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Understanding the Complex Structure of CeO_2/TiO_2 Nanocatalyst. Key Contributions of the Combined Use of HAADF, X-EDS and EELS Spectroscopies

R Manzorro[1,2], JA Pérez-Omil[1,2], JJ Calvino[1,2] and S Trasobares[1,2*]

[1.] Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Campus Río San Pedro, Puerto Real, Cádiz, Spain.
[2.] IMEYMAT. Instituto de Microscopía Electrónica y Materiales, Universidad de Cádiz, Spain
* Corresponding author: susana.trasobares@uca.es

Catalytic nanomaterials are usually submitted to different thermal treatments under controlled atmospheres in order to improve their performance [1]. In the particular case of ceria-based catalysts, such treatments aim at increasing their oxygen-handling capabilities and may involve high temperatures. For titania-supported ceria systems, CeO_2/TiO_2, these thermochemical processes lead to complex materials with mixtures of phases with different composition, structure or oxidation states at the nanometer scale. The broad variety of crystal structures with varying cerium-titanium concentrations[2, 3] makes the identification of these phases a challenge that can only be resolved with the combined use of structural and analytical information with high spatial and energy resolution. Electron Energy Loss Spectroscopy is a powerful technique which does not only provide information about the crystal composition but also, in the case of cerium and titanium, changes on the chemical environment implies a modification of the Energy Loss Near Edge Structure (ELNES)[4]. In the present study DUAL-EELS will be combined with X-EDS, HAADF images acquisition and image simulation to explore the features of the CeO_2/TiO_2 system.

The CeO_2/TiO_2 systems have been prepared in two steps: first, one CeO_2 monolayer has been deposited on the surface of preformed TiO_2 crystallites by hydrothermal methods and then the sample has been submitted to a severe heat treatment under reducing conditions (SRMO) followed by an oxidation step also at high temperature (SRSO). In order to understand the influence of the thermal process, the structure and chemical information of both samples will be compared. The characterization has been carried out on a FEI Titan Cubed Themis 60-300 microscope operated at 80kV equipped with a monochromator, which allows reducing the energy resolution of the zero loss peak spectrum from 600 meV to 75 meV. Such a system permits also to monitor slight ELNES modifications and therefore to distinguish between different phases.

Low magnification HAADF images corresponding to the CeO_2/TiO_2 SRMO and SRSO samples (figures 1A and B respectively) illustrate the complexity of these systems, where crystals with diverse sizes and intensities are observed. Changes in the intensity of the particles may suggest the presence of phases with different chemical composition. In addition, the SRMO sample shows the existence of brighter interfaces (marked with red arrows in figure 1A) that do not appear in the SRSO catalyst. These brighter layers at the interfaces suggest a higher cerium concentration.

Regarding the SRMO sample, analytical electron microscopy techniques confirm the presence of a mixture of pure TiO_2 crystals and mixed oxide crystals with a Ce/Ti composition in the range of 30/70 to 70/30. Figure 1C illustrates a Ce-$M_{4,5}$ and Ti-$L_{2,3}$ elemental map, extracted from the EELS Spectrum Imaging (SI) data, showing a mixed Ce-Ti oxide crystal supported on TiO_2. Moreover, a lower content of cerium is observed all over the TiO_2 crystal and that there is an enrichment of cerium both at the surface and at the crystal interface. Several spectra extracted from the SI data (positions 1 to 4) acquired at different energy dispersion values evidence differences in the cerium concentration and Ti-$L_{2,3}$ fine structure.

In the case of the SRSO, significant modifications have been found with respect to the SRMO one. In fact, the ELNES structure of the Ti-$L_{2,3}$ features pointed out differences in terms of the level of incorporation of Ce into the titanium oxide structure.

The whole set of experiments performed on these nanostructured CeO_2/TiO_2 catalysts have revealed that the structural characterization and phase identification on such a complex system demands the simultaneous use of several electron microscopy techniques, such as EELS, X-EDS and HAADF imaging. In particular, the combination of compositional X-EDS with high energy resolution ELNES analysis on the Ti-$L_{2,3}$ edge provides key information [5].

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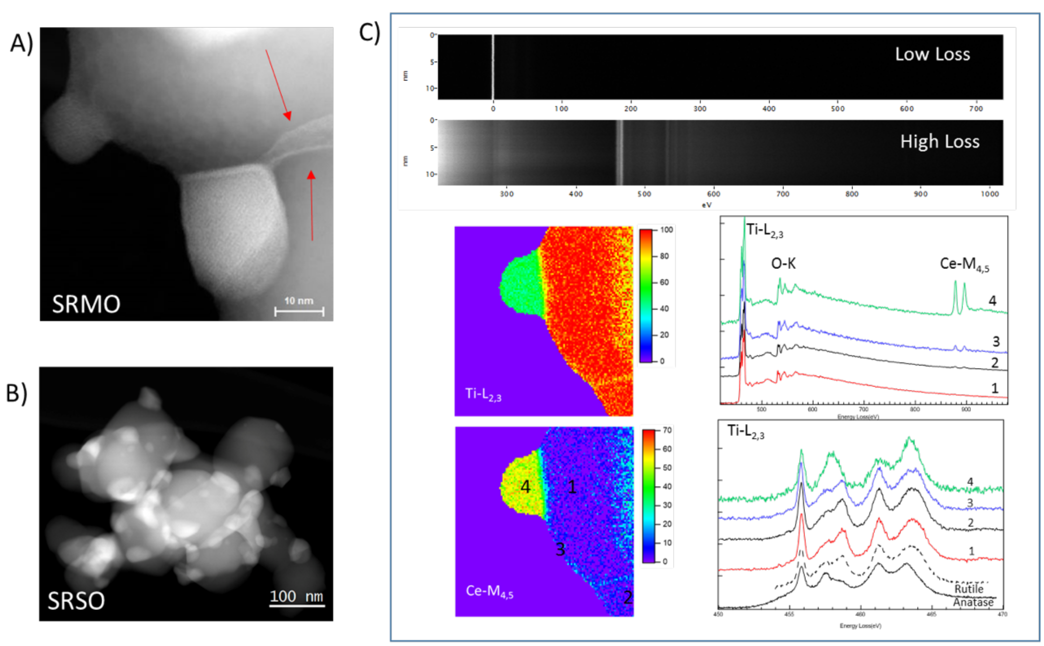

Figure 1. A) and B) HAADF images of the CeO_2/TiO_2 sample after the SRMO and SRSO treatment respectively. C) EELS results for the SRMO sample showing the Ce-$M_{4,5}$ and Ti-$L_{2,3}$ elemental maps and several spectra extracted from SI data acquired with an energy dispersion of 0.25 and 0.025 eV/Ch.

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