Structural studies of mesoporous ZrO$_2$-CeO$_2$ and ZrO$_2$-CeO$_2$/SiO$_2$ mixed oxides for catalytical applications

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Abstract

In this work the synthesis of ZrO$_2$-CeO$_2$ and ZrO$_2$-CeO$_2$/SiO$_2$ were developed, based on the process to form ordered mesoporous materials such silica SBA-15. The triblock copolymer Pluronic P-123 was used as template, aiming to obtain crystalline single phase walls and larger specific surface area, for future applications in catalysis. SAXS and XRD results showed a relationship between ordered pores and the material crystallization. 90% of CeO$_2$ leaded to single phase homogeneous ceria-zirconia solid solution of cubic fluorite structure (Fm$ar{3}$m). The SiO$_2$ addition improved structural and textural properties as well as the reduction behavior at lower temperatures, investigated by XANES measurements under H$_2$ atmosfere.

Keywords: ceria, zirconia, mesoporous

1. Introduction

Mesoporous materials have interesting properties, such as high surface area, adjustable size and shape of pores, several different structures and compositions which provide potential applications in catalysis, adsorption, sensors, drug delivery and nanodevices[1]. The extension of silicon-based materials synthesis to other metal oxides is extensively pursued, since ordered mesoporous materials such as MCM-41 and SBA-15 present excellent textural/structural properties[1][2][3][4][5][6].

Zirconia-Doped Ceria (ZrO$_2$-x%CeO$_2$, ZDC) is a largely studied material due to its physical-chemical properties that are useful for applications in three-way catalysts and as anodes in Solid Oxide Fuel Cells (SOFC). Among these properties, a high surface area is pursued since the gas permeation in the material allows a high gas reaction rate. Also, ceria-based materials present the ability to store/release oxygen during rich/poor fuel conditions, which is correlated to the Ce$^{4+}$ ↔ Ce$^{3+}$ redox reaction[7][8][9][10][11][12].

Several authors report the synthesis of mesoporous ceria-zirconia materials[13][14][15][16][17] but few present a detailed study of the porous network via SAXS and the evolution of the pore ordering regarding the materials crystallization. Therefore, the aim of this work was to explore different synthesis methods to produce ZDC samples and fully characterize their physical chemical properties for future applications. In particular, the strategy to build a SiO$_2$ palisade was analyzed as an attempt to avoid shrinkage during calcination.

2. Experimental

2.1. ZrO$_2$-CeO$_2$ and ZrO$_2$-CeO$_2$/SiO$_2$ preparation

Anhydrous chloride method: 2 g of Pluronic P-123 (BASF) was previously stirred in 10 mL of ethanol, a total of 13.8 mmol of anhydrous ZrCl$_4$ and CeCl$_3$ (Aldrich) were solubilized in another 10 mL of ethanol and added to the polymer mixture (Ce/Zr molar ratios of 0.5 and 0.9). Approximately 2 mL of water were added to the solution, and the
Zr/Ce precursor salts and polymer were stirred for 24 hours. The solution was placed in an open Petri dish for thermal treatment (with water vapor) in the oven at 60 °C, until dried. Sample names: Z50AC and Z90AC (50 and 90 mol% CeO2).

Hybrid method (10 mol% Si): 2 g of Pluronic P-123 was previously stirred in 10 mL of ethanol and 1 mL of HCl (2 mol/L). Then 0.15 mL (total 10 mol%) of TEOS (Tetraethyl orthosilicate, Aldrich), the Si precursor, was added dropwise in the solution and stirred together for 30 minutes. After that 6 mmol of ZrCl4 and CeCl3·7H2O (Aldrich) were solubilized in another 10 mL of ethanol and added to the polymer mixture (Ce/Zr molar ratio of 0.9). NH4OH was added to achieve a pH of 3 and the remaining solution was stirred for 24 hours. The solution was placed in a Teflon autoclave for hydrothermal treatment in the oven at 60 °C for 1 day, and dried in a water bath for 5 hours. Sample name: Z90H10.

Palisade method (10 and 30 mol% Si): based on the last synthesis, the P-123 polymer and TEOS (total 10 and 30 mol%) were stirred previously for 6 hours before adding the same Zr/Ce salt precursors with Ce/Zr molar ratio of 0.9. Then NH4OH was added to achieve a pH of 3 and the remaining solution was stirred for 24 hours. The solution was placed in a Teflon autoclave for hydrothermal treatment in the oven at 60 °C for 1 day, and dried in a water bath for 5 hours. Sample names: Z90P10 and Z90P30.

The calcination process to remove all the samples’ template was performed in a tubular oven, with a temperature heating rate of 1 °C/min, until 540 °C in N2 atmosphere, an isotherm in 540 °C with 2 hours in N2 and 2 hours in air.

2.2. ZrO2–CeO2 characterization

In-situ SAXS experiments were carried out at the SAXS-1 beamline of the Brazilian Synchrotron, LNLS. The wavelength was set at 1.5498 Å. High-intensity (low-resolution) configuration, without crystal analyzer, was chosen with 2θ from 18° to 102°, with a 0.05° step, and counting times between 2.5–3.0 s/step.

2.3. ZrO2–CeO2/SiO2 characterization

The X-ray powder diffraction measurements were carried out at the XPD beamline of the Brazilian Synchrotron, LNLS. The wavelength was set at 1.5498 Å. Isotropic atomic displacement (temperature) factors were assumed. The least-square refinement analysis was performed on the samples calcinated until 540 °C. The software Fullprof[19] was used to refine the structural parameters through a least-squares method. The peak shape was assumed to be a pseudo-Voigt function with asymmetry parameters. The background of each pattern was fitted by a 5 degree polynomial function. Isotropic atomic displacement (temperature) factors were assumed. The least-square method was adopted to minimize the difference between the observed and simulated powder diffraction pattern. The R’s values indicated the agreement between the observed and calculated quantities. The refinement was done, reducing R’s values and the quality factor goodness of fit (SGoF), until they reach the convergence[20][21][22][23][24].

Nitrogen adsorption isotherms were performed for all samples (with and without Si) with a NOVA (Quantachrome) porosimeter. Thermal treatment to dry the samples was made for 2 hours in 200 °C and measurements were taken in 77 K (N2). The pore size distribution, pore volume and pore radius were calculated using BJH method[25]. The specific surface area was calculated using the BET method[26][27].
The cerium oxidation state was evaluated by in situ XANES experiments at the Ce L_{III}-edge. The spectra were collected at the D04B-XAFS1 beamline at the LNLS in transmission mode using a Si(111) monochromator. The samples with SiO_2 were diluted with boron nitride (BN), and pressed into 15 mm diameter pellets (around 4-5 mg of sample and 70 mg of BN). The pellets were placed in a quartz tubular furnace sealed with Kapton windows. These measurements were acquired during temperature-programmed reduction (TPR) under a 5% H_2/He gas mixture (total flow of 50 mL/min) at temperatures in the range of 25 to 500 °C at a heating rate of 10 °C/min. The data were analyzed with the WinXAS software [28].

3. Results and discussion

3.1. ZrO_2-CeO_2

In-situ SAXS experiments were carried out in order to analyze the process of template removal in the samples. Both as-synthesized samples present one diffraction peak, revealing partial spatial correlation between its pores before the calcination process.

For the 50% CeO_2 content (sample Z50AC) depicted in figure 1, the intensity of the peak decreased as the temperature increased, reaching a maximum around 170 °C and then, decreased showing the loss of the ordered mesoporous structure. Figure 3 shows the radius of gyration (R_G) from Guinier plot (log[I(q)] versus q^2) for both CeO_2 contents.

For the 90% CeO_2 content (sample Z90AC), depicted in figure 2, the intensity of the peak increased as the temperature increased, reached a maximum around 170 °C and then, decreased showing the loss of the ordered mesoporous structure. Figure 3 shows the radius of gyration (R_G) from Guinier plot (log[I(q)] versus q^2) for both CeO_2 contents.

The radius of gyration is related to the mean size of the scattering particles or pores in the sample [29, 30]. For mesoporous materials, this parameter can be related to the pore size. Before 174 °C, for both CeO_2 content, there was a shrinking of the pore size, due to the decomposition of
the polymer template, which is expected for SiO₂ systems[31]. Between 200 to 300 °C the radius of gyration increased, suggesting the pores walls are breaking. After 300 °C, both samples lost the ordered mesoporous network after the total removal of the polymer (540 °C). At the end of the calcination process there was a final radius of gyration around 80 Å for both ceria contents, showing a shrinkage of the pores structure.

Figure 4 shows the X-ray powder diffraction results for the Z50AC and Z90AC samples, calcinated until 250 °C and 540 °C.

For Z50AC sample there were no crystalline phases when it was heated until 250 °C. After 540 °C treatment, the crystalline structure was composed of tetragonal (P42/nmc) and cubic fluorite (Fm$\bar{3}$m) ZrO$_2$–CeO$_2$ crystallographic phases[32,33]. For the Z90AC sample several peaks were observed after it was heated until 250 °C, from chloride and oxychloride phases (Zr(ClO$_4$)$_2$)$_4$ and Ce(ClO$_4$)$_2$[1]. There was a single cubic fluorite type phase (Fm$\bar{3}$m) after calcination until 540 °C.

Rietveld results are presented on table[1] showing the difference between the two ceria contents. For Z90AC there were larger lattice parameters, leading to a higher cell volume, the cubic phase crystallite size is also larger. From the lattice parameters it was possible to evaluate the amount of zirconia that was incorporated in to the ZDC lattice[33]. For Z50AC, it was estimated that the compositions of the tetragonal and cubic phases were ZrO$_2$-15 mol% CeO$_2$ and CeO$_2$-5 mol% ZrO$_2$, respectively. Besides, the fitting results suggested that a small part of amorphous ZrO$_2$ was still present in this sample.

Table 1: Structural parameters of Rietveld analysis for 50 and 90% CeO$_2$ calcinated samples (until 540 °C). Where a and c are lattice parameters, weight percentage of crystalline phases, V is the lattice volume, D is the average crystallite size. $R_p$, $R_w$, $R_{exp}$, $\chi^2$ and $S_{GOF}$ are the Rietveld standard agreement factors.

| Phase          | Z50AC | Z90AC |
|----------------|-------|-------|
| Cubic          | Fm$\bar{3}$m | P42/nmc | Fm$\bar{3}$m |
| a/Å            | 5.409(15) | 5.621(5) | 5.490(6) |
| c/Å            | 5.216(5) | -     | -     |
| V/$Å^3$        | 158.236(8) | 68.41(7) | 158.364(3) |
| D/nm          | 16.3(3) | 6.63(9) | 29.8(9) |
| $R_p$          | 7.31   | 6.82   |
| $R_w$          | 7.57   | 6.05   |
| $R_{exp}$      | 2.45   | 2.90   |
| $\chi^2$       | 9.56   | 5.3    |
| $S_{GOF}$      | 3.1    | 2.1    |

Nitrogen physisorption results are presented on figure[3] and table[2].

Table 2: Nitrogen physisorption results: Specific surface area $S_{BET}$, pore volume $V_p$, mean pore diameter $D_p$.

| Samples   | $S_{BET}$ (m²/g) | $V_p$ (cm³/g) | $D_p$ (Å) |
|-----------|------------------|---------------|-----------|
| Z50AC     | 47.3             | 0.18          | 28.0      |
| Z90AC     | 46.1             | 0.21          | 20.7      |

The Z50AC sample presented a type IV isotherm and H₂ hysteresis. The BJH pore size distribution (PSD) showed one peak at a mean pore diameter of 28.0 Å. For higher ceria content, the Z90AC sample, presented hysteresis more characteristic of H₁ type, with capillary condensation happening only at P/P$_0$ higher values, indicating lower pore sizes and inter-particle porosity contribution. The PSD showed a higher dispersion of pores size for higher ceria content, with medium pore diameter around 20.7 Å. The BET specific surface area and pore vol-

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1 Phases indexed with MDI Jade 6.5 software.
ume were independent of the ceria content. The t-
plot analysis showed absence of micropores for both
ceria contents. The radius of gyration calculated by
SAXS (fig. 3) was higher than the average pore di-
diameter measured from adsorption mostly because
of inter-particle porosity contribution on the sur-
face adsorption.

These results indicate that the crystallization
process is an important step, which guides the
mesoporous structure of these oxides. And, even
loosing the ordered pore structure, the ZDC sam-
ple present good textural properties.

3.2. ZrO$_2$-CeO$_2$/SiO$_2$

In order to increase the mechanical stability two
different one-pot synthesis with low SiO$_2$ content
and 90% CeO$_2$ (single phase cubic structure) were
tested (sec. 2). SAXS results are showed in figure
6 and table 3 where there are results before and after calcination for all samples.

Since the first sample from hybrid method
(Z90H10) showed a disordered porous structure af-
after calcination until 540 °C, samples from palisade
method (Z90P10 and Z90P30) were heated until in-
termediate temperatures (300, 350 and 400 °C) in
order to evaluate the ordered porous structure ev-
olution. The presence of several peaks in the low
angle region of SAXS measurements indicates that
the material has an ordered porous structure and,
more than one peak indicates which structure was
formed after the synthesis.

Table 3: SAXS parameters: Area under the peaks \( A_P \), total area under the SAXS curve \( A_T \), ordering factor \( f \), where \( f = A_P/A_T \), and radius of gyration, \( R_G \).

| Samples | \( A_P \) (arb. u.) | \( A_T \) (arb. u.) | \( f \) | \( R_G \) (Å) |
|---------|-----------------|-----------------|-----|--------|
| Z90H10  | 14              | 39              | 0.36| 124.2  |
| as prepared |                |                 |     |        |
| calcined | -               | 7784            | 0   | 114.3  |
| Z90P10  | 19              | 26              | 0.71| 112.7  |
| as prepared | 63               | 107             | 0.51| 90.9   |
| 300°CC  | -               | 442             | 0   | 117.5  |
| 350°CC  | -               | 1954            | 0   | 128.7  |
| 400°C  | -               | 5126            | 0   | 114.4  |
| calcined | -               | 298             | 0.24| 115.0  |
| Z90P30  | 73              | 298             | 0.24| 112.6  |
| as prepared | 2               | 30              | 0.07| 118.5  |
| 300°CC  | -               | 807             | 0   | 136.7  |
| 350°CC  | -               | 4187            | 0   | 125.5  |
| 400°C  | -               | 9476            | 0   | 132.6  |
| calcined | -               |                 |     |        |

The ordering factor \( f \) was defined as the area of
the peaks after subtracting the scattering baseline
\( A_P \) divided by the total area under the peaks
without the baseline removal \( A_T \), so \( f = A_P/A_T \).
Since the area under the SAXS curve is propor-
tional to the scattering pores/particles, it was pos-
sible to compare samples having higher ordering re-
lying on the pore structure.
Studying the interplanar distances from uncalcined samples in fig. 6, the results obtained for samples prepared by the hybrid and palisade methods were similar. Comparing interplanar distances $d^1$ from the first peak and $d^2$ for the second peak, it was possible to index a lamellar structure where the lattice parameter for the pores, $a_p$, is $1/d_{00}=h/a_p$. Therefore $a \sim d_{10} = 116 \AA$ for Z90H10 and Z90P10. The sample Z90P30 presents two peaks, closer to a 2D hexagonal structure with average lattice parameter $a_p = 180 \AA$, calculated using $\frac{1}{d_{h,k,l}^2} = \frac{4}{a_p^2} \frac{h^2+k^2+l^2}{h^2+k^2+l^2}$ (for this case, hkl = 100 and 200).

From hybrid and palisade method with 10 mol% Si it was possible to infer that stirring the polymer and TEOS prior to Zr/Ce addition during preparation resulted in higher areas (higher porosity) therefore higher ordering factor. As the temperature increased, the total area increased, since the intensity of SAXS depends mostly on the structure density contrasts. Both samples of the palisade method maintained their ordered pores until 350 °C, where there were no more peaks on the SAXS curves. The ordering factor decreased as the temperature increased. The radius of gyration for Z90P10 decreased at 300 °C, indicating a abrupt shrinkage of the structure, while for Z90P30 the radius increased at 350 °C which could suggest the rupture of the walls of the 2D hexagonal structure.

Figure 4 shows the diffraction patterns for calcined Z90H10. Z90P10 and Z90P30 were analysed after heated until 300, 350, 400 °C and calcined (540 °C). Rietveld results are presented on table 4.

XRD measurements followed the same temperatures from SAXS experiments, to study what undergoes with the increase of the temperature and the crystalline structure.

For Z90P10 the crystallization started only at 350 °C, later than previous sample with the same ceria content. Z90P30 at 350 °C presented an amorphous phase, showing a even later crystallization, at 400 °C. Sample Z90H10 showed a smaller crystallite size. From Rietveld results there were no significant changes on the overall crystallographic structure of the ZDC synthesized with Si, the lattice parameters are similar from cubic single-phase solid solutions synthesized by gel-combustion routes [33].

N$_2$ physisorption results are showed on figure 8 and table 5.

Hybrid method sample resulted in a type H$_2$ hysteresis, while both palisade samples presented between H$_2$ and H$_3$ type. From PSD curves a higher silica content resulted a narrower PSD.

From t-plot analysis [34], the Z90H10 sample showed micropores in its structure (V$_p^{t-plot} = 0.012$ cm$^3$/g and S$_p^{t-plot} = 8.1$ m$^2$/g), while Z90P10 and Z90P30 only presented mesopores. The addition of the Zr/Ce precursors after the previous P-123 and TEOS solution resulted in a higher surface area, but slightly lower pore volume. Higher silica content resulted in higher surface area and pore volume, showing the advantage of a silica palisade to improve the material texture.

In situ XANES results are presented on figure 9.
Table 4: Structural parameters of Rietveld analysis for 90% CeO$_2$ (Z90H10, Z90P10 and Z90P30) calcinated samples (until 540°C). Where a and c are lattice parameters, weight percentage of crystalline phases, V is the lattice volume, D is the average crystallite size, R$_p$, R$_{exp}$, χ$^2$ and S$_{GoF}$ are the Rietveld standard agreement factors.

| Samples   | Phase | a/A  | V/A$^3$ | D/Å  | R$_p$  | R$_{exp}$ | χ$^2$ | S$_{GoF}$ |
|-----------|-------|------|---------|------|--------|-----------|-------|-----------|
| Z90H10    | Cubic | 5.41(14) | 158.38(7) | 18.59(9) | 8.24  | 10.5      | 4.2   | 1.9       |
| Z90P10    | Cubic | 5.41(14) | 158.38(7) | 18.59(9) | 9.71  | 12.0      | 4.4   | 2.1       |
| Z90P30    | Cubic | 5.41(14) | 158.38(7) | 18.59(9) | 9.19  | 11.9      | 4.1   | 2.0       |

The analysis method described by Zhang et al [35] was used to quantify the fraction of Ce$^{3+}$ in the samples. It consists of a least-squares fit to the experimental data with the WinXAS software, using four Gaussian profiles and one arctangent function (fig. 9 inset) [28].

Figure 8: Nitrogen physisorption isotherms and the PSD for: (a) Z90H10 isotherm, and (b) PSD. Z90P10 (c) isotherm, and (c) PSD. Z90P30 (e) isotherm, and (f) PSD.

Figure 9: Ce$^{3+}$ fraction for Z90P10 and Z90P30 with temperature, under temperature programmed reduction (TPR) with 5% H$_2$/He. Inset shows the CeO$_2$ XANES spectrum at Ce L$_{III}$-edge.

Pure CeO$_2$ spectrum at L$_{III}$-edge has 2 main peaks, A and B, which refers to Ce$^{3+}$ final states from 2p to 5d transitions. The peak C occurs due to dipole transitions and it is characteristic to Ce trivalent state. And the pre-edge peak D corresponds to multiple scattering processes [35, 36, 37, 38]. Therefore the Ce$^{3+}$ fraction = C/(A+B+C) where A, B and C represent the area of the fitted peaks. Fig. 9 shows that with the increase of temperature under reduction conditions the samples shift from Ce$^{4+}$ to Ce$^{3+}$. At 500°C Z90P10 reached reduction of 28%, and Z90P30, 54%.

Although there is not total reduction of Ce$^{3+}$ to Ce$^{4+}$ in the studied temperature range, the increase of the silica content from 10 to 30 mol% and the improvement on the superficial area (from 73 to 120 m$^2$/g, respectively) promoted a higher reduction of Ce$^{4+}$ under lower temperatures compared to materials synthesized via gel-combustion routes [38, 39].

4. Conclusions

In this work new synthesis of ZDC was reported using soft template method. Three new synthesis methods with low SiO$_2$ content were developed to
increase mechanical stability of the pores. The lost of the ordered structure of the pores was correlated to the amorphous-crystalline transition of ZrO$_2$–CeO$_2$ at 300 °C. Although there were no ordered pores, the samples showed proper textural properties for applications in catalysis as well as SOFC anodes. A higher pore ordering was obtained and kept until 350 °C, compared to other materials in the literature. Better textural properties were obtained, specially higher specific surface area. And finally, in situ XANES results revealed a high reduction rate of Ce$^{3+}$, which is directly correlated to higher catalytical activity.

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