EUROPEAN SYNCHROTRON RADIATION FACILITY
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# Experiment Report Form

The aim of this investigation is to conduct *in situ* studies of XAS at the metal K- edge on supported Pd catalysts to understand the nature of PdO-Pd transformation and the role of support in assisting/prohibiting this transformation. We focused our work primarily on the Pd K-edge, Ce L3 and K-edge to investigate the conversion of PdO under oxidising and reducing conditions.

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

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- 1st September for experiments carried out up until January of the same year.

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>In situ studies of palladium supported ceria catalyst | **Experiment number**: |
| **Beamline**: | **Date of experiment**:<br>from: 13/11/2015 to: 17/11/2017 | **Date of report**: |
| **Shifts:** | **Local contact(s)**: Manuel MONTE CABALLERO | *Received at ESRF:* |

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## Report:

The aim of this investigation is to conduct *in situ* studies of XAS at the metal K- edge on supported Pd catalysts to understand the nature of PdO-Pd transformation and the role of support in assisting/prohibiting this transformation. We focused our work primarily on the Pd K-edge, Ce L3 and K-edge to investigate the conversion of PdO under oxidising and reducing conditions.

Supported palladium catalysts have found several applications in the field of catalysis, in particular, methane combustion, hydrogenation and for diesel oxidation (in combination with other metals). Owing to its successful applications in these fields, several studies have focussed on the oxidation and reduction properties of palladium supported catalysts and more importantly the transformation of PdO to Pd metal in air at elevated temperatures, where it has been shown, for example, that the conversion of PdO to Pd during the high temperature methane oxidation reaction has a profound effect on catalyst reactivity[1-7]. We carried out a range of experiments. First we examined the heating of Pd/Ceria sample in air to determine whether the process of reduction, similar to $Pd/Al_2O_3$ observed in our earlier work, takes place at 950C. In figure 1 we show the XANES data collected during the heating process along with the Fourier transform of the Pd K-edge EXAFS data. Whilst we observe some minor changes above 900$^o$C in the XANES and reduction in the magnitude of the FT, we interpret this as primarily due to the PdO stabilisation by ceria lattice and perhaps prevent the PdO-Pd-PdO transformation.

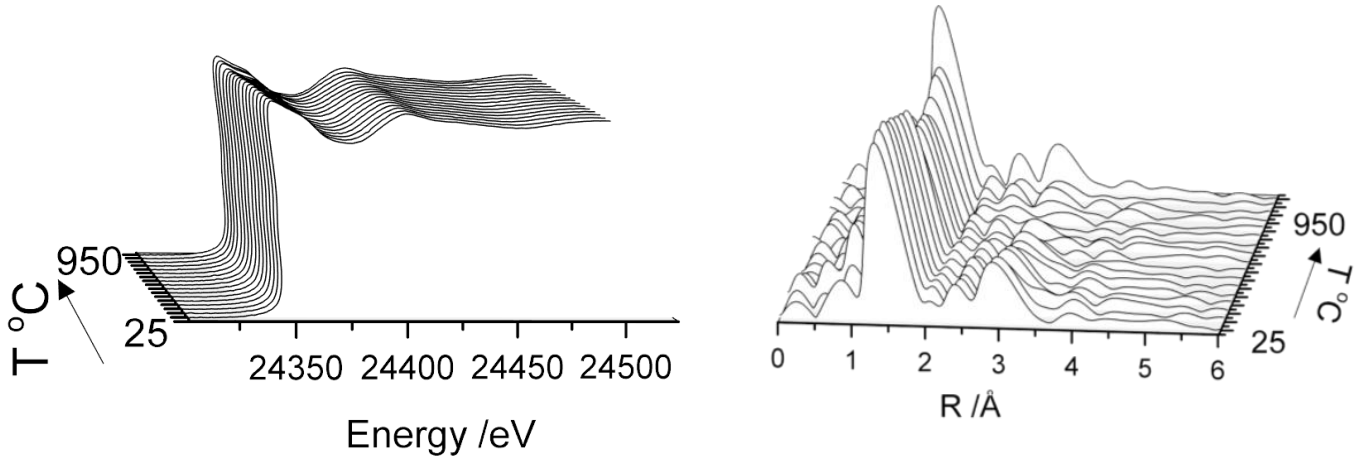


**Fig.1 Pd K-edge XANES (left) and FT of the Pd K-edge EXAFS recorded during heating 5%Pd/$CeO_2$ from room temperature to 950C in Air.**

On the other hand PdO is converted predominantly to Pd metallic phase when heated in air above 850C and upon cooling below ca 650C, the metallic Pd is converted back to PdO, shown in Figure 2.

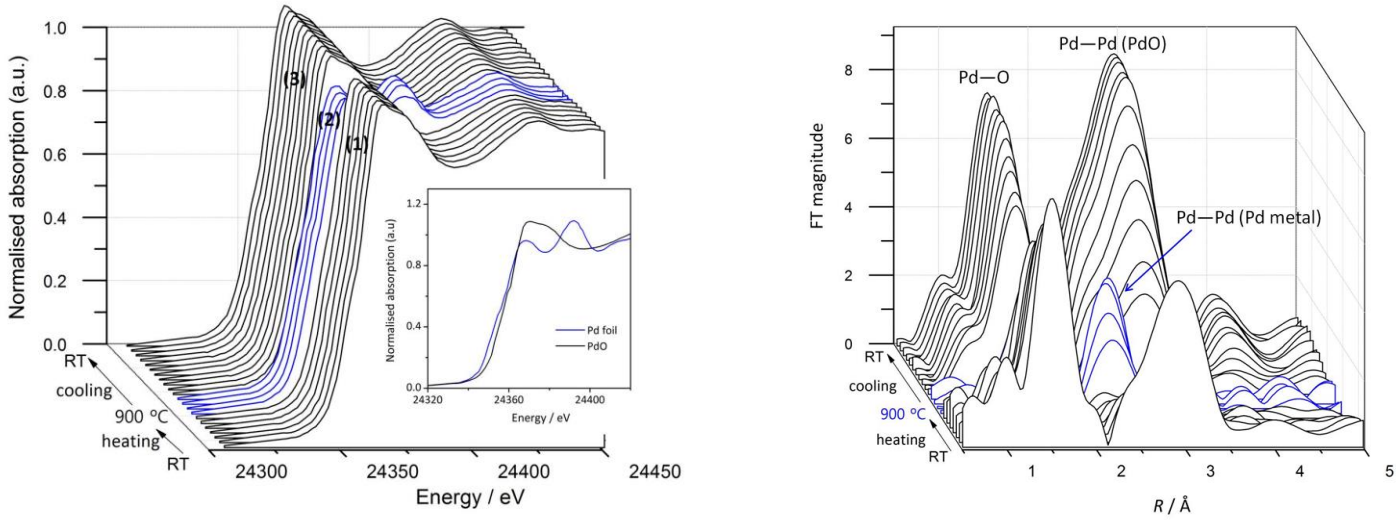


**Fig.2 Pd K-edge XANES (left) and FT of the Pd K-edge EXAFS recorded during heating 5%Pd/$Al_2O_3$ from room temperature to 950C in Air[8].**

The analysis of the EXAFS data is in progress to complete this part of the work. In addition to this, we carried out reduction in hydrogen at both Ce L3, Ce K edges to establish the changes in ceria. In particular we observed that in presence of Pd, the reduction of CeO2 (Ce(IV) occurs at much lower temperatures ca 100C compared to the one without Pd. Surprisingly the part of the reduced Ce(IV) ions are reoxidised to Ce(IV). In order establish this effect is primarily due to the metal support interaction or not, a recylcing of the reduction experiment is necessary to further understand the unusual behaviour of the supported ceria catalyst

**Reference**

1.R. B. Anderson, K. C. Stein, J. J. Feenan and L. J. E. Hofer, *Industrial and Engineering Chemistry*, 1961, **53**, 809-812; 2. D. Ciuparu, M. R. Lyubovsky, E. Altman, L. D. Pfefferle and A. Datye, *Catalysis Reviews-Science and Engineering*, 2002, **44**, 593- 649. 3. E. M. Cordi and J. L. Falconer, *Journal of Catalysis*, 1996, **162**, 104-117. 4. R. J. Farrauto, M. C. Hobson, T. Kennelly and E. M. Waterman, *Applied Catalysis a-General*, 1992, **81**, 227-237. 5. M. Lyubovsky and L. Pfefferle, *Catalysis Today*, 1999, **47**, 29-44. 6. A. K. Datye, J. Bravo, T. R. Nelson, P. Atanasova, M. Lyubovsky and L. Pfefferle, *Applied Catalysis a-General*, 2000, **198**, 179-196. 7. S. W. Yang, A. Maroto-Valiente, M. Benito-Gonzalez, I. Rodriguez-Ramos and A. Guerrero-Ruiz, *Applied Catalysis B-Environmental*, 2000, **28**, 223-233. 8. J. Keating, G. Sankar, T. Hyde and S. Kohara, *PCCP*, 2013,**15**, 8555-8565