Structural Analysis of Mesoporous SiO_2:ZrO_2-90%CeO_2

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The synthesis of ZrO_2-x%CeO_2 ordered mesoporous structures for catalytic applications is a research area under development. These systems are also potential candidates as anodes in intermediate temperature solid oxide fuel cells (IT-SOFC) due to an enhancement on their surface area [1-5]. The ordered mesoporous structure can be formed by the use of a polymeric template. The crystallization of the as-synthesized amorphous zirconia-ceria walls occurs at low temperature, around 300ºC, promoting the collapse of the ordered network during the usual calcination process, necessary for the removal of the directing structure agent [6]. In this work, an attempt to preserve the ordered mesoporous structure after the polymeric template extraction was developed by depositing a palisade of silica over the triblock copolymer micelles before the growth of zirconia-ceria walls.

Samples containing 10 mol% of Si were prepared using TEOS as Si source, anhydrous $CeCl_3$ and $ZrCl_4$ precursors and Pluronic P-123 triblock co-polymer in an acidic medium (2molL^{-1} HCl). The Ce/Zr atomic composition was x=0.9, which lead to a 100% cubic structure of the nanocrystalline walls, as determined X-ray diffraction (XRD).

Small Angle X-ray scattering (SAXS) measurements were performed in order to analyse the mesoporous (2-50nm) structure and XRD experiments were used to investigate the wall structure. Table 1 presents the improvement of surface areas obtained with the growth of the silica palisade.

Table 1: Superficial Area for samples with Ce/Zr=0.9mol.

Samples	Superficial Area (m^2/g)
Zr-Ce wt. 30% Si (Anh. Chlorines)	128.1
Zr-Ce wt. 10% Si (Anh. Chlorines)	72.7
Zr-Ce wt. 0% Si (Anh. Chlorines)	46.1
Zr-Ce wt. 0% Si (Nitrates)	8.7

The as-synthesized samples yielded better ordered porous structures compared to samples prepared without the palisade, but the usual calcination process up to 540ºC destroyed the ordered network. Even though, the N_2 adsorption/desorption measurements showed a significant increase of the superficial area (Table 1). New synthesis with large pores, using a swelling agent and 30% Si content will be reported, as well as other strategies to remove the template.

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