. The data of Figure 3 show that despite the large metallic Pd particles present on the catalyst, the structure of Pd remains dynamic. The fact that changes related both to the Pd containing phase and the YFeO<sub>3</sub> phase are visible and occur indicates that YFeO<sub>3</sub> is involved in the dynamic changes. This dynamics can be observed by XRD combined with PSD. Given the strong interaction of the perovskite matrix with the X-rays, this information is of difficult access using X-ray absorption spectroscopy.

The experiments confirm that XRD of high quality can be obtained on technically relevant catalysts with low precious metal content. However, information on the crucial active species can be obtained by application of PSD to the high energy XRD set of data. In a single snapshot the whole structure of the material is obtained. The detailed time-resolved kinetics of each phase and of the structural information is obtained that is difficult to get by other methods.

Data evaluation is on-going.

Dr. M. Di Michiel and the team of ID15B are greatly acknowledged for their crucial contribution to the success of the campaign.

## References

(1) D. Ferri, M.A. Newton, M. Di Michiel, S. Yoon, G.L.

Chiarello, V. Marchionni, S.K. Matam, M. Aguirre, A. Weidenkaff, F. Wen, J. Gieshoff, *PCCP* **15** (2013) 8629.