

Report on beam time: CH9276, ID24

Dr. Ana Iglesias-Juez, Prof. Marcos Fernandez-Garcia, (CSIC, Madrid)

Studying the dynamic size dependent redox properties of CeZrO₄ in the presence and absence of Pd nanoparticles at the Zr K-edge using time resolved dispersive EXAFS.

Within the 18 shifts allocated to this proposal we were to mount, and carried out combined experiments using X-ray absorption at the Zr K-edge, 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 were devoted to analysing; i) the formation of unexpected noble metal carbide upon a CO atmosphere [1]; and ii) the role of Pd particle size of both CO and NO elimination [2]. This beam time aimed to analysing the behaviour of the CeZrO₄ component and the metal-promoter interface in real, alumina-supported TWCs systems. The project parallels the equivalent investigations of working catalysts and powder materials using high energy diffraction on ID15b [3] which were jointly delineated to tracking down the structural redox relationship in the Ce-Zr promoter (in presence and absence of Pd). With the Zr K-edge experiments we expect to add information concerning the structural situation of the Ce-Zr promoter at a local level upon cycling conditions, typical of TWCs operation. This must help in interpreting on physical basis the main Ce-Zr promoter role, related to the so-called oxygen storage capacity (OSC), which is in turn related to the oxygen handling properties of the promoter and the exchange of this molecule with the gas phase as well as the active, noble metal function [4,5,6].

Previous studies using un-supported CeZrO₄ materials were able to quantify the Ce⁴⁺-Ce³⁺ redox change involved in the oxygen capture/release of the Ce-Zr promoter upon oxidative/reductive model atmosphere, representative of cycling conditions [7]. As was previously suggested, the Ce redox par is significantly promoted in the Ce-Zr promoter with respect to the bare CeO₂ oxide by changes of the Zr neighbouring coordination. So, as a first goal of the present project we analyse Zr behaviour in a 33 wt. % CeZrO₄/Al₂O₃ (33ZCA) support and the 4 wt. % Pd-loaded (4Pd33ZCA) catalysts upon CO/NO cycling conditions and compare this with previous studies concerning un-supported systems [7] or XAS studies concerning the Pd behaviour [6].

Figure 1 shows the Zr K-edge XANES region for the samples in He at 673 K and difference spectra upon specific situation occurring during CO/NO cycling conditions.

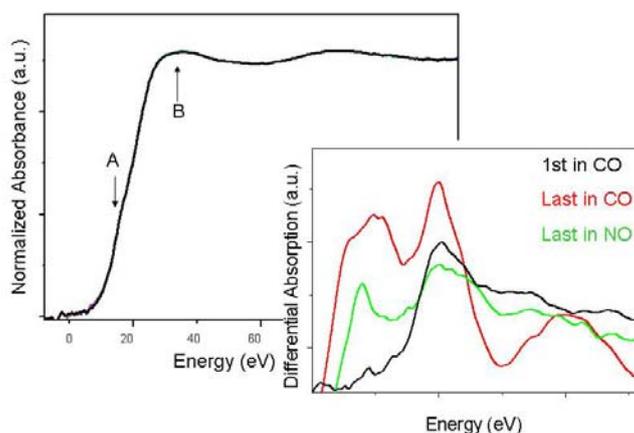


Figure 1. Zr K-edge XANES spectra for 4Pd33ZCA during a CO/NO cycling atmosphere at 673 K; a) upper panel, initial sample in He; b) lower panel, difference spectra for specific situations.

The plot displays changes in the edge region; in the here called A region, corresponding to the $s \rightarrow p/d$ pre-edge transition [8], the difference spectra show an increase of intensity in presence of CO, and the opposite in an NO atmosphere. This can be interpreted as a cycling change going from cubic-type (8-coordinated) situations obtained near the end of the NO step to other less symmetric ones (presumably with loss of oxygen; see below) in presence of CO, ending up with the expected growth of the pre-edge intensity. Region B of the spectra indicates concomitant changes in the overall s/p unoccupied electronic density of states [8]. Changes in the Zr local environment without any Zr redox modification are thus observed, in consonance with previous results. Interesting to note is the fact that this is possible using the time-resolution of the Dispersive-XAS experiments (0.2-0.3 seconds in the present case) with its inherent limitation on energy resolution; as Fig. 1 shows, the relatively small XANES effects derived from symmetry changes are clearly visible in the experiment, in spite of the potential energy resolution limitation mentioned. So, this graph opens the path for Zr-based XANES time-resolved studies, a tool previously un-exploited in the literature in the context of TWCs studies [4-7].

More interesting is the quantification of the O handling properties around the Zr environment using EXAFS. Fig. 2 displays the Fourier Transform of the EXAFS signal during a CO/NO cycle and the intensity of the two Zr-O contributions observed at first coordination shell distances.

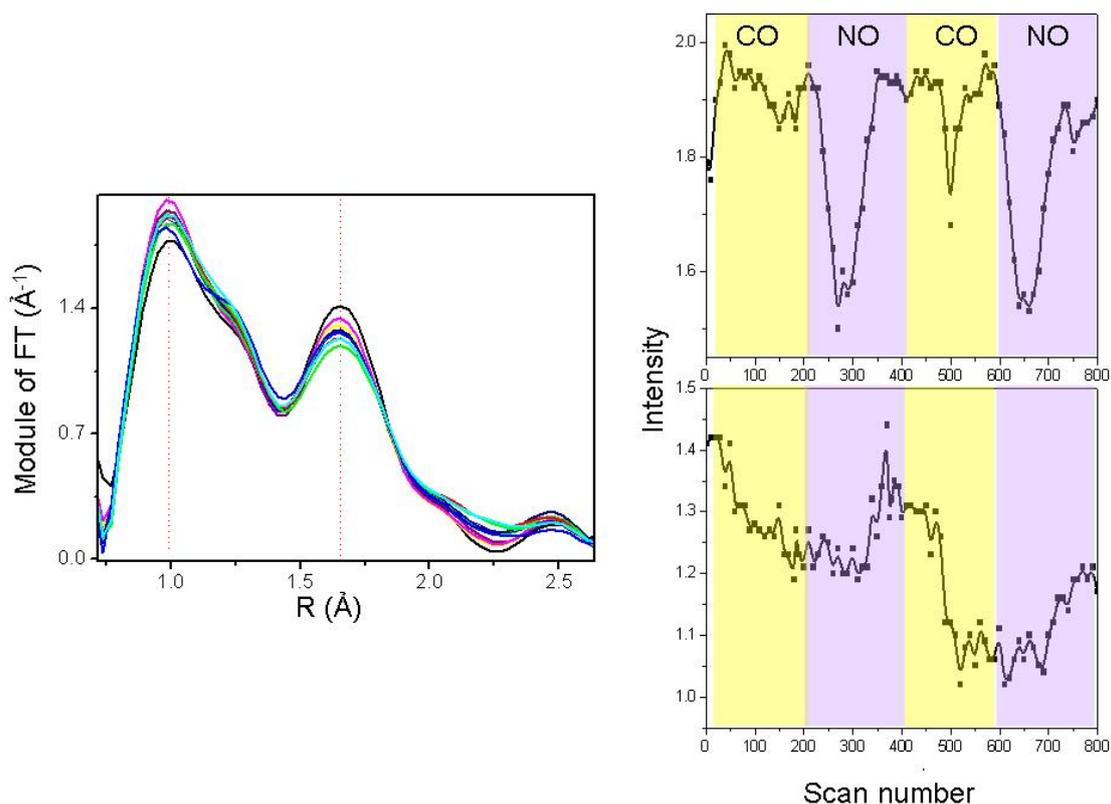


Figure 2. Fourier transform in the Zr-O first shell coordination distance and intensity of the two contributions observed. Upper/Lower intensity panels correspond to the high/low R contributions.

The first important result of the EXAFS study is that the alumina-supported samples describe two well defined Zr-O contributions at first shell distances. This is not observed in unsupported CeZrO_4 materials [7] and is a constant over the samples analysed in this beam time. More crucially, the two contributions behave differently upon the CO/NO cycling. As the intensity of the signal shows, the 1st peak is roughly constant upon CO and suffers an ordering process upon NO while the 2nd has an intensity decrease upon CO and increase on presence of NO. This clearly shows that our samples has a rather distinctive Zr-O environment in which a multitude of phenomena occur while

eliminating oxygen upon CO and restoring it upon NO. Although the overall behaviour is similar for all the Ce-Zr loadings studies (10 and 33 wt %; promoter sizes of 1 and 2.5 nm), the fine details (particularly the oxygen partitioning between the two contributions) seem different although precise knowledge will require detailed EXAFS fitting analysis which is currently underway [9].

So, as a summary of the report, we believe the Zr handling of oxygen is, as reported, crucial for the OSC function of TWC systems but the present study uncovers structural details not known up to the moment. The combined analysis of XAS and HRXRD works will outline the main physical basis of the Ce-Zr promoter OSC function, lending a complete, local and long range order structural picture of the physico-chemical phenomena behind the promoter key role on TWC systems. In particular, by building up a correlation between of Pd and the Ce-Zr behaviour we expect to detail the physical grounds of the OSC mechanism in real, TWC systems [9]

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References

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