

TEM Investigation of the Synthesis of Rh/CePrO_x Catalysts

P. Rodríguez-Luque*, J.C. Hernandez*, S. Trasobares*, J.A. Pérez-Omil*, S. Bernal*, O. Stephan**, C. Colliex**, J.J. Calvino*

* Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica. Facultad de Ciencias. Universidad de Cádiz. Puerto Real, 11510-Cádiz. Spain

** Laboratoire de Physique des Solides. Université Paris Sud. 91400-Orsay. France.

Noble metals (Pd, Rh, Pt, Ru, Au) dispersed over the surface of mixed oxides of ceria with transition elements (Zr) or other lanthanides (Tb, Pr) are good candidates for applications related with Environmental Catalysis [1]. Systems based on Ce-Pr mixed oxides, which show significant improvements in the redox properties with respect to pure ceria, are particularly interesting [2].

It is well established that pure praseodymium oxide is sensitive to leaching of Pr³⁺ species during treatments with slightly acidic aqueous solutions [3]. The usual routines to prepare supported noble metal phases include, as a first step, the impregnation of the supports with aqueous solutions of some precursor of the corresponding metal. These solutions are usually highly acidic. In the case of Ce-Pr mixed oxides impregnation with such solutions could induce severe modifications of the oxide nanostructure and, at the same time, modify the final properties of the supported metal phase.

In this contribution we focus on the application of different TEM techniques to unveil the modifications of CePrO_x mixed oxides, both at the bulk and the surface levels, during the preparation of a Rh supported catalyst using the incipient wetness impregnation method with an aqueous Rh(NO₃)₃ solution. The structure of both the metal and the support has been investigated with HREM, X-EDS and EELS. Spectra acquired both in spot and in the Spectrum Imaging mode have provided key nanoanalytical information about the compositional changes taking place during the catalyst synthesis. To sort out the effects of the impregnation step, CePrO_x oxides were characterized before and after the deposition of the noble metal. TEM information has been complemented with SEM and UV-VIS spectroscopy data.

FESEM as well as low magnification TEM images indicate that impregnation with the rhodium nitrate solution induces changes in the texture of the mixed oxide crystallites. By using a specific quantitative image analysis procedure developed in this work, we have detected in CTEM BF images the presence of crystallites with a more microfaceted surface in the impregnated sample. Likewise FESEM images show the presence of a larger fraction of small size crystallites and small pores after impregnation.

UV-VIS data obtained from small aliquots taken from the impregnating solutions indicate, Table 1, the presence of significant amounts of both Pr³⁺ and Ce⁺³ species in solution, this confirming the occurrence of leaching of these elements out of the fluorite matrix in the mixed oxide. From the composition of the oxides and data in Table 1, it is clear that Pr³⁺ is the cation preferentially affected by this dissolution process. Reprecipitation of these dissolved lanthanide cations with Rh³⁺ species during the drying stage of the synthesis could explain the textural modifications suggested by SEM and CTEM data.

X-EDS analysis performed in spot mode (0.5 nm probe) on ultrathin sections of the samples reveal the occurrence of severe redistribution of the lanthanide cations in the mixed oxide as a consequence of Pr^{3+} leaching. Figure 1 summarizes the findings of the nanoanalytical study of a $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_2$ sample. As can be noted in this figure, the composition of the oxide crystallites before impregnation, both at the surface and the bulk, is close to the nominal value within a narrow composition window. After impregnation the material becomes much more heterogeneous in composition. Large composition deviations are specially observed at surface locations, where both Ce rich and Pr rich spots can be found. Much smaller deviations observed in bulk position may be caused by the effects of the surface. These changes detected by X-EDS indicate the occurrence of a redistribution of the cations at the first surface exposed layers of the oxide after impregnation. The detailed analysis of EEL spectra recorded from the oxide and the metal supported catalyst confirm this process which affects both the real composition of the material at the surface level and, as also suggested by HREM images, to the state of the supported phase. These changes should be taken into account to understand the catalytic behavior of these materials.

References

- [1] M. Shelef, G.W. Graham and R.W. McCabe, in: *Catalysis by Ceria and Related Materials*, ed. A. Trovarelli (Imperial College Press, London, 2002) ch. 10.
- [2] W. Chuna, G.W. Grahama, J.A. Lupescua, R.W. McCabea, M.M. Koranneb, and R. Brezny, *Catal. Letters*, 106(3-4) (2006) 95
- [3] Z.C. Kang and L. Eyring, *J. Solid State Chem.* 75 (1988) 60.
- [4] This work has received financial support from MEC (MAT2005-00333), the EU FEDER Program and the Junta de Andalucía (FQM-110, FQM-334)

TABLE 1. Concentrations of Ce^{3+} and Pr^{3+} species in the impregnating solution, after contact with Ce-Pr mixed oxides of two different compositions.

Support	[Ce] mg/L	[Pr] mg/L
$\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_x$	166 ± 1	3820 ± 33
$\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_x$	119 ± 1	991 ± 4

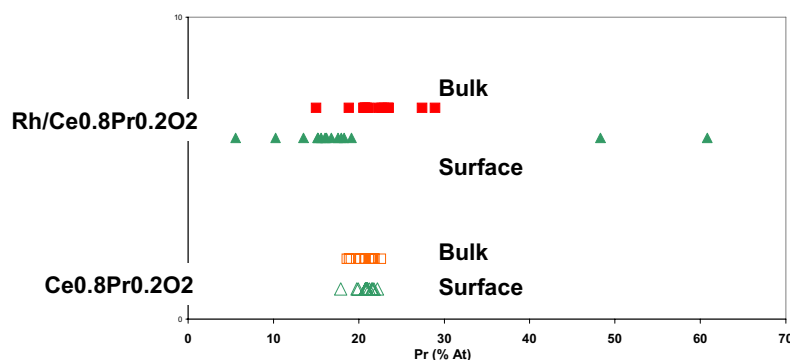


FIG. 1. Ce/Pr ratio values as determined from spot X-EDS analysis in a $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_2$ sample before (rows at the bottom) and after (upper rows) impregnation to deposit $\text{Rh}(\text{NO}_3)_3$. Surface and bulk locations are shown separately. Note the large increase in the composition range at the surface of the supported metal catalyst with respect to the bare oxide.