

Electron Microscopy Investigation of Redox Materials with Applications in Environmental Catalysis. Achievements and Challenges.

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Materials composed of nanosized particles of noble metals (Pt, Rh, Pd, Ru) dispersed over the surface of mixed oxides with fluorite-type structure based on ceria, CeMO_x ($M=\text{Pr, Tb, Zr, Mn}$), find application as catalysts in a variety of processes related to Environmental Protection [1]. Three Way Catalysis is undoubtedly the field in which they have nowadays a real practical impact [1,2]. Nevertheless currently they are also considered good candidates as mediators of other Environmental Catalysis processes which also involve redox reactions. In this respect we could mention the catalytic Wet Air Oxidation (CWAO) of organic substances present as pollutants in industrial waste waters [3], autothermal reforming of methane or ethanol [4], the gasification of biomass [5], the low temperature Water Gas Shift reaction (LTS) [6] or the selective oxidation of carbon monoxide in the presence of large quantities of hydrogen [7].

Electron Microscopy techniques have been systematically used in our laboratory to understand a number of topics related with this kind of materials [8,9], from the influence of the synthesis procedures on the nanostructural properties; the role of the supported metal phases on the redox properties; the evolution of metal-support interaction effects in this family of catalysts or the deactivation/regeneration processes affecting these materials. The wide spectrum of techniques that Electron Microscopy offers constitute an unique window to reveal the details of the structural and/or compositional changes underlying all these themes. This contribution aims at summarizing the most remarkable findings, to highlight the role of Electron Microscopy as a key tool to rationalize redox chemistry of these materials, and of course to identify some points in which further EM research is currently lacking.

Focusing on the investigation of the redox properties, HRTEM images and image simulation studies have been key to understand topics like: 1) the blockage of the redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ in catalysts prepared from chlorine-containing metal precursors by nucleation of a CeOCl phase; 2) the onset of decoration/alloying phenomena affecting the metal particles; 3) the influence of metal-support epitaxial growth on the oxidation behaviour of the metal particles. Likewise, the combined use of SEM, EDS(SEM), HRTEM and EDS-TEM allows having a clear picture of one of the hot topics in TWC catalysis, the sensitivity of the supported metal phase to deactivation by sintering.

Rationalizing the behavior of catalytic materials unavoidably involves the investigation of the effects of diverse thermochemical treatments to the samples under investigation. To our knowledge, one of the most serious limitations of conventional EM to Noble Metals supported on ceria oxide systems is their tremendous sensitivity to air after any redox treatment. Severe and fast reoxidation of most of these materials upon contact to air precludes the use of ex-situ investigations to obtain reliable conclusions about the supports. In-situ microscopy is called to play a major role at this respect [10]. Data in Fig. 1 provide an insight into the capabilities of in-situ EM on these materials.

Thus, by recording in-situ EELS data, we have been able to gain valuable information about the mechanism of the reduction process of a Ce-Pr mixed oxide under hydrogen and vacuum. Our results indicate a stepwise reduction of the oxide which begins with the transformation of the more reducible Pr^{4+} ions into Pr^{3+} . Only at high temperatures, after the complete reduction of Pr^{4+} , a change of the more hardly reducible Ce^{4+} species into Ce^{3+} starts to take place. Parallel, in-situ HREM evidences suggest that oxygen vacancies associated to the reduction of praseodymium do not become ordered into superstructures. Only at higher temperatures, when reduction of cerium takes place such superstructures have been identified, Figure 1c. The comparison of in-situ experiments like this with data coming from TEM observations on samples prepared ex-situ in microreactors and transferred into the microscope under anaerobic conditions may provide a reliable insight into the structural and composition aspects of the redox chemistry of both the supports and supported metals.

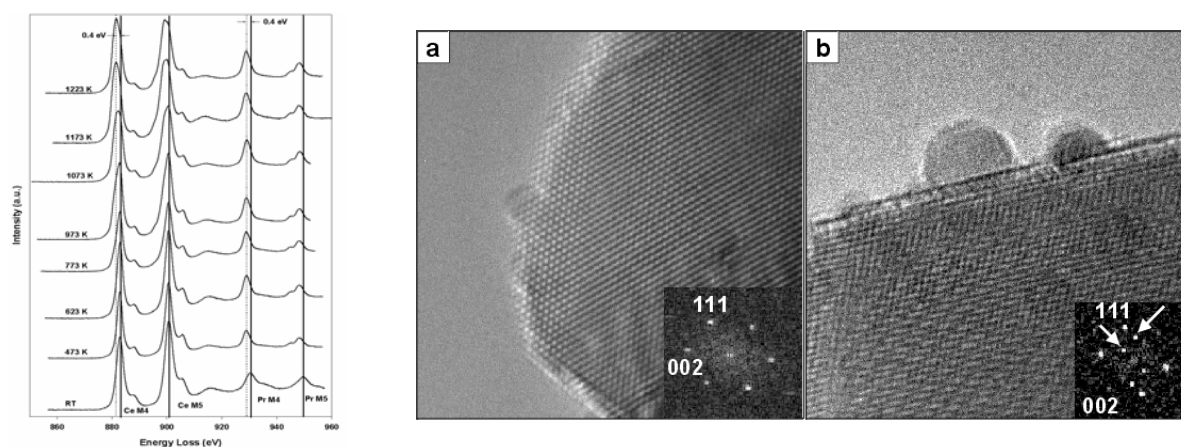


Fig. 1.- (left) In-situ EELS spectra of a $\text{Rh}(1\%)/\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-x}$ catalyst after treatment in H_2 at increasing temperatures. Solid lines mark the position in the energy loss scale of the M4, M5 lines maxima characteristic of Ln^{4+} species; dashed lines mark those corresponding to Ln^{3+} species; HREM images of the catalyst reduced at 473 K (a) and 1223 K (b). Superlattice spots marked in (b)

We acknowledge MCYT (MAT-2002-02782), Junta de Andalucía (FQM-110 and FQM-334) and Haldor Topsoe A/S for supporting us to perform in-situ EM studies at their R+D installations.

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