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ESRF	**Experiment title:** Interactions of protic solvents with Pd supported on TiO_2, CeO2, $CeZrO_4$, and $LaFeO_3$ perovskites	**Experiment number:** 31-01-11
Beamline: BM31	**Date of experiment:** from: 20.09.2016 to: 25.10.2016	**Date of report:** 23.1.2017 *Received at ESRF:*
Shifts: 15	**Local contact(s):** Hermann Emerich	

Names and affiliations of applicants (* indicates experimentalists):

Mark A. Newton[1]*, Davide Ferri[2]*, Chris Mulligan[3]*

1- Department of Physics, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL, UK
2- Paul Scherrer Institut (PSI), CH-5232 Villigen, Switzerland
3- Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, UK

Report:

The experiment requested about 3 shifts for installation and beamline alignment. Initially, issues related to the liquid pumping unit were encountered. The XAS spectra were affected by the pulsing of the peristaltic pump, which was replaced by a syringe pump (used in the past for similar experiments [1]). Additionally, initial in situ experiments were affected by inappropriate degassing of the solution that resulted in bubbles, whose presence could be recognized in the XAS spectra by the loss of intensity at repeated intervals. Once this issue could be fixed (2nd day) the quality of the spectra (30-40 s/spectrum) at the Pd K-edge (24.35 keV) was good and analysis could be pushed to 12-13 $Å^{-1}$.

The purpose of the experiment was to analyze the influence of the presence of a solvent (50 vol% H_2O/50 vol% ethanol) on the oxidation state of Pd-based catalysts. Previous experiments had shown that this mixture is able to reduce supported PdO, the PdO particle size being critical [1]. In this experiment, various metal oxide supports have been tested, including Al_2O_3, $Al_2O_3/CeZrO_2$ and $LaFeO_3$ in order to monitor the state of Pd as a function of the stability of the Pd-O bond in such catalysts. Because these kind of catalysts can be used in synthesis reactions, e.g. C-C coupling [2], we have additionally followed the state of Pd upon addition of a base (0.1 M K_2CO_3) to the solvent: an additional element ubiquitous to C-C coupling catalysis

The experiments consisted in a heating ramp from ambient temperature to 80°C at 1°C/min while measuring quickEXAFS spectra as a function of temperature and of position within the catalyst bed [1]. For this purpose, the cell was moved repeatedly in order to obtain EXAFS spectra in 9 different positions within the bed to monitor the evolution of any reduction gradients. This is the reason of the slow temperature ramp. While we were able to confirm previous measurements obtained on independent Pd/Al_2O_3 catalysts, we decided to study a commercially available and reduced 5 wt% Pd/Al_2O_3 following this protocol. EXAFS showed that this material is in its native state comprised of very small and ostensibly reduced Pd nanoparticles (ca. 10-20 atoms). The same catalyst was calcined at 500°C for 5 h to yield an equivalent PdO sample allowing us to compare two different starting structures of the Pd component. The small reduced Pd particles were found to increase in size as of ca. 40-50°C; the PdO based sample reduced only at

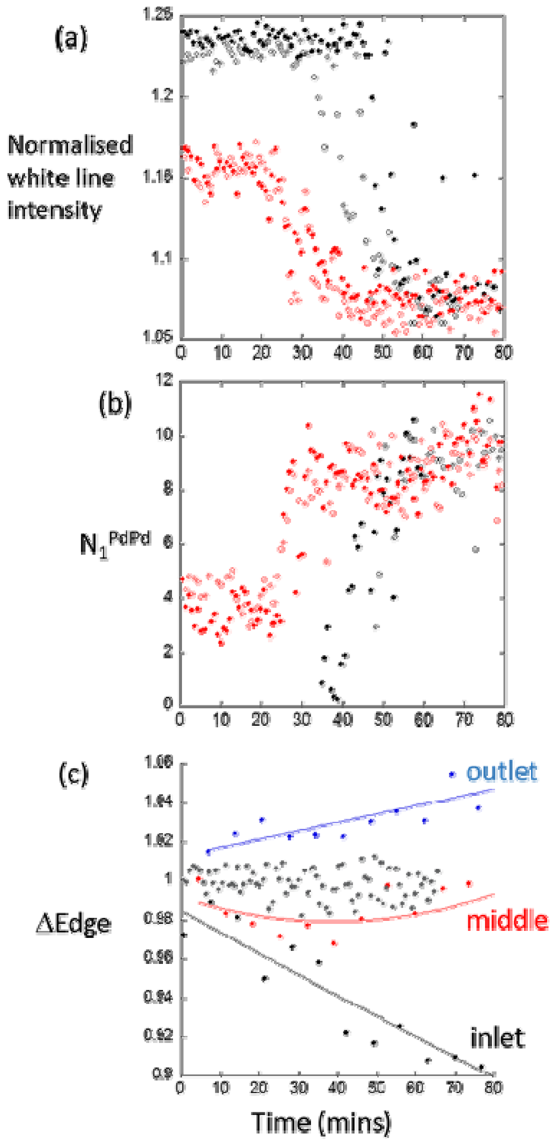

Figure 1. (a) Temporal variation of the Pd K-edge XANES white line and (b) of the PdPd coordination (N_1^{PdPd}) indicative of the formation of *fcc* Pd^0 nanoparticles of fresh (red) and calcined (black) 5 wt% Pd/Al_2O_3 in the space-resolved experiment under solutions of ethanol/H_2O (open symbols) and ethanol/H_2O/0.1M K_2CO_3 (filled symbols). (c) Variation of the intensity of the Pd K-edge jump (relative to those obtained from an initial mapping of the wet bed at RT). Grey correspond to variations observed under 50:50 ethanol/H_2O. Black, blue, and red symbols are the variations in edge jump intensity measured at three inducated axial positions within the beds during heating under the 50:50 ethanol/H_2O/0.1M K_2CO_3. The attainment of 80°C occurs at ca. 55 mins. Lines are used to guide the eye.

temperatures in excesss of 70°C. Addition of 0.1 M K_2CO_3 to the solvent mixture had two effects. First, it caused a retardation in the PdO reduction of calcined Pd/Al_2O_3 by ca. 20°C. Second, the intensity of the edge jump increased measurably while moving to the end of the catalyst bed within the cell while it decreased at the inlet (Figure 1c). This strongly suggests the induction of a mass transport of Pd along the bed as a result of the addition of the K_2CO_3. Beside Pd/Al_2O_3, reduction was measured in the case of $LaFeO_3$-based catalysts as well. In the absence of K_2CO_3, the oxidised Pd present did not reduce. However, in the presence of K_2CO_3 reduction of the PdO was again evidenced as was considerable loss of absolute edge-jump intensity as an axial function of the bed position. Again therefore the base appears to induce a leaching of the Pd in the absence of any halogenated component in the solvent mixture. We note that this material was previosuly shown to promote Suzuki C-C coupling [2] and that both Pd reduction, the strong structural changes observed in the support, and Pd leaching were attributed to the presence of the aryl halide reactant of the reaction scheme. Our measurements show that, at tenfold lower concentrations of the base used for that reaction, i.e. K_2CO_3, and in the absence of the aryl halide reduction of octahedral Pd and its solubilisation can occur under relatively mild conditions.

The EXAFS measurements will be complemented by transmission electron microscopy measurement of the fresh and used samples. In a preliminary measurement, TEM could verify the detachment of Pd particles (ca. 3-4 nm) from Al_2O_3 in the presence of K_2CO_3. Additionally, two distinct structures are evident in the TEM image of $LaFePdO_3$ identically treated, which suggest the destruction of the $LaFeO_3$ structure associated with reduction of octahedral Pd.

The data collected on Pd/Al_2O_3 are being summarized in a scientific publication.

Extensive data evaluation of the EXAFS data is on-going. H. Emerich is greatly acknowledged for his support during the allocated beamtime.

References

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