



**Experiment title: Redox and Size-effects on TWCs catalytic performance under operando conditions**

**Experiment number:**  
CH-2743

**Beamline:**  
ID24

**Date of experiment:**  
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**Shifts:**  
18

**Local contact(s):**  
Dr. M. A. Newton

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**Names and affiliations of applicants (\* indicates experimentalists):**

Prof. M. Fernández-García (\*)

Dr. A. Martínez-Arias (\*)

Dr. A. Kubacka

Instituto de Catálisis (CSIC), Campus Cantoblanco, 28049-Madrid, Spain

**Report:**

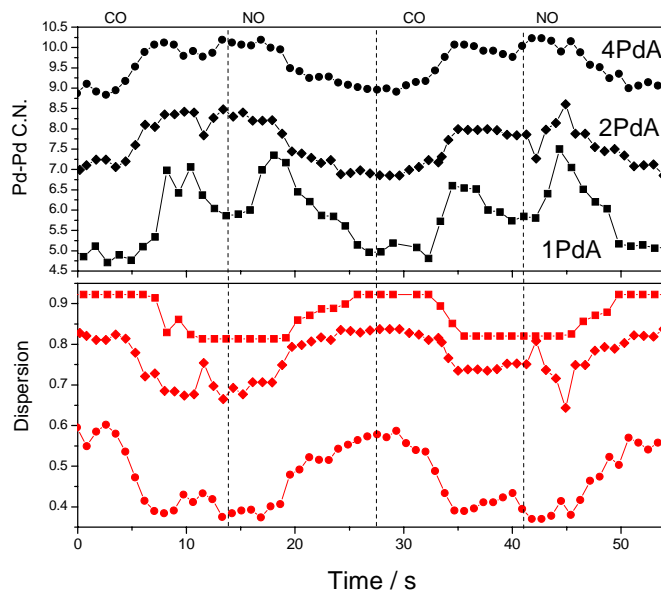
Alumina-supported Pd catalysts promoted with Ce-Zr mixed oxides (CZ component) are widely employed as three-way catalysts (TWCs) for the control of toxic emissions in the exhaust of petrol-fuelled automobiles. Analysis of the noble metal interactions with the CZ promoter and the carrier during “real” operation conditions is necessary to understand the physical basis of the catalytic behavior of TWCs. This goal requires the analysis of all components of TWCs subjected to rapid changes (1-3 Hz) of the exhaust gas mixture, which may have stoichiometric (equal molar ratio of reducing and oxidant molecules;  $\lambda = 1$ ), oxidizing ( $\lambda > 1$ ), and reducing ( $\lambda < 1$ ) nature, and using working temperatures [1].

XAFS experiments were carried at the beam line ID24 with a Si(311) monochromator in Laue-configuration and using a CCD detector. A plug-flow reactor were used to subject the samples to an atmosphere containing 0.1 %  $C_3H_6$  + 0.1 % NO + 1 % CO (Ar balance) and variable quantities of oxygen (or model less complex mixtures) in order to go from oxidizing to reducing conditions and vice versa in a step change. Results at the Pd K-edge were taken with a typical temporal resolution of 50-200 ms (depending on Pd loading, experimental conditions, etc.) and lasted several seconds.

Our previous experiments were focusing on the main physico-chemical phenomena occurring upon such cycling conditions and aimed to uncover the structure-activity relationship details governing the behavior of these systems [2]. Moreover, by making a long (e.g. XRD) vs. local (e.g. XAS) analysis of structural effects we detailed most of the noble-metal dynamic behavior, which is a complex response to the gas atmosphere and includes morphological size-shape changes but also formation of several phases among which some are expected (metallic, oxidized Pd) and others less commonly observed and essentially unexpected (Pd carbides) in the experimental conditions of operation [3].

During this run we tried to investigate the size and redox dependence of such behavior. Size dependence was focused in the noble metal component while redox dependence concerns both the noble metal and the promoter. So, for a step by step study we initially started the study with a Pd on alumina series containing samples with 0.5, 1.0, 2.0 and 4.0 wt % of the precious metal. Initial estimation of the particle size after reduction indicates a particle size (for all samples where EXAFS can be measured in dynamic conditions; e.g. loading above 1 wt. %) below 1, 1.5 and 2.5 nm for, respectively, 1, 2, and 4 Pd samples. The influence

on size was first analyzed in connection with CO and NO elimination upon oxygen presence/absence. While upon stationary conditions the first reaction is essentially a surface insensitive reaction the second is not, so a complex and different chemistry is expected for both reactions as a function of the Pd morphological properties. In order to test it, we first measured/fitted EXAFS data obtained upon cycling (CO/NO) conditions and calculated the dispersion (Pd surface fraction) variations observed throughout such conditions (Fig. 1).



Using such information we normalized the chemical information extracted from DRIFTS (mostly adsorbed molecules) and Mass spectrometry (gas phase reactants and products). Contrarily to stationary conditions, the Pd phase transformation from metallic to carbide generates a clear size-sensitivity for the CO oxidation reaction. Also, NO reduction seems more complex than presumed from stationary results. In fact, we detected a significant contribution from a NO dissociation pathway practically unadverted in literature reports. The analysis of this reaction path allowed to interpret the size-sensitivity of NO reduction by effect of two elemental steps NO dissociation (at low temperatures) and N-N coupling (dominant at high temperatures) [4].

In a second stage of the study, we are now dealing with some of the redox effects of importance and particularly, with the size-dependence of the oxygen release and storage of the promoter by using a combination of XRD and XAS data. The extensive data concerning this point is currently undergoing analysis and we believe that this highly successful demonstration of a new experiment (mainly a XRD/XAS comparative analysis, together with the use of DRIFTS and MS) will lead to several highly quality publications in 2010.

Lastly, we would like to thank Dr M. A. Newton for the extensive support he has given this experiment. Without his support and know-how it could not have been the success that it has turned out to be.

## References

- 1.- "Catalysis by ceria and related materials". A. Trovarelli (ed.). Imperial College Press (London), 2002.
- 2.- M. A. Newton, C. Belver, A. Martínez-Arias, M. Fernández-García. *Nature Materials*, **2007**, *6*, 528-532.
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- 4.- A. Kubacka, A. Martínez-Arias, M. Fernández-García, M. Di Michel, M. A. Newton, *J. Catal.* **2010**, *270*, 275-284.