	Experiment title: Combined XRD-IR study of heterogeneous catalysts at work under red-ox conditions	**Experiment number**: CH-3197
Beamline: ID15B	**Date of experiment**: from: 25.1.2011 to: 30.1.2011	**Date of report**: 19.8.2011
Shifts: 15	**Local contact(s)**: Jerôme Andrieux	*Received at ESRF:*

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Report:

A description of a typical experiment performed within the allocated beam time is provided here. The data refer to a concentration modulation experiment consisting in the periodic switch between two gas flows, i.e. CO and O_2 pulses (both gases 1 vol% in He) at 300°C over 2 wt% $Pd/Ce_{1-x}Zr_xO_2$ (briefly, 2PdCZ). The two gases are admitted to the cell for an equal time (25 sec each pulse). During pulsing, time-resolved DRIFT spectra and hard-XRD data have been continuously and synchronously collected. A full modulation period is defined as the time required to conclude a full O_2 vs CO sequence. A modified DRIFT cell for a combined use with X-rays has been used as the reactor.[1] Online MS analysis of the exhaust gas of the reactor cell has been performed as well simultaneously. Only the issues related to the evaluation of the XRD data are demonstrated here. Crucial to the experiment is the synchronization of the acquisition of XRD and DRIFT data. From then on the modulation experiment was determined by the infrared spectrometer. Typically, the subsequent trigger signal for EXAFS data collection was provided at each CO pulse of the modulation experiment.

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).[2] 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
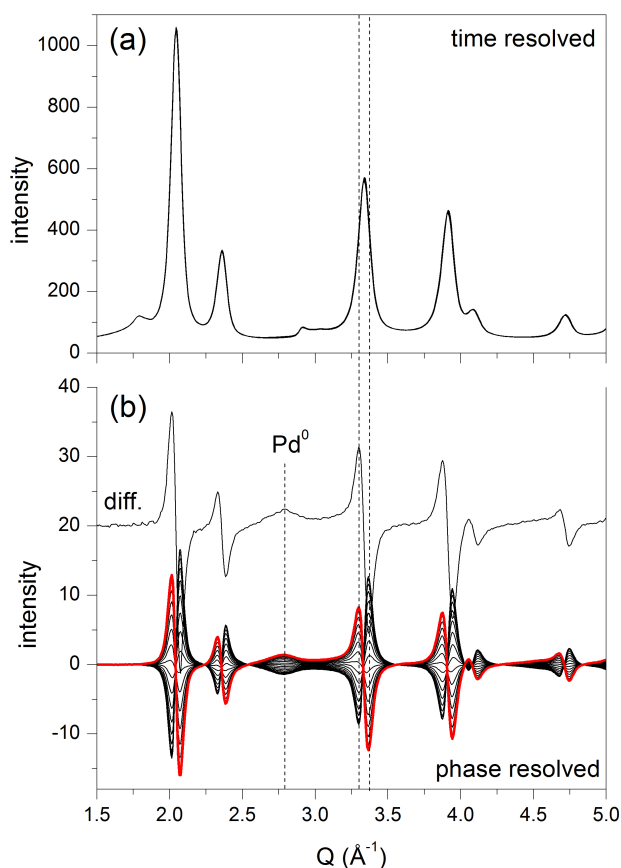

Figure 1. (a) time resolved hard-XRD data during CO vs. O_2 modulation experiment at 300°C on 2PdCZ; (b) corresponding phase-resolved data and difference XRD. The bold red XRD is used to guide the eye.
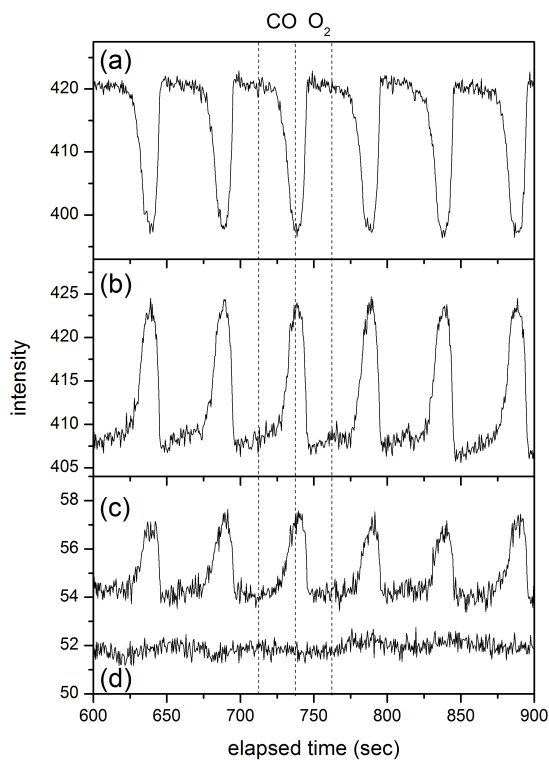
Figure 2. Temporal evolution of the signals marked in Fig. 1 from the averaged time-resolved XRD data of 2PdCZ: (a) 3.4, (b) 3.3, (c) 2.8 Å^{-1} and (d) 2.8 Å^{-1} for CZ.

filtered out and do not appear in the phase-resolved data.

The time-resolved hard-XRD data collected during a modulation experiment (100 XRD x 25 periods, Fig. 1a) exhibit the reflections of cubic CZ but hardly display any tangible change. No information is available about the state of Pd. This is typically associated with the fine dispersion of PdO particles induced by CZ.

The corresponding phase-resolved XRD data (Fig. 1b) exhibit only the very subtle changes associated with the signals responding to the modulation experiment. All signals of the CZ support shift repeatedly to lower and back to higher Q values in response to the CO and the O$_2$ pulses, respectively. This behaviour qualitatively describes the reduction and the re-oxidation of CZ typically associated with its oxygen storage capacity (OSC). Importantly, the data also exhibit additional features at ca. 2.8, 3.1 and 4.5 Å^{-1} not characteristic of CZ. These broad signals correspond to metallic Pd reflections and describe the change in the state of the Pd active phase. No Q shift is observed. The sole intensity change is associated with the relative increase of long range order attributed to PdO reduction. Therefore, the modulation data can capture the reversible reduction and re-oxidation of PdO and CZ.

From the PSD envelopes one can precisely assess the temporal behaviour of the structural changes using the 100 averaged time-resolved XRD patterns. The detailed structural-dynamic behaviour of the system can be then uncovered. This is shown in Fig. 2 exhibiting the kinetics of three selected signals (the ones marked in Fig. 1). Reduction of both PdO and CZ occurs much slower than re-oxidation. This is the effect of the OSC of CZ that is able to provide oxygen during the reducing pulse. The signal at 2.8 Å^{-1} is unambiguously associated with reduced Pd for comparison with the same signal in an identical experiments with CZ (Fig. 2d).

All the above information needs to be coupled to the synchronously measured DRIFT and MS data to obtain detailed structural information. Rietveld refinement of selected XRD data is on-going with the aim to estimate the amount of oxygen exchanged during the CO vs. O$_2$ pulsing.

A number of samples treated under various conditions have been analysed in this way and the evaluation is on-going.

The experiment of Figs. 1-2 shows that combination of XRD (and IR) with MES is a powerful tool.
1) The PSD approach provides some sort of surface sensitivity to XRD; it extracts what cannot otherwise be seen, i.e. the Pd nano-particle behaviour hidden below the static background of XRD.
2) The data of Fig. 1b should allow the quantification of the Pd particle size corresponding to the situation of maximum reduction extent. This is hardly possible by other methods.
3) The method allows to treat difficult samples for other techniques (e.g. XAS) and to get comparable detailed time-resolved structural information that is otherwise difficult to get.

References
(1) M.A. Newton, B. Jyoti, A.J. Dent, S.G. Fiddy, J. Evans, *Chem. Comm.* (2004) 2382.
(2) D. Ferri, M. Santhosh Kumar, R. Wirz, A. Eyssler, O. Korsak, P. Hug, A. Weidenkaff, M.A. Newton, *PCCP* **12** (2010) 5634.