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Synthesis, structural and morphological characterization of CeO_2 – ZnO nanosized powder systems from Pechini´s method

C. Peverari, A. M. Pires, R. R. Gonçalves, O. A. Serra.*
Dept. Química, FFCLRP, USP, Av. Bandeirantes 3900, 14040-901, Ribeirão Preto, SP, Brazil.

Abstract: This work reports on the investigation of nanosized CeO_2-ZnO systems prepared by Pechini´s method. The structural and morphological characterization of CeO_2-ZnO systems as well as the characterization of CeO_2 and ZnO separately, showed that the employed method result in powders with spheroidal particles whose size are in the range 30 - 200 nm, which is appropriate to provide homogeneous suspensions. The ZnO present in the prepared mixed oxides seems to increase particle size distribution and to influence the arrangement of the particles after powder dispersion.

Keywords: cerium oxide; zinc oxide; nanopowder; Pechini´s method.

Introduction

Ultrafine nm-sized particles have attracted much attention since they often exhibit physical and chemical properties that are significantly different from those of bulk materials [1]. In particular, materials with high surface area have importance in two major fields: ceramic science and catalysis [2]. In recent years, nanotechnology has created excitement in a wide array of sectors in both the scientific and financial communities. Cosmetic chemists may not have realized that their industry has been leading the way in nanotechnology for the last 10 years with the use of one of the first nanotechnological products, nanoscaled (<100 nm) inorganic UV absorbers or "nanopowders".

Cerium oxide is a major compound in the useful rare earth family and has been applied as a useful glass-polishing material, ultraviolet absorbent and automotive exhaust promoter [3]. Fine particles of cerium oxide of very small size can become potential new materials that maybe useful for fine UV absorbent and high-activity catalysts. Many studies have reported the synthesis of nanosized particles of ceria with various purposes. However, because of its high catalytic activity for the oxidation of organic material, CeO_2 has seldom been used commercially as a sunscreen material. So, the introduction of ZnO should reduce the oxidation catalytic activity of cerium oxide.

Zinc oxide, for instance, is a versatile material with many applications, including antireflection coating, transparent electrodes in solar cells [4], gas sensor [5], varistor [6,7], surface acoustic wave devices, electro-luminescence and photo-luminescence devices [8-11] and UV blocking materials [12-14].

Therefore, this work reports on the synthesis, by Pechini´s method, and the structural, morphological and spectroscopic characterization of CeO_2-ZnO systems in order to better understand how ZnO modifies the nanostructured CeO_2, in the search for a new UV filter material.

Material and Methods

CeO_2-ZnO mixture preparation from Pechini´s method

Rare earth (Ce^{3+}) and zinc nitrates solutions were mixed with citric acid in an appropriate stoichiometry, Ce^{3+}: Zn^{2+}. The mixture was heated

and stirred in a hot plate at 60°C, and then ethylene glycol was added and heated at 90°C, resulting in a polymeric resin (polyester). The yellowish resin was fired at 500°C, and the obtained powder mixed oxides was heated at 900°C, in air, for 4h [15]. CeO_2 and ZnO powder samples were prepared separately by using the same Pechini´s method and a mixture of $1CeO_2$:1ZnO was also obtained grinding both oxides in an agate mortar in order to compare with the mixed oxide samples.

Samples Characterization

The crystalline phase identification was performed by X-ray diffraction, XRD (SIEMENS D5005 X-ray diffractometer). The size distribution and powder shapes were observed using transmission electron microscopy, TEM, (Philips CM200 microscope equipped with Digital Spectrometer – Prism PGT – Princeton Gamma Tech) and scanning electron microscopy, SEM (Scanning Electron Microscope Zeiss DSM 940A). For TEM measurements, powder samples were suspended in ethanol and supported in a copper grid. For SEM images acquirement the powders were dispersed in isopropanol, supported in aluminum stubs and after drying, coated by a gold thin layer using sputtering system. For diffuse reflectance spectroscopic (DRS) measurements the powders were ground in agate mortar and compacted in a black holder. Spectrofluorimeter SPEX–FLUOROLOG II with excitation and emission double monochromators was used to record DRS spectra by synchronously monitoring of both monochromators at the same wavelengths [16].

Results and discussion

The XRD patterns of the synthesized powders are shown in Fig. 1. For all samples, reflection planes that perfectly match to both indexed CeO_2 cubic structure, space group Fm3m (225) and ZnO hexagonal structure, space group P63mc (186) [17] are detected. No peak of any other phase, such as zinc cerate or cerium zincate, is observed indicating that the employed method leads to a mixture of CeO_2 and ZnO phases in all systems. The X-ray pattern of the mechanical mixture $1CeO_2$:1ZnO containing the nanosized oxides included in the Fig. 1 shows that the relative intensity of CeO_2 reflection peaks are higher then the ZnO one, although both oxides are present in the same ratio. This difference in intensity due to the different oxide X-ray absortivity explains why in the $2CeO_2$:3ZnO, $3CeO_2$:2ZnO and $4CeO_2$:1ZnO systems the reflection planes characteristic for CeO_2 are more evident than the ZnO ones.

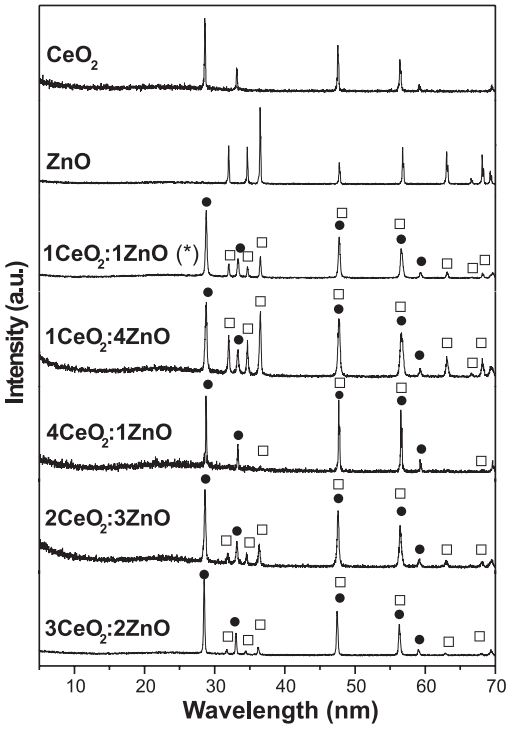

Figure 1. X-ray powder diffraction patterns of CeO_2, ZnO, and the mixed oxides $1CeO_2$:4ZnO; $4CeO_2$:1ZnO; $2CeO_2$:3ZnO and $3CeO_2$:2ZnO, where ● refers to CeO_2 pattern and □ to ZnO one. $1CeO_2$:1ZnO (*) sample refers to the X-ray pattern of a mechanical mixture.

TEM analysis was performed in order to evaluate particle shape and size distribution, Fig. 2. It is possible to observe that cerium and zinc oxides, as well as their mixtures, have spheroidal particles whose sizes were estimated and listed in Table 1. TEM images also reveal the nanocrystal planes of the particles, with their superposition in some cases.

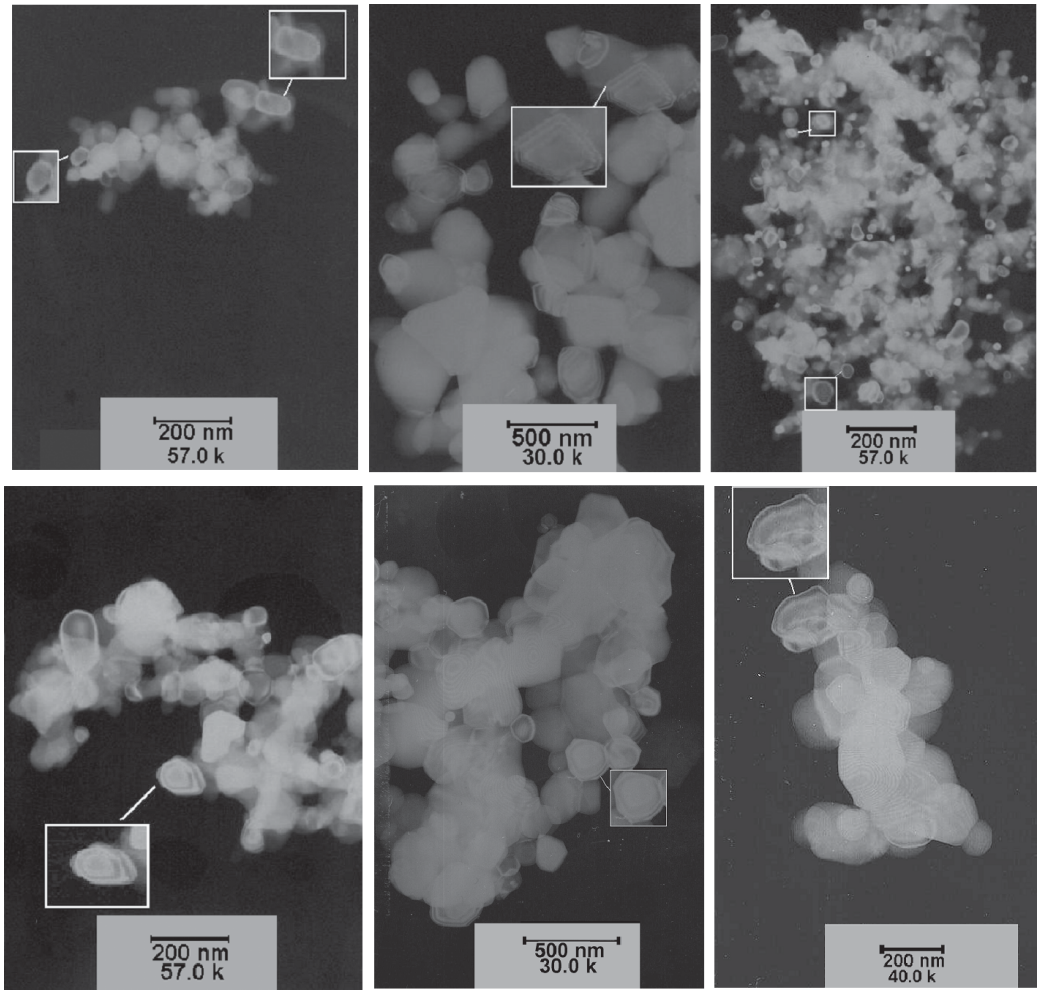

Figure 2. TEM images of the pure oxides **(a)** CeO_2 and **(b)** ZnO and prepared systems **(c)** $1CeO_2$:4ZnO, **(d)** $4CeO_2$:1ZnO, **(e)** $2CeO_2$:3ZnO and **(f)** $3CeO_2$:2ZnO.

Table 1. Particle size estimate for the oxide particles from TEM image analysis (Fig. 2).

Sample	Smallest particle size (nm)	Biggest particle size (nm)
CeO_2	30	60
ZnO	60	200 – 400
$1CeO_2$: 4ZnO	30	----
$4CeO_2$: 1ZnO	30	150
$2CeO_2$: 3ZnO	50	220
$3CeO_2$: 2ZnO	50	140 - 170

In the case of the $1CeO_2$:4ZnO system, Fig. 2c, as it is difficult to well define the border of the biggest particles, only the small ones were estimated. Analyzing Table 1, it is possible to verify that the oxide mixtures present a wide particle size distribution, whereas the pure oxides separately show extreme values, i.e., CeO_2 displays the smallest particles and ZnO the biggest ones. Therefore, during TEM analysis, EDS (energy-dispersive spectroscopy) was performed in order to investigate individual particles in an attempt to establish some relationship between particle size and composition. As the pure oxides present extreme values, one would expect that in the mixtures CeO_2 could form the small particles and ZnO the big ones. However, no conclusive relationship was observed, because both big and small particles in some cases presented both metals, Ce and Zn, in their composition. Therefore, the inclusion of ZnO in the CeO_2 system increases the final particle size distribution even when ZnO is present in a lower proportion ($4CeO_2$:1ZnO).

The morphological general aspect of the powder particles can be observed by the SEM images, shown in Fig. 3. They reveal how the individual particles observed by TEM agglomerate after dispersion in a solvent and drying. For the CeO_2 sample, Fig. 3a, and the mixtures where this oxide is present in higher proportion, Fig. 3d and Fig. 3f, the agglomerates of spheroidal particles show similar aspect. However, ZnO particles, Fig. 3b, as well as the ones observed in the $2CeO_2$:3ZnO, Fig. 3c and $1CeO_2$:4ZnO, Fig. 3e systems, seem to be arranged in layers that form plates. So, ZnO must also be influencing the particles arrangement in the mixtures.

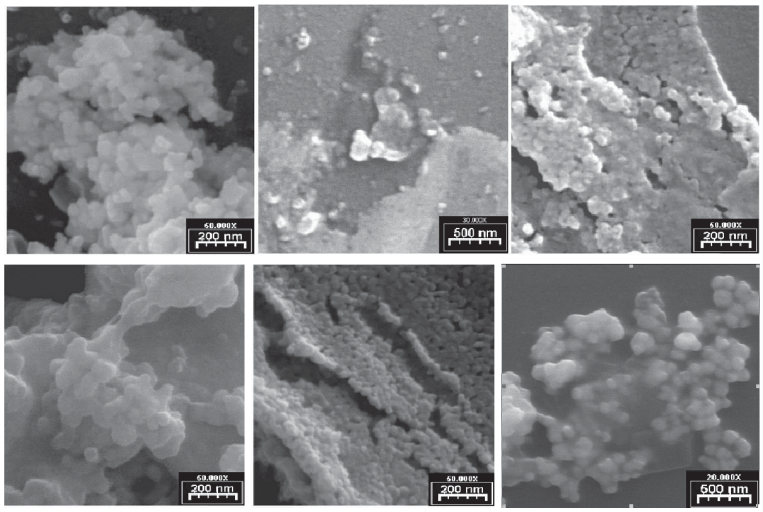

Figure 3. SEM images of **(a)** CeO_2, **(b)** ZnO, **(c)** $1CeO_2$:4ZnO, **(d)** $4CeO_2$:1ZnO, **(e)** $2CeO_2$:3ZnO and **(f)** $3CeO_2$:2ZnO nanoparticles.

In the powder reflection spectra, low reflectance values indicate high absorption in the corresponding wavelength region. Fig. 4 shows the reflection spectra of pressed powders of CeO_2-ZnO systems, compared to those of the pure CeO_2 and ZnO powders. CeO_2, ZnO and CeO_2-ZnO systems (1:4, 2:3, 3:2 and 4:1) have the same low reflectance behavior in the UV region, and a reflectance rate of almost one in the visible. The reflectance rate of pure CeO_2 is lower than that of the other samples. The most significant region in the UV-B (290-320 nm) is above 300 nm, where all samples, except for ZnO, present reflectance rate below 0.5, which means high absorption power. All systems show high absorption over the whole UV-A region (from 320 to 400 nm), and their reflectance increases sharply

above 370 nm, except for the pure CeO_2 powder. It is important to emphasize that all CeO_2-ZnO compositions, independent of the stoichiometry, present higher absorption than the pure oxide powders in the UV region. In the visible region, the ZnO powder shows the expected high constant reflectance, which is responsible for its resultant white color, whereas the CeO_2 powder exhibits a yellowish color due to its lower reflectance. The CeO_2-ZnO mixtures, on the other hand, show intermediate reflectance indices, which probably imply the decrease in the pale-white resulting color.

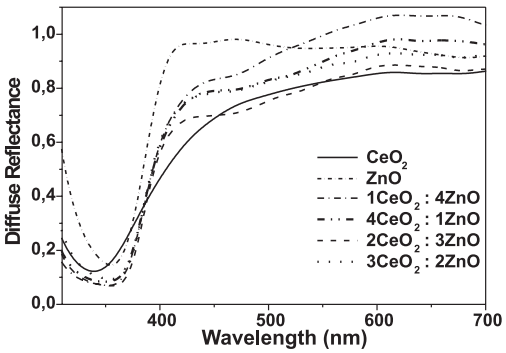

Figure 4. Reflectance spectra of CeO_2, ZnO and the CeO_2-ZnO nanopowder systems.

Conclusions

A new material consisting of nanopowders of the mixed oxides CeO_2 and ZnO, was prepared by Pechini´s method in an appropriate stoichiometry. This method leads to powders with spheroidal particles, whose size range from 30 to 200 nm, which is appropriate to provide homogeneous suspensions. The ZnO present in the prepared mixed oxides seems to increase particle size distribution and to influence the arrangement of the particles after dispersion in a solvent and drying. Moreover, CeO_2–ZnO nanopowder systems, independent of the stoichiometry applied, present higher absorption than the pure oxide powders in the UV. Also, the intermediate reflectance indices of these mixed oxides probably imply a decrease in their pale-white resulting color. Therefore, the findings of the present study suggest that CeO_2–ZnO nanopowder systems are promising candidates for use in a specific application, and Pechini´s method is adequate for the obtention of such nanopowders compounds.

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C. Peverari, A. M. Pires, R. R. Gonçalves, O. A. Serra. Síntese e caracterização estrutural e morfológica de partículas nanométricas do sistema CeO_2 – ZnO a partir do método Pechini

Resumo: Neste trabalho investigou-se o sistema nanométrico CeO_2-ZnO preparado pelo método Pechini. As caracterizações estrutural e morfológica foram realizadas para o sistema CeO_2-ZnO assim como para CeO_2 e ZnO separadamente, o que demonstrou que o método empregado resulta em pós com partículas de tamanho entre 30 a 200 nm. A presença do ZnO nas misturas dos óxidos preparados aumenta a distribuição no tamanho das partículas e também influencia o arranjo das mesmas após a dispersão dos pós.

Palavras-chave: óxido de cério; óxido de zinco; nanopartículas; método Pechini.

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