EUROPEAN SYNCHROTRON RADIATION FACILITY
ESRF User Office
BP 220, F-38043 GRENOBLE CEDEX, France
Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Report on beam time: CH9264, ID15b

Dr. Ana Iglesias-Juez, Prof. Marcos Fernandez-Garcia, (CSIC, Madrid), Dr. Mark A. Newton (ESRF) ,

Time resolved high energy diffraction (HXRD)/diffuse reflectance infrared spectroscopy (DRIFTS) study of the size dependent redox properties of $CeZrO_4$ in the presence and absence of Pd nanoparticles.

Within the 18 shifts allocated to this proposal we were to mount, test and demonstrate the exceptional potential of a new experimental methodology (first applied in project MA-617; 2008), fusing time resolved hard X-ray diffraction, infrared spectroscopy, and mass spectrometry for the *in situ* time-resolved study of powder materials such as catalysts. The project follows previous results focussed on the Pd noble metal role on Three-way catalysts (TWCs) upon cycling conditions typical of motor operation. Under a CO/NO cycling atmosphere our last contributions unveil details concerning; i) the formation of an unexpected noble metal carbide upon CO and its elimination under NO [1]; and ii) the role of Pd particle size in alumina supported systems on both CO and NO elimination [2]. This beam time aimed to analysing the behaviour of the $CeZrO_4$ component and the metal-promoter interface in real ceria-zirconia-promoted, alumina-supported TWCs systems.

Figure 1 shows representative data obtained for a 33 wt. % $CeZrO_4/Al_2O_3$ (33ZCA) support and the 4 wt. % Pd-loaded (4Pd33ZCA) catalysts upon CO/NO cycling conditions with different repetition times (13.86 and 21.40 seconds).

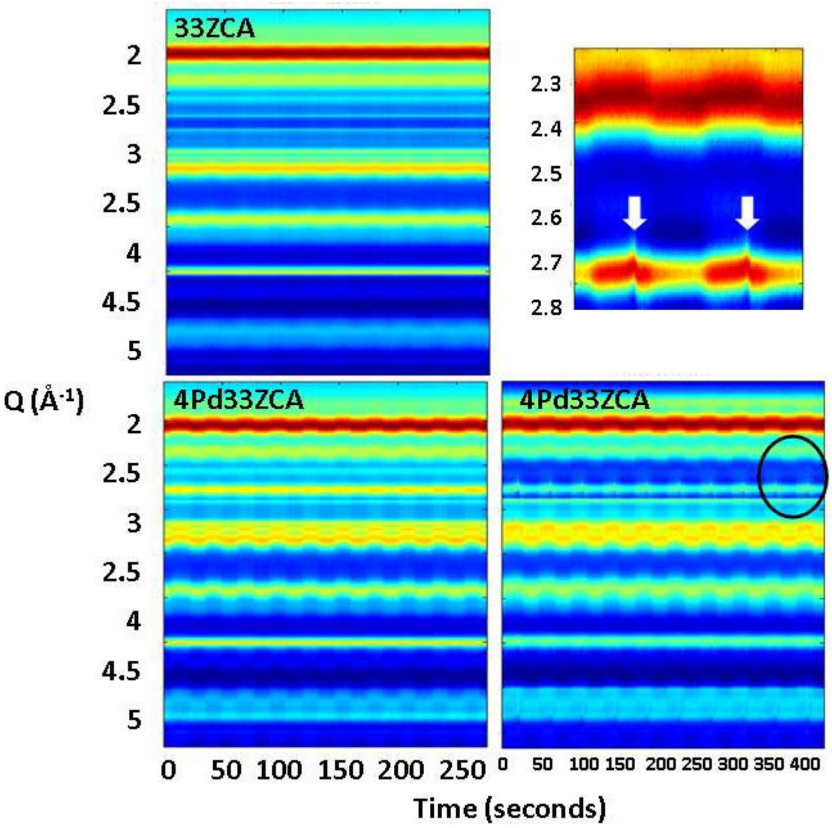


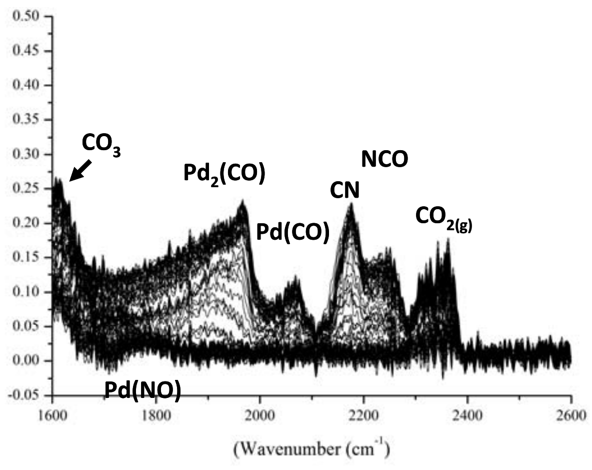
Figure 1. Colour maps showing the diffraction pattern behaviour of 33ZCA and 4Pd33ZCA systems during redox cycling (as indicated) at 673K. Diffraction images were collected using 90 keV X-rays and at a repetition rate of 2.5Hz. Two cycling times (13.86 and 21.40 s) are presented.

Within the range of Q space shown in Figure 1 (which is not the maximum that can be achieved with the current setup) a variety of aspects of the structural reactive behaviour of these systems are very clearly divined, giving complementary information to the Zr K-edge experiments run at ID24 [3]. The structural new information of the CeZrO4 phase can be summarised as;

i) an increased resistance of the Pd nanoparticles to structural modification (size/shape/disorder) in the face a changing redox potential of the feed. The plot provides evidence of the absence of Pd changes for the sorter cycling time, in conditions where our previous reports on alumina-supported systems [1,2] showed the alteration of the Pd metal phase by presence of C intertitials species (e.g. formation of a PdC_x phase) upon CO and their removal upon NO in absence of the Ce-Zr promoter. Comparing with an alumina supported Pd system with equal primary particle size allows eliminating any Pd-size influence on the phenomenon. Such PdC_x phase is therefore only observed for a 4Pd33ZCA sample at significant longer times, where the $CeZrO_4$ redox capability is essentially exhausted (see inset of Fig. 1 in the top left corner).
The noble metal behaviour uncovered is thus new and adds new chemistry-related facets to the well known roles played by the Ce-Zr promoter in the oxygen control (the so called, OSC –oxygen storage capacity) and noble metal size dispersion stabilization [4,5]. Results clearly show the alteration of the noble metal chemistry by adequate oxygen handling through the metal-promoter interface.

ii) A dependence of the noble metal – promoter redox behaviour (e-g- oxygen exchange) with the promoter particle size. Although this is expected and our work is currently undergoing, with a combined XAS/XRD approach we intend to analyse quantitatively this behaviour and establish the size-dependence of the phenomenon. A quantitative analysis not only require working with several Ce-Zr containing samples with different promoter size but also samples with different Pd loadings as the Pd particle size and Pd-promoter degree of contact depends on the Ce-Zr loadings. This means that the full analysis requires the study of 3-4 Pd loadings per Ce-Zr loading and will take a significant amount of time.

The simultaneous DRIFTS measurements were used to interpret the new aspect showed by the XRD results and related to suppressing the formation of PdCx phases during the CO cycle through efficient oxygen release. Fig. 2 IR provides evidence that CO dissociation within the adsorbed CO adlayers is still occurring in the 4Pd33ZCA system. This comes directly for the burst in CN/CNO formation observed upon changing the atmosphere from CO to NO. This would suggest that the OSC function of the $CeZrO_4$ promoter effectively reintegrates much of the "lost" C(a) species back into the overall CO oxidation process within the reducing cycle of the experiment through several intermediates species as surface carbonates.



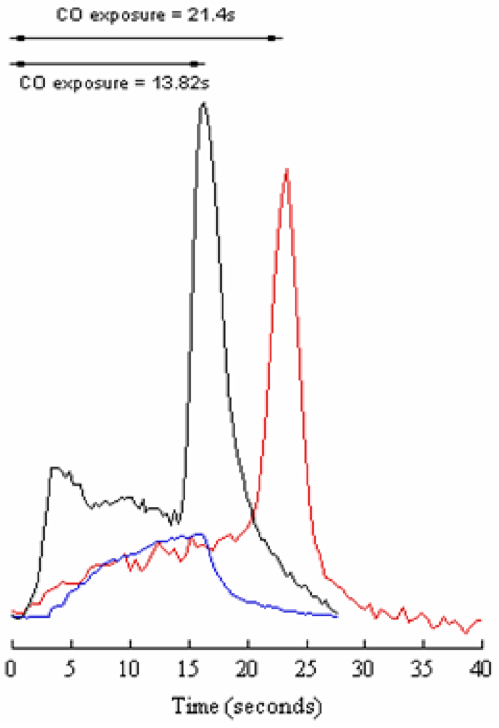


Figure 2. DRFITS results (right) and intensity of the NCO species (left) observed for 4Pd33ZCA systems during redox cycling (blue; 13.86 s; red; 21.40 s; for comparison black, 2 wt. % Pd-Al_2O_3 *13.86 s) at 673 K. Two cycling times (13.86 and 21.40 s) are presented.*

So, as a summary of the report, we believe that these HXRD/DRIFTS results uncover fundamental aspects of the TWC behaviour not known previously and which may allow defining precisely the multiple roles of the Ce-Zr promoter OSC function upon reaction conditions. A manuscript concerning the fate of the Pd phase upon cycling conditions is now under preparation [6] while a more general HXRD/XAS/DRFITS/MS study on the promoter-size dependence of the oxygen handling upon cycling conditions is expected to be completed during this year [7].

Finally, we would lie to thank Dr M. Di Michiel 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.

From an overall perspective we note that the only significant (beamline) limitation to the furtherment of this experiment currently lies in the computing hardware and software available to run the Pixium 2D detector. We were restricted to collecting data at 2.5 Hz because of these issues. It is clear, however, that the full potential (an order of magnitude faster) of the pixium is not currently able to be exploited because of these numerous issues and we would urge that these are resolved on ID15 as soon as is possible.

References

1.- M. A. Newton, M. Di Michiel , A. Kubacka, M. Fernández-García. *J. Am. Chem. Soc.*, 2010, 132, 4540.
2.- A. Kubacka, A. Martínez-Arias, M. Fernández-García.M. M. Di Michiel , A. Newton, *J. Catal.*, 2010, 270, 275.
3.- A. Iglesias-Juez, M. Di Michiel, M.A. Newton, M. Fernández-García, CH-2976 report.
4.- See for instance, J. Kaspar, P. Fornasiero in "catalysis by ceria", ed. Trovarelli, Imperial College press, 2002.
5.- A. Martinez-Arias, J. C. Conesa, M. Fernandez-Garcia, J. A. Anderson, in, "Supported metals in Catalysis", Eds., J. A. Anderson, M. Fernandez-Garcia, 2005, 283.
6.- A. Newton, M. Di Michiel , A. Kubacka, A. Martínez-Arias, M. Fernández-García., in preparation.
7.- A. Kubacka, A. Iglesias-Juez, M. Fernández-García.M. M. Di Michiel , A. Newton, in preparation.