



Experiment title: Synchronous QuickEXAFS-IR-MS analysis of supported metal nano-particles: a modulation excitation spectroscopy approach

Experiment number:
CH-3313

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Report:

The beamtime was dedicated to the application of modulation excitation spectroscopy (MES) [1] to QuickEXAFS data collected on various supported Pd nano-particle catalysts. The experimental conditions to obtain concentration modulation spectroscopy were provided by 30 alternate switches between 1 vol% CO and 1 vol% O₂ in He as carrier gas. QuickEXAFS data were collected at monochromator speed of 4000 over the energy range 24 to 25.5 keV by 10 eV steps (1500 points), resulting in an acquisition time of 5.3 sec/scan (upwards or downwards). A dedicated EXAFS-XRD-IR cell [2] has been used to combine QuickEXAFS with IR data approximately at the same position within the catalyst bed. MS has been coupled online to the spectroscopic experiment. Unfortunately, a hardware problem hindered us from completing IR experiments.

Figure 1 shows a comparison between a series of non-energy corrected single shot QuickEXAFS spectra of 5.3 sec and averaged over 10 consecutive scans of Pd/Al₂O₃ catalysts (PdA) with a nominal Pd loading of 0.5, 1, 2, 3.5 and 5 wt%. Spectra were recorded with a 5 mm sample pathlength at the Pd K-edge using the Si(111) monochromator crystal.

Averaging over 10 scans improves the quality of the QuickEXAFS data, especially in the EXAFS region.

A typical MES experiment where CO vs O₂ modulation is applied to the 0.5 wt% and 2 wt% Pd/Al₂O₃ catalysts is shown in Figure 2. The raw spectra, the time-resolved spectra averaged over 25 CO vs O₂ modulation periods (out of 30) and the resulting phase-resolved spectra are shown from left to right.

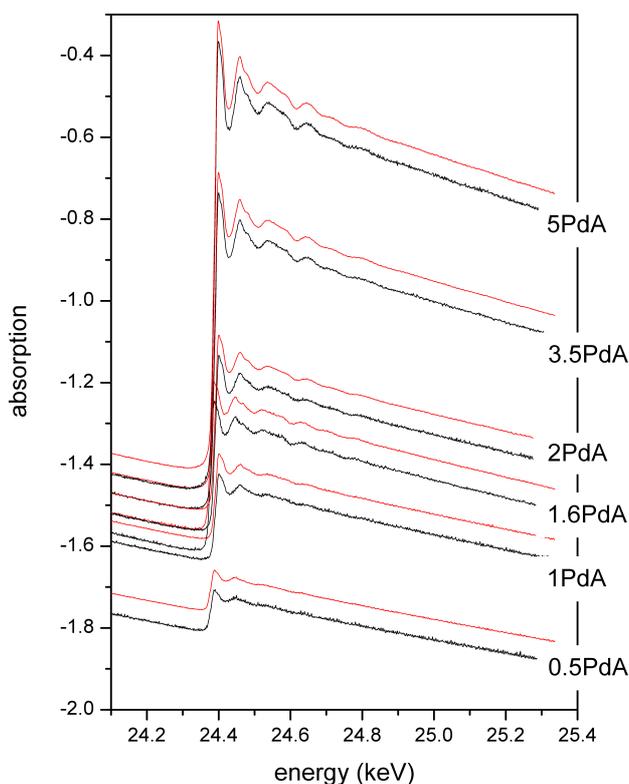


Figure 1. Raw and averaged (10 scans) QuickEXAFS data for PdA catalysts at room temperature.

The green spectra are the first QuickEXAFS spectra recorded right before the triggering of the MES experiment by the EXAFS and represent the (oxidized) state prior to MES. The subsequent series of time-resolved and averaged spectra show that during the experiment, the state of Pd oscillates repeatedly between partly oxidized and reduced. The initial oxidized state cannot be recovered at 300°C during CO vs. O₂ switches. The data of Figure 2 allow to clearly follow the dynamic oxidation state of Pd along the modulation periods. The details of this dynamic behaviour can be clarified in association with the MS data, not shown here, and possibly IR data under identical conditions. The spectra also display an overlapping frequency function clearly visible in the EXAFS region in Figure 2. The function gains importance with the decreasing

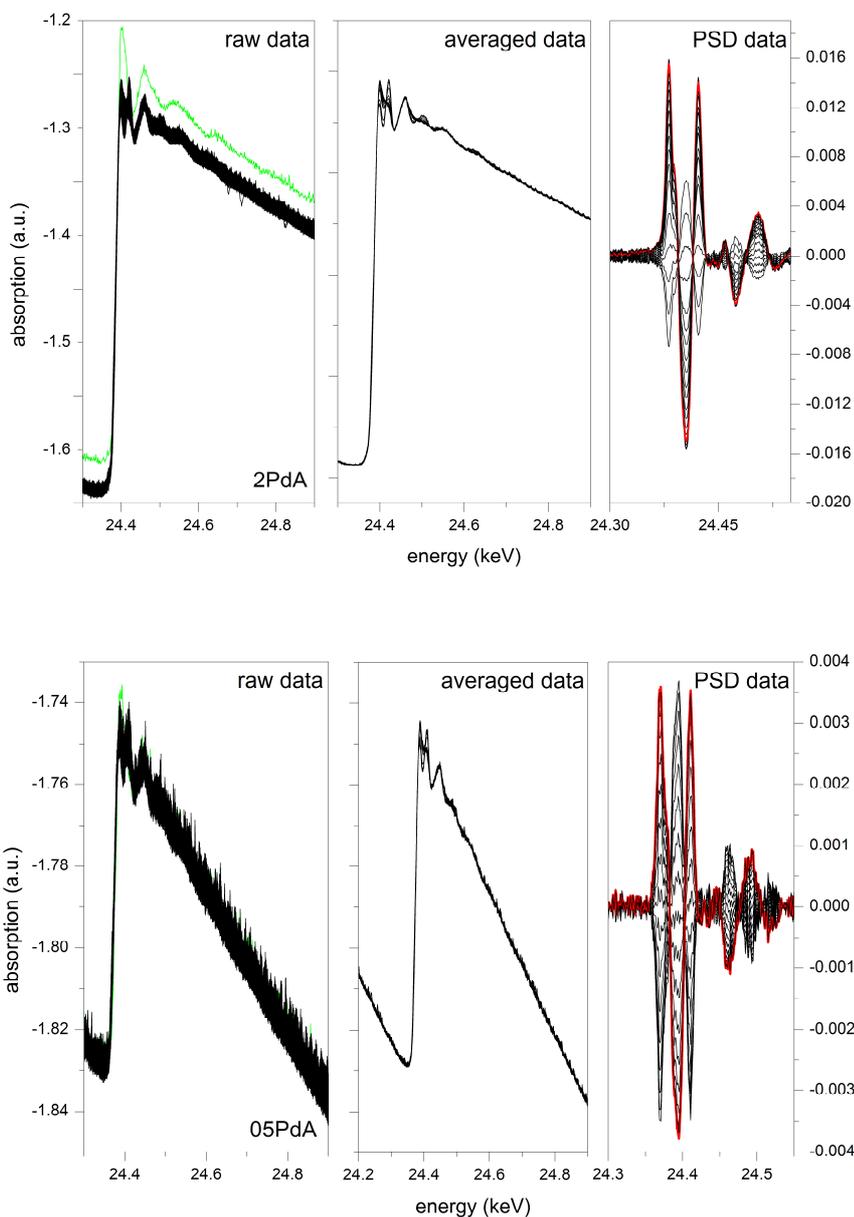


Figure 2. CO vs O₂ MES experiment on 05PdA (bottom) and 2PdA (top).

environmental conditions. Similar features can be obtained for 1.6 wt% Pd/Al₂O₃-Ce_{1-x}Zr_xO₂ (A:CZ=1:1), traditionally more difficult because of the CZ component.

References

- [1] Ferri, Santhosh Kumar, Wirz, Eyssler, Korsak, Hug, Weidenkaff, Newton, *PCCP* **12** (2010) 5634.
- [2] Newton, Jyoti, Dent, Fiddy, Evans, *Chem. Commun.* (2004) 2382.

Pd loading and with difficult catalyst samples with strongly absorbing metal oxide supports. The function seems to be provided, though partly, by the electronic control of the monochromator position at the rocking curve. This does not prevent to collect high-quality spectra at least with transparent metal oxide supports such as Al₂O₃. Any artefact and any signal not responding to the modulation frequency are filtered by PSD, which shows only the signals responding to the external stimulation. Averaging of the QuickEXAFS spectra over the modulation periods considerably increases the S/N ratio, especially for poorly absorbing samples as 05PdA. The PSD enables to investigate structural changes that cannot be captured within the set of time-resolved data.

Finally, experiments on LaFe_{0.95}Pd_{0.05}O₃, a more difficult strongly absorbing sample, clearly show the unprecedented adequate energy resolution achieved needed to differentiate the PdO₆ feature in the whiteline that is crucial for operando-in situ studies under