Local Structure of the Metal-oxygen Bbonds in $ZrO_2\mbox{-}CeO_2$ Nanopowders

Ismael Oscar Fábregas^a, R.O. Fuentes^a, D.G. Lamas^a, M.E. Rapp^a, N.E. Walsöe de Reca^a, A.F. Craievich^b, M.C.A. Fantini^b, ^aCINSO (Centro de Investigaciones en Sólidos), CITEFA-CONICET, Argentina. ^bInstituto de Física, Universidade de São Paulo, Brazil. E-mail: ifabregas@citefa.gov.ar

Zirconia-ceria solid solutions are being widely employed in current automotive three-way catalysts as oxygen storage promoters due to their excellent catalytic properties. These properties have been proposed to be related to the local structure of the metal-oxygen bonds in these materials.

In this work, the local structure around Zr and Ce atoms in compositionally homogeneous, nanocrystalline ZrO₂-CeO₂ powders was investigated by the technique named extended X-ray absorption fine structure (EXAFS). These experiments were carried out at the D04B XAS-1 beamline of LNLS (Brazilian Light Facility). ZrO₂-15, 40, 50, 60, 65, 70, 80 and 90 mol% CeO₂ nanopowders were synthesized by a pH-controlled nitrate-glycine gel-combustion process. While Ce-O coordination sphere has a cubic symmetry in the whole composition range, the Zr-O coordination shows a tetragonalto-cubic symmetry change as the CeO₂ content is varied. This transition was found to be at (85±5) mol% of CeO₂, in agreement with a previous synchrotron XRD study. For compositions with a tetragonal crystal structure, a 5+2 model was found for the Zr-O bond, while the coordination number was 5 for the cubic solid solutions. The coordination number of Ce was close to 8 for all the compositions. Finally, we also demonstrated that the local structure determined by EXAFS agrees well with the long-range structure deduced by XRD. Keywords: EXAFS, zirconia-ceria, nanocrystalline materials