



CeO₂ thin film supported on TiO₂ porous ceramics

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ABSTRACT

The work demonstrates an easy and simple method for obtaining a TiO₂ porous ceramic coated with a CeO₂ thin film (COTF) on the surface. Replica technique used a 30 PPI polyurethane sponge and TiO₂ ceramic suspension. Dip coating technique was used to coat the material surface and cerium polymeric resin synthesis was obtained by polymeric precursors method. Thermal analysis indicated a thermostable material from 500 °C. X-ray diffraction analysis of calcined CeO₂, at 600 to 900 °C, resulted in monophasic and crystalline with a fluorite type cubic structure. Scanning electron microscopy made it possible to monitor COTF formation and growth from islands shape to a more homogenous form over 10 depositions.

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1. Introduction

Porous ceramics (PCs) are advanced ceramics subclasses which have been widely studied due to characteristics and properties that favor technological applications, such as high porosity combined with permeability, being ideal for use as catalytic supports and gas sensors [1–4].

Currently, there are numerous methods for obtaining PCs, being the most employed: sacrificial phase method, foam gelcasting method and polymeric sponge or replica method [5–7]. Replica technique, one of the most cited due to its simplicity and versatility, consists of a polymeric sponge impregnation in a ceramic suspension, to obtain a replica, undergoing a heat treatment process [8].

PCs are essential materials in catalytic converters manufacture, denominated Three Way Catalyst (TWC), which perform exhaust gases purification, transforming harmful gases produced by combustion process into less toxic to the environment gases [9]. TWC are normally formed by refractory oxides with a high surface area, called magnesium cordierite monoliths (2MgO.2Al₂O₃.5SiO₂), with a honeycomb structure, porous and usually impregnated with noble metals, such as platinum (Pt), palladium (Pd) and rhodium (Rh). CeO₂, due to its high oxygen storage capacity, has been widely applied in redox reactions, characteristic in which it has attracted

scientific research aimed at heterogeneous catalytic reactions [10–12].

According to Oliveira et al. [13], Ce compounds have properties, such as redox potential range (+3/+4), high oxygen ions mobility in the crystalline network and high affinity for oxygen, nitrogen and sulfur, which give it technological applicability. Studies report that CeO₂ is used as a catalytic support and in activation and inactivation of catalysts [11,12,14].

In this study, we report an innovative approach to the gas redox system for a possible application in automotive catalysts.

2. Materials and methods

200 g TiO₂ ceramic suspension (TOCS), 150 mL distilled water, 4 mL deflocculant (ammonium polyacrylate) and 1 mL HNO₃(conc) were processed in a ball mill, for 24 h, at 600 rpm. Polyurethane sponge with a 30 pores per inch (PPI) porosity (PRO-314 Blue - ProEspuma®), in a cube form, was used as a polymeric mold. The sponge was chemically pre-treated by remaining immersed in a 1.5 mol L⁻¹ HNO₃ solution, for 12 h, and then, washed with distilled water and dried at room temperature. Then, the sponge was immersed and withdrawal from TOCS, being withdrawn solution excess, and heat treated at 80 °C, for 30 min, and at 110 °C, for 60 min, both with a 1 °C min⁻¹ heating rate. After drying, sponge decomposition and TiO₂ porous ceramics (TOPC) sintering were carried out using three temperatures: 500 °C and 1000 °C, for 60 min, and 1500 °C, for 300 min; at different rates heating:

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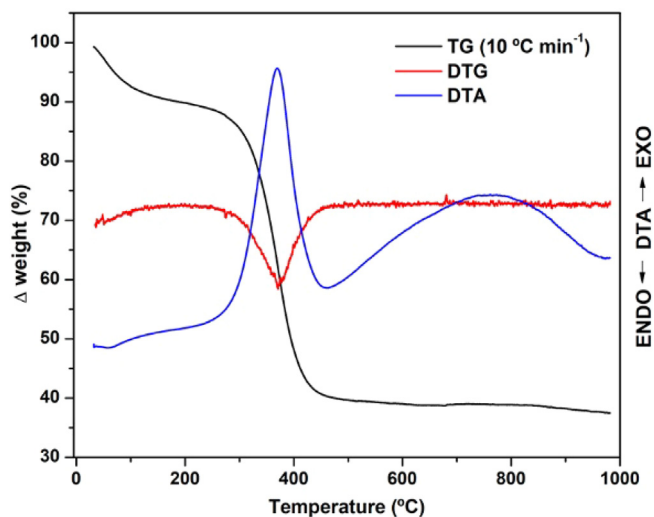


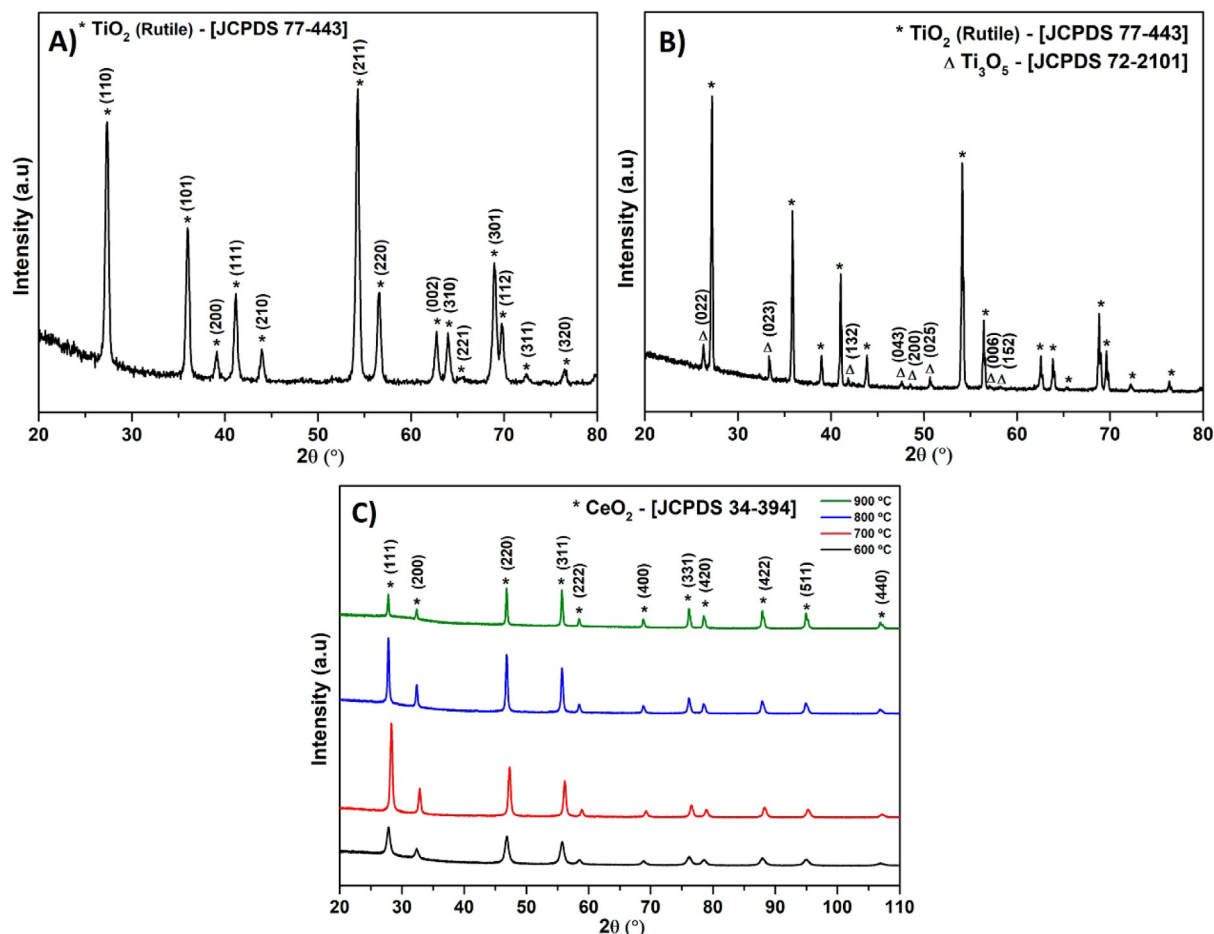
Fig. 1. TG/DTA of pre-calcined CeO_2 powder at 300°C , disaggregated and sieved in a 270 mesh screen.

$0.5^\circ\text{C min}^{-1}$, 2°C min^{-1} and 3°C min^{-1} , respectively. To obtain the CeO_2 thin film (COTF), a polymeric cerium resin (PCR), previously prepared by polymeric precursors method (PPM), was used with the following stoichiometric ratio, according to Pechini patent [15] 1 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$: 4 mol citric acid: 16 mol ethylene gly-

col. A citric acid aqueous solution was added to $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ aqueous solution for Ce metal complexation process, which remained for 30 min under stirring, at 60°C . pH of the resulting solution was adjusted to 6. For Ce polyesterification reaction, ethylene glycol was added to the Ce complexation resulting solution, under stirring, at 50°C , for 12 h.

Ceramic coating process with Ce to form films was carried out by the dip coating technique, that is, TOPC immersion in polymeric resin. Then, a ceramic was left to rest on paper towel, for 24 h, to remove excess resin and prevent pore poisoning, and, subsequently, sintered at 900°C , for 120 min, with a 5°C min^{-1} heating rate. The material immersion and burning process was repeated until the tenth time, to guarantee the film formation.

For Organic matter decomposition and CeO_2 thermal stability determination, thermogravimetric (TG) analysis and differential thermal analysis (DTA) of CeO_2 powder (COP), obtained from resin pre-calcination at 300°C , were performed, respectively. The material was subjected to heating from 35 to 980°C , at a heating rate $10^\circ\text{C min}^{-1}$, with a $50\text{ cm}^3\text{ min}^{-1}$ synthetic air flow. In order to identify the phase and CeO_2 crystalline structure evolution, an X-ray diffraction (XRD) analysis of heat treated at 600 to 900°C COP, of TiO_2 powder and of sintered at 1500°C TiO_2 ceramic powder was performed. For analyzes, a diffractometer was used, with copper tube ($\text{Cu-K}\alpha$, $\lambda = 1.5406\text{ \AA}$), at 40 kV and 60 mA. Diffraction spectra were obtained in the range of 2θ , between 20 and 80° , in continuous mode, at $0.02^\circ 0.12\text{ s}^{-1}$. To evaluate and characterize the morphological structure of the ceramic surface coated with CeO_2 , a scanning electron microscopy (SEM) analysis was



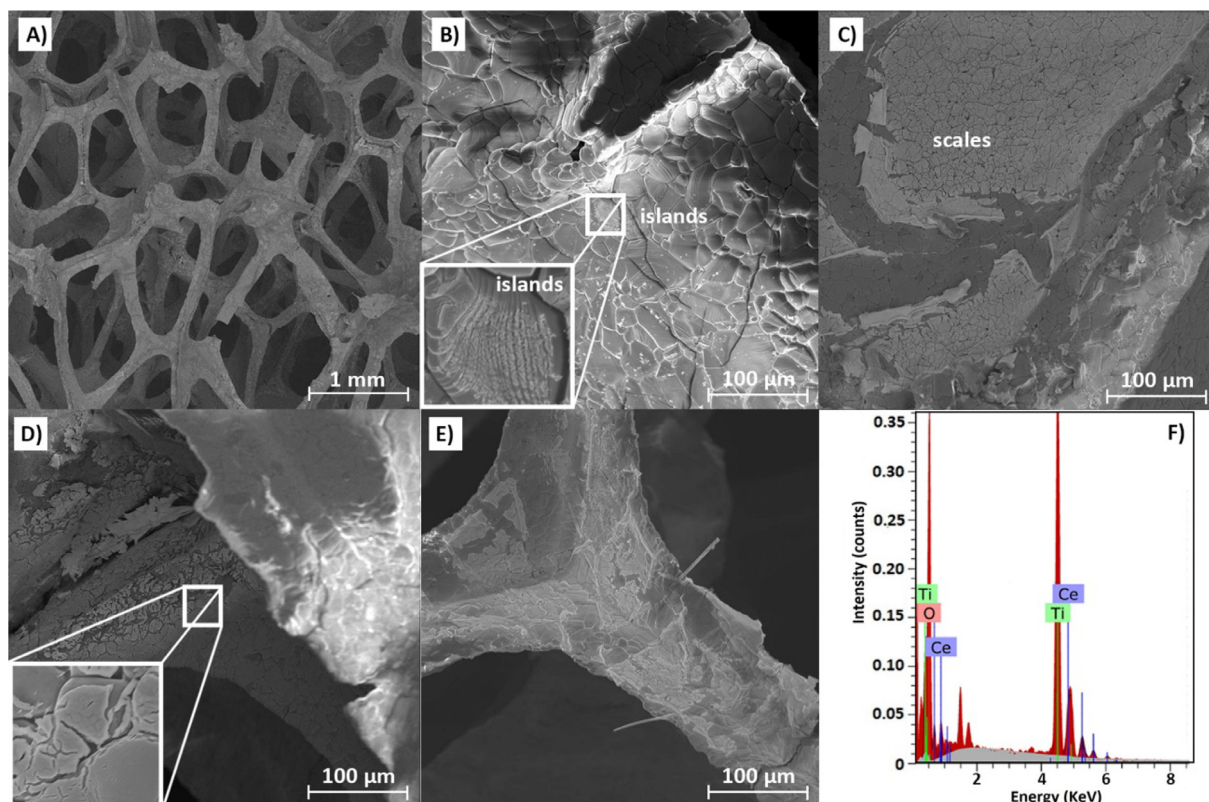


Fig. 3. Micrographs of thin films, obtained by SEM, of TOPC immersed in CPR, calcined at 900 °C, for 120 min: (a) uncoated TOPC sintered at 1500 °C, for 300 min; (b) 2 depositions; (c) 4 depositions; (d) 8 depositions; (e) 10 depositions; (f) EDS spectrum after 10 depositions.

performed, with *retro*-scattered electronic incidence, coupled to an energy dispersive spectroscopy (EDS) detector.

3. Results and discussion

Mass loss events of the pre-calcined material are shown in Fig. 1. By TG/DTA, two material mass loss events were observed. First event occurs from room temperature to 200 °C, being attributed to the output of H₂O (humidity), which is weakly bound by hydration, and of adsorbed gases (CO₂ e N₂) on the material surface [16], corresponding to the endothermic peak, at 62 °C, on the DTA curve. Second event occurs from 250 to 450 °C, and it refers to the volatile output from organic matter decomposition by oxidation reactions, derived from citric acid and ethylene glycol [16], corresponding to the exothermic peak at 380 °C, on the DTA curve. Above 500 °C, a thermostable compound was obtained, from which temperature was used as a reference to obtain the single-phase CeO₂ thin film. Between 600 and 800 °C, no exothermic signal was observed in DTA curve, probably associated with CO₂ recombination, as no inert gas was used as an atmosphere in the analysis.

XRD patterns of TiO₂ and CeO₂ powder to identify and monitor the crystalline phase formation are shown in Fig. 2. TiO₂ powder diffractogram presents well-defined, crystalline and monophasic peaks, which is characteristic of rutile phase with a tetragonal structure, belonged to the spacial group P4₂/mm (Fig. 2a). While TOPC powder showed narrower and more intense peaks, which can be related to a higher degree of crystallinity, a second phase Ti₃O₅, with an orthorhombic structure and CmCm spatial group, related to low intensity peaks after sintering the material at 1500 °C, was observed (Fig. 2b) [17]. XRD pattern of CeO₂ powder by PPM also reveals crystalline peaks, characteristics of a fluorite type

cubic structure, belonging to Fm3m space group and the CeO₂ phase formation at the studied temperatures (Fig. 2c). An important factor observed was that the phase transformation and the crystallinity increase occurred due to the increase in material calcination temperature [18], which corroborates TG/DTA results, making it impossible to obtain CeO₂ phase below 500 °C.

Based on TG/DTA results, the process of immersion and deposition in 10 layers and sintering at 900 °C was performed to form a CeO₂ thin film. Its growth, formation and identification on the material surface was analyzed by SEM/EDS (Fig. 3). Fig. 3a shows a porous, uncoated ceramic, sintered at 1500 °C, with interconnected structure, hollow rods and triangular profiles. The evolution of CeO₂ deposition on the ceramic surface (Fig. 3b) illustrates an island shape at specific points after 2 depositions. With the increase in depositions number, scales formation is observed (Fig. 3c). After 8 depositions (Fig. 3d), CeO₂ coating was observed more homogenously on the material surface. After 10 depositions (Fig. 3e), a regular covering on the surface is observed without changing the morphology. EDS spectrum, shown in Fig. 3f, identifies peaks related to titanium (Ti) and cerium (Ce) present after 10 depositions of CeO₂ supported on a TiO₂ porous matrix. Indicative of CeO₂ phase presence on the surface, from 500 °C, according to TG (Fig. 1) and XRD (Fig. 2) analyzes, which corroborates with the results of a thermostable, monophasic and crystalline compound, respectively.

4. Conclusions

In this study, a CeO₂ thin film, obtained by polymeric precursors method, was deposited on a TiO₂ porous ceramic matrix, obtained by the replica technique, presenting monophasic CeO₂, with fluo-

rite type cubic structure and crystalline, according to TG/DTA and XRD results. Through morphological analysis (SEM/EDS), it was possible to monitor the thin film growth and formation on ceramic surface up to 10 depositions, showing the possible application for automotive catalysts.

CRediT authorship contribution statement

Alley Michael Silva Procópio: Conceptualization, Methodology, Validation, Investigation, Visualization, Writing - original draft, Project administration. **Jaqueline Carmo Lima Carvalho:** Visualization, Writing - review & editing. **Thales Henrique Resende Silveira:** Investigation, Writing - review & editing. **Aislan Lúcio Valério:** Investigation, Writing - review & editing. **Isabela Cristina Fernandes Vaz:** Conceptualization, Visualization, Writing - review & editing. **Ana Cristina Tolentino Cabral:** Conceptualization, Visualization, Writing - review & editing. **Márcio Roberto Freitas:** Conceptualization, Methodology, Writing - review & editing, Supervision. **Mercês Coelho Silva:** Conceptualization, Resources, Writing - review & editing, Supervision. **Francisco Moura Filho:** Conceptualization, Methodology, Resources, Visualization, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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