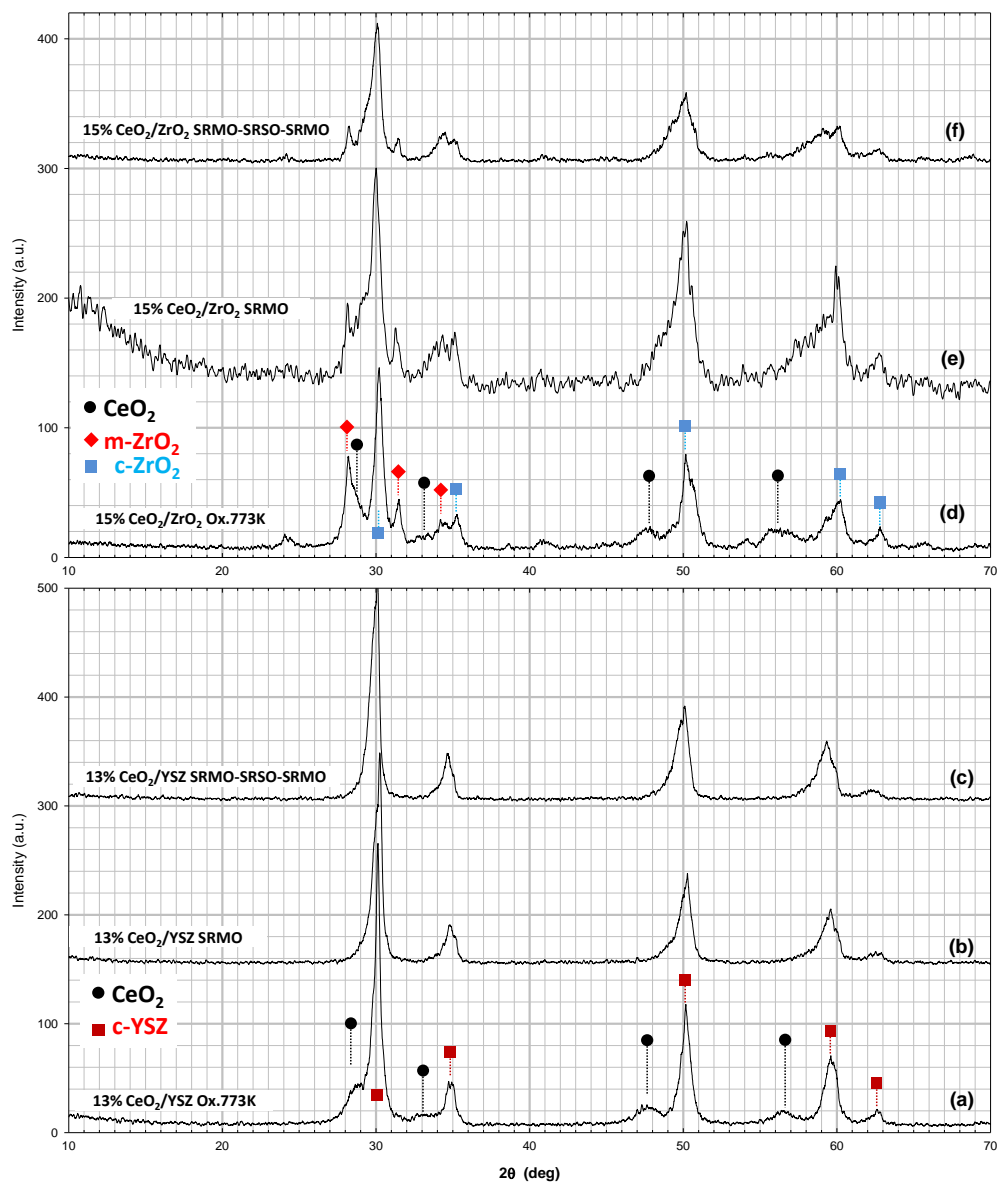


# **Rational Design of Nanostructured, Noble Metal Free, Ceria-Zirconia Catalysts with Outstanding Low Temperature Oxygen Storage Capacity**

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## **SUPPORTING INFORMATION**

## 1. XRD



**Figure SI.1** XRD diagrams of the catalysts supported on YSZ (a-c) and pure zirconia (d-f). Applied treatments are indicated over each diagram.

Figure SI.1 shows the X-ray diffractograms corresponding to the  $\text{ZrO}_2$  and YSZ supported ceria samples. In the case of the as-synthesized, oxidized at 773K, YSZ supported ceria catalyst sample, Figure SI.1(a), peaks belonging to cubic YSZ and cubic ceria are observed. After the

SRMO treatments, Figure SI.1(b), the ceria peaks disappear and an asymmetry in the YSZ peaks is now noticeable. These data are in good agreement with the TEM studies, which evidenced the growth of a cerium-zirconium surface layer on top of the YSZ crystals after this treatment with an epitaxial relationship. The asymmetry of the XRD peaks may be related with a relaxation of the layer structure. Finally, after the SRMO-SRSO-SRMO treatment, Figure SI.1(c), the width of the peaks is reduced. This suggests an improvement of both cristallinity and structural coherence between the cerium-zirconium, oxidized pyrochlore, surface layer and the YSZ support.

Concerning the pure-ZrO<sub>2</sub> supported sample, X-ray diffractograms corresponding to the as-synthesized, oxidized at 773K, sample, the sample after SRMO and after SRMO-SRSO-SRMO treatments are shown in Figure SI.1(d-f). When pure zirconia is used as a support for ceria, structural modification trends similar to those already described for the YSZ catalyst take place. The major difference in this case being that the initial diffraction pattern contains peaks corresponding to both monoclinic and cubic zirconia.

## 2. XPS Studies

X-ray Photoelectron Spectra were obtained on a Kratos Axis Ultra DLD instrument, and recorded with monochromatic Al K $\alpha$  radiation (1486.6 eV). The instrument was operated in the fixed analysis transmission mode (FAT), using a pass energy of 20 eV. The Kratos coaxial charge neutralization system was used to compensate charging effects, and the binding energy scale was calibrated with respect to Zr 3d<sub>5/2</sub> component at 182.64 eV.<sup>1</sup> The spectrometer was

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<sup>1</sup> Cies, J. M., del Río, E., López-Haro, M., Delgado, J. J., Blanco, G., Collins, S., Calvino, J. J. and Bernal, S. (2010), *Angew. Chem. Int. Ed.*, 49: 9744–9748

connected to a catalytic cell which allowed the reduction of samples and their anaerobic transfer to the analysis chamber.

Figure SI.2(a) shows the values of the Ce 4d/Zr 3d (a) and Ce 3d/Ce 4d (c) intensity ratios estimated from the analysis of the spectra of the 15% CeO<sub>2</sub>/ZrO<sub>2</sub> and 13% CeO<sub>2</sub>/YSZ catalysts after different pretreatments. Before commenting the graphs, we should mention that the estimated values for the Inelastic Mean Free Path (IMFP) of Ce 4d and Ce 3d photoelectrons in our samples, using the *NIST Electron Effective-Attenuation-Length Database (Version 1.3)*,<sup>2</sup> are about 3.13 nm and 1.71 nm respectively. Thus, if we take into account that 95% of the XPS signal originates from a layer whose thickness is about 3 times the IMPF value, our XPS data are generated by a layer about 9 nm thick in the case of the Ce 4d signal and only about 4 nm thick when the Ce 3d signal is considered. Concerning Zr, the sampling depth for Zr 3d signals is similar to that of Ce 4d core level

Note that in the case of the two oxidized catalysts, the value of the Ce 4d/Zr 3d ratios are in the range 0.4-0.5. This clearly indicates that Ce concentrates within the first surface layers of the nanocrystallites. In effect, for the two catalysts we have prepared, 15% CeO<sub>2</sub>/ZrO<sub>2</sub> and 13% CeO<sub>2</sub>/YSZ, the expected value for the Ce/Zr ratio in the case that Ce was homogeneously distributed in the bulk of the crystallites would be 0.18 (=15/85), a number which is much lower than the one observed by us. Moreover, as evidenced by our STEM data, 9 nm is a distance much larger than the characteristic size of the ceria-zirconia nanostructures we have detected, which in some cases were only about 1 nm thick. Therefore the thickness analyzed by XPS

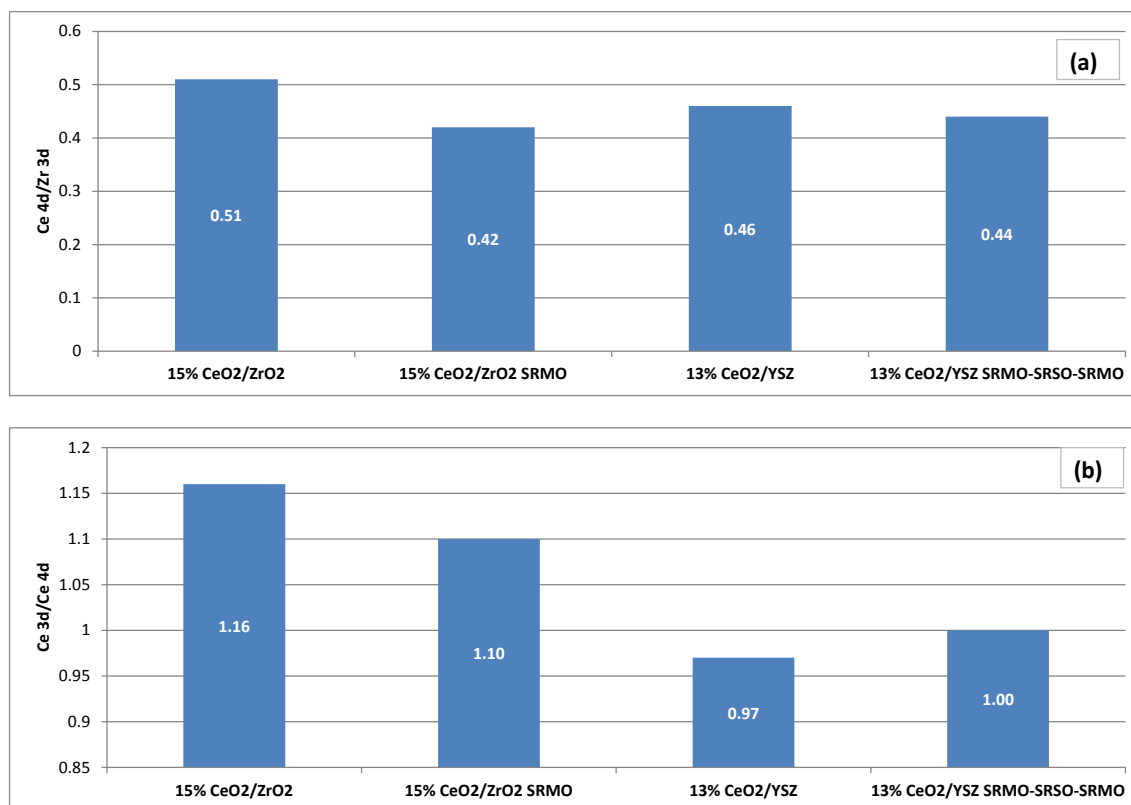
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<sup>2</sup> C. J. Powell and A. Jablonski, NIST Electron Effective-Attenuation-Length Database - Version 1.3, National Institute of Standards and Technology, Gaithersburg, MD (2011)

includes regions where most likely only Zr is present. In other words, XPS is very likely overestimating the Zr contribution to the Ce/Zr ratio.

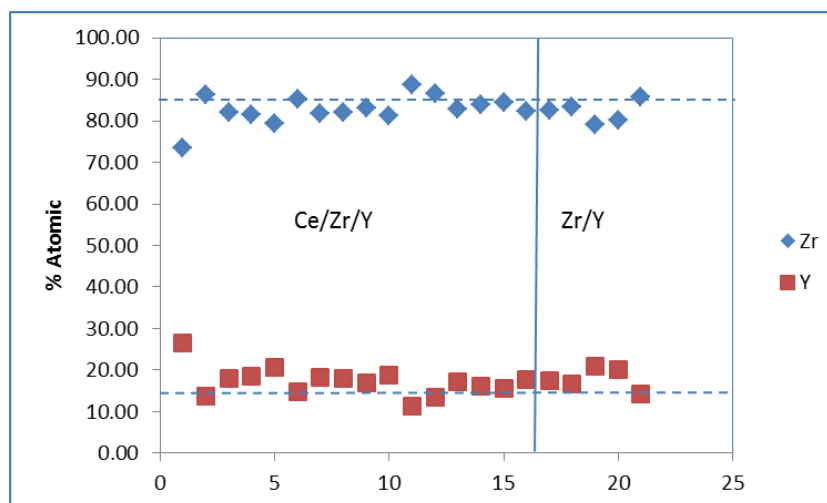
A very important aspect of the Ce/Zr ratios detected by XPS refers to their evolution with catalyst pretreatments. In the case of the 15% CeO<sub>2</sub>/ZrO<sub>2</sub> catalysts the application of the SRMO treatment gives rise to a small decrease of the Ce 4d/Zr 3d ratio, from 0.51 to 0.42. Such decrease must be motivated by the transformation of the initial ceria supported particles obtained after the first calcination at 773K into the oxidized pyrochlore phase particles where both Ce and Zr are mixed. Further application of the second SRSO-SRMO redox cycle does not modify this ratio value at all. The behavior of the 13% CeO<sub>2</sub>/YSZ sample is slightly different. The initial Ce/Zr ratio value is already smaller, 0.46, and does not modify significantly with further pretreatments. Thus, it changes only from 0.46 in the oxidized catalyst to 0.44 after the SRMO-SRSO-SRMO cycle. These latter observations suggest that the intermixing of Ce and Zr in the initial catalyst was improved even after the initial oxidation treatment. The larger structural coherence between the initial ceria and cubic YSZ components must be at the roots of this behavior and provides further evidence to the synthetic strategy foreseen by us.

The modification of the Ce 3d/Ce 4d ratio with pretreatments, Figure SI.2(b), also supports a higher initial mixing of Ce and Zr in the catalyst based on YSZ. Thus, this value changes from 1.16 to 1.10 on going from the oxidized sample to the SRMO one in the 15% CeO<sub>2</sub>/ZrO<sub>2</sub> catalyst, whereas it starts at a lower value, 0.97, in the case of the 13% CeO<sub>2</sub>/YSZ oxidized at 773K and does not change significantly after SRMO.



**Figure SI.2.** Values of the Ce 4d/Zr 3d and Ce 3d/Ce 4d integrated intensity ratios estimated from the XPS spectra of the studied samples

### 3. XEDS Studies



**Figure SI.3.** XEDS analysis with representative results of composition fluctuation from site to site in different crystallites.

