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Unexpected malformations in
Xenopus tropicalis



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Catalytic combustion of soot over ceria-zinc mixed oxides catalysts supported onto cordierite

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ABSTRACT

Modified substrates as outer heterogeneous catalysts was employed to reduce the soot generated from incomplete combustion of diesel or diesel/biodiesel blends, a process that harms the environment and public health. The unique storage properties of ceria (CeO_2) makes it one of the most efficient catalysts available to date. Here, we proposed that ceria-based catalysts can lower the temperature at which soot combustion occurs; more specifically, from 610°C to values included in the diesel exhausts operation range ($300\text{--}450^\circ\text{C}$). The sol-gel method was used to synthesize mixed oxide-based catalysts ($\text{CeO}_2\text{:ZnO}$); the resulting catalysts were deposited onto cordierite substrates. In addition, the morphological and structural properties of the material were evaluated by XRD, BET, TPR- H_2 , and SEM. Thermogravimetric (TG/DTA) analysis revealed that the presence of the catalyst decreased the soot combustion temperature by 200°C on average, indicating that the oxygen species arise at low temperatures in this situation, promoting highly reactive oxidation reactions. Comparative analysis of soot emission by diffuse reflectance spectroscopy (DRS) showed that catalyst-impregnated cordierite samples efficiently oxidized soot in a diesel/biodiesel stationary motor: soot emission decreased by more than 70%.

Introduction

Particulate matter (PM) is naturally present in the atmosphere. The majority of the PM released into the atmosphere stems from fossil fuels combustion. The PM generated by diesel engines affects the human health negatively indeed, environmental pollution from diesel exhausts has risen dramatically, increasing the prevalence of lung problems among the population, mainly in urban centers (Harrison and Yin, 2000; Wichmann, 2007; Müller et al., 2006; Bünger et al., 2012; Tsai et al., 2012). This situation calls for strict PM emission control (Russell and Epling, 2011; Neeft et al., 1996; Twigg, 2007). Awareness

about the need to abate soot release by the diesel engine exhausts has increased, as noted from the environmental legislation on exhaust specifications (van Setten et al., 2001; Vouitsis, et al., 2003).

The hazardous nature of diesel soot has led researchers to develop devices that can diminish soot emission from engines, in the hope that new technologies will help remedy the problems soot causes (Simonsen et al., 2008; Cousin et al., 2007). One strategy has been to design catalytic filters or traps that combine retention and oxidation or gasification of the soot emitted from diesel engines (Tikhomirov et al., 2006; Gálvez et al., 2012). These filters may employ catalysts that promote low-temperature combustion of carbonaceous materials, to reduce the amount of diesel soot, and they should exhibit high performance at low temperatures, since exhaust gases cool down to 280--

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450°C. Hence, it is mandatory that catalysts which are active enough to ignite soot within the above temperature range are developed. However, systems that increase the temperature to burn soot are not necessary, because this would require greater energy expenditure (Tighe et al., 2012; Kumar et al., 2012).

The catalytic diesel particulate combustion is based on a heterogeneous reaction involving solid soot particles, exhaust gas, and the solid catalyst in intimate contact with the filter (van Setten et al., 2001). In turn, the catalytic activity of the solid is related to the chemical composition, structure, particle size, and specific surface area of the catalyst. Many catalysts mixed with metal oxides and noble metals can function as traps. The most often used materials can adsorb oxygen and generate reactive oxygen species that oxidize soot (Liang et al., 2008; Gupta et al., 2010; Li et al., 2007). Oxides containing metals are the most active for soot combustion, because they can perform redox cycles during the process. The redox reaction disturbs the charge balance of the mixed-valence binary oxides, but the creation of oxygen vacancies ensures electroneutrality. Researchers have tested several kinds of catalysts such as oxides (Wagloehner and Kureti, 2012; Saab et al., 2007; Zouaoui et al., 2012; Kaspar, et al., 1999), mixed oxides (Wu et al., 2011; Uner et al., 2005; Wang et al., 2012), alkaline or heavy metal oxides (Kumar et al., 2012; Jiménez et al., 2008; Peralta et al., 2011; Neyertz et al., 2012), and precious metals (Guan et al., 2011; Homsí, et al., 2011; Yamazaki, et al., 2011; Hirata et al., 2011). Ceria (CeO_2) doping with these metals oxides improves the oxygen exchange capacity of the oxide and raises the soot combustion rate. Ceria contain oxygen vacancies, because many $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox sites are rapidly formed and removed. The result is remarkable oxygen storage capacity (Homsí, et al., 2011; Vicario et al., 2009; Shimizu et al., 2010), a function known as oxygen storage/release capacity. In more general terms, this behavior is referred to as redox and oxygen-vacancies behavior; it accounts for the characteristics of CeO_2 reduction and oxidation, confirming that these materials generate active species that consume soot (Aneggi et al., 2006; Thrimurthulu et al., 2012). This happens because O_2 adsorbs onto the catalyst, subsequently increasing the mobility of active oxygen species (Trovarelli, 2002; Azambre et al., 2011; Sun et al., 2012; Acerbi et al., 2012).

The immobilization of small amounts of oxides with catalytic properties on matrixes with high specific surface area leads to new surface species with structural features that control the activity and selectivity of the new composite materials. The combination of two or more metal oxides on the surface of a support produces a complex system with multiple functions stemming from each oxide, often eliciting new properties. The role of ceria is to assist generation of the atomic oxygen species and transfer them from the gas phase to the lattice consisting of mixed oxides

and the soot surface (Aouad et al., 2009; Jeguirim et al., 2010).

In this article we prepared the mixed binary oxide $\text{ZnO}:\text{CeO}_2$ over cordierite by the sol-gel method and evaluated the catalytic activity of the supported mixed oxide in diesel soot particulate oxidation. We used X-ray powder diffraction (XRD), scanning electronic microscopy (SEM), Raman spectroscopy, diffuse reflectance spectroscopy (DRS), and thermal analysis (TG and DTA), to analyze the structure of the catalyst.

1 Materials and methods

1.1 Preparation of the mixed binary oxide powder supported onto cordierite

The solid system $\text{CeO}_2:\text{ZnO}$ was synthesized from an ethanolic suspension of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and a $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution (0.4 mol/L), at a Ce/Zn molar ratio of 2:3. The mixture was heated under reflux, and 200 μL of lactic acid (85%) was successively added, until $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ dissolved completely and a stable transparent sol arose. The sample was then dried until ethanol was eliminated. The powder was calcined at 650°C for 3 hr under air atmosphere, to eliminate the organic material.

The cordierite ceramic substrates ($5\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{MgO}$, Umicore[®], Brazil) were modified using the $\text{CeO}_2:\text{ZnO}$ impregnation method; they were cut into a cylindrical shape (3.5-cm height and 2.5-cm diameter), for use in the catalytic tests. The impregnation process consisted of immersing the ceramic substrate into the $\text{CeO}_2:\text{ZnO}$ sol at 50°C for 5 min, followed by heating at 650°C for 3 hr; this procedure was repeated four times. The mass of catalyst that adhered to the monolith after the impregnation procedure was gravimetrically determined for each preparation, by weighing the vacuum-dried cordierite samples before and after the impregnation procedure. The amounts of loaded catalyst varied around 10% in mass with relation to the initial mass of the substrate.

1.2 Characterization of the prepared materials

Nitrogen adsorption data were obtained on a Nova 2200 (Quantachrome, USA) analyzer using a liquid nitrogen bath (77 K) and high-purity nitrogen as adsorbate; the specific surface area was calculated by the BET equation. The samples were previously dried for 5 hr under low pressure (ca. 60 mmHg), at 120°C.

The structural characterization of the catalysts (powder) was accomplished on a D5005 (Siemens, Germany) X-ray diffractometer (XRD) operating with a copper tube ($\text{Cu-K}\alpha$ radiation, 1.541 Å) under 40 kV and 30 mA. The scan

speed was 2°/min; the 2 θ values ranged from 20° to 90°.

The redox behaviour of the CeO₂:ZnO catalysts was examined by H₂-TPR in a Pulse ChemiSorb 2705 (Micromeritics, USA) device consisting of a tubular quartz reactor coupled to a TCD detector, to monitor H₂ consumption. The reducing gas was 5% H₂ in N₂. Experiments were conducted from room temperature to 800°C at heating rate was 10°C/min.

The oxygen storage capacity (OSC) measurements were carried out in an atmospheric glass fixed bed reactor placed in an electrical oven connected to a QMS200 quadrupole mass spectrometer (Pfeiffer, Germany) and a TCD. The sample (200 mg) was placed in the reactor and heated up to 400°C under continuous helium flow (50 mL/min), at atmospheric pressure. At this temperature, 10 pulses of 10% O₂/He were introduced, to completely oxidize the sample; He flow was passed through the sample for 10 min, to purge to desorb the excess of weakly adsorbed O₂ in the sample. Then, ten pure CO pulses were injected before a new 10 min purging step with He. The oxygen storage capacity was calculated from the first CO pulse. Then, the oxygen storage complete capacity (OSCC) was evaluated from the total amount of CO consumed at the end of the CO pulse series. OSCC corresponds to the total amount of reactive oxygen.

The morphology and particle size of the materials were evaluated by scanning electron microscopy. The micrographs were acquired on a EVO50 (Zeiss, Germany) equipment and a JEM-100cx II (JEOL, Japan). An IXRF Systems 500 Digital Processing accessory was used for elemental quantification.

For diffuse reflectance spectroscopy (DRS) measurements, the powders were ground in an agate mortar and compacted in a black holder. The measurements were performed on a USB4000 (Ocean Optics, Germany) spectrometer equipped with an R400-7-VIS/NIR reflection/backscattering probe (400 μ m core diameter optical fiber) and an LS-1 tungsten-halogen lamp. The DR spectra were recorded in the 300–700 nm and 300–1000 nm ranges, with integration time of 100 ms and a distance of 0.5 cm between the samples and the probe, which was kept at 90° in relation to the sample surface (backscattering geometry). The visible spectra of the filter papers impregnated with soot were also recorded in the same apparatus.

Micro-Raman spectra were collected in the backscattering configuration using a T64000, (Horiba-Jobin Yvon, USA) spectrometer equipped with a nitrogen-cooled charge coupled device detector. The argon ion (Ar⁺) laser line with $\lambda = 514.5$ nm was used as the excitation source, focused onto the sample with the aid of an BX41 (Olympus, USA) microscope and a long working distance objective with 100x magnification. The incident laser power was 3.5 mW.

1.3 Catalytic activity

The potential of the catalysts was firstly evaluated by thermal analysis of the combustion of mixtures containing each catalyst and the soot model - Printex-U[®], Degussa (DeSousa Filho et al., 2009) at a ratio of 9:1 (W/W), respectively. For loose contact conditions, the catalyst and soot were simply mixed with a spatula. The catalytic ability was evaluated through dynamic tests comprising a diesel combustion stationary motor. The emissions produced by diesel burning in the engine were captured by means of quantitative papers, used as filters. Impregnation into the filter papers was compared by DRS. Clean filters (without soot deposition) were used as diffuse reflectance internal standards; i.e., blank samples, DRS = 100% (Silva et al., 2011).

2 Results and discussion

2.1 Catalyst characterization

Nitrogen physisorption analysis (Fig. 1) revealed that deposition of CeO₂:ZnO onto cordierite changed the BET surface area slightly, but it did not affect the catalytic activity or the texture significantly. CeO₂:ZnO exhibited moderately high surface area, 28 m²/g and average pore size of 23.2 nm, for a type IV structure with an H3 hysteresis-loop, indicating a certain degree of mesoporosity.

We investigated the redox properties of selected samples by H₂-TPR and plotted the H₂ consumption profiles in Fig. 2, where the TCD signal is proportional to the amount of consumed H₂. H₂ consumption (730 μ mol/g) must be due to the reduction of Ce⁴⁺ and Zn²⁺ cations (Wang and Luo, 2008; Yao and Yao, 1984). The first peak, centred at around 370°C in the profile of CeO₂, refers to reduction of the Ce⁴⁺ layers; the second peak, centred at 670°C,

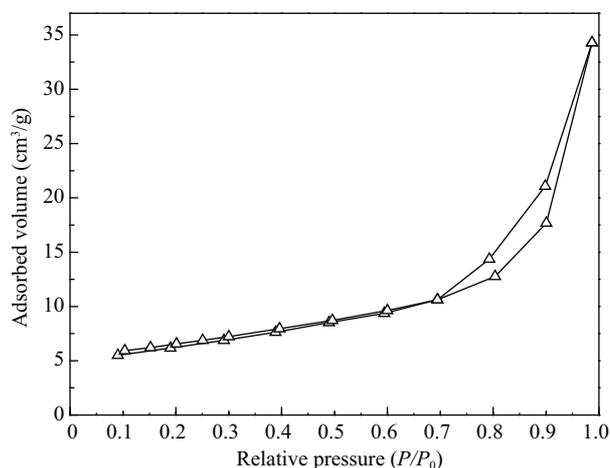


Fig. 1 CeO₂:ZnO nitrogen adsorption/desorption isotherms.

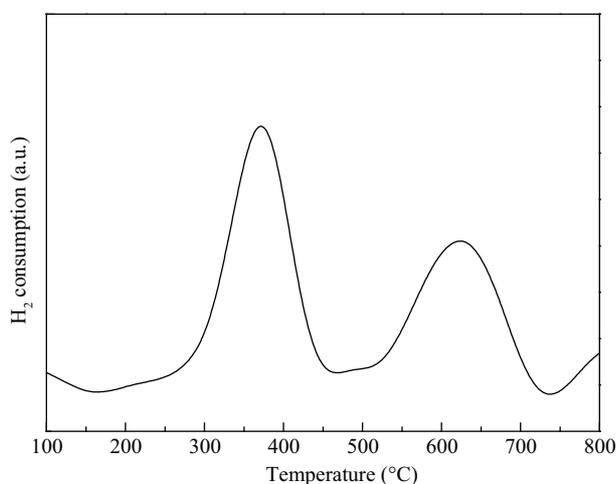


Fig. 2 Temperature-programmed reduction profile of the $\text{CeO}_2\text{:ZnO}$ catalyst.

corresponds to Zn^{2+} reduction, indicating that Ce^{4+} ions exist in the ZnO host and facilitate cerium reduction. This suggests enhanced oxygen mobility within the $\text{CeO}_2\text{:ZnO}$ lattice, with consequent creation of vacancies. A synergistic interaction between Ce and Zn in the mixed solid solution gives rise to low-temperature reduction (Wang et al., 2012). These results agree with the OSC data, which had demonstrated that $\text{CeO}_2\text{:ZnO}$ has higher oxygen storage capacity ($268 \mu\text{mol O/g}$ for OSC and $320 \mu\text{mol O/g}$ for OSCC). We also measured at 400°C for the catalyst. The storage capacities are expressed as $\mu\text{mol O/g}$, which corresponds to the amount of oxygen removed by reduction with CO, to produce CO_2 .

The XRD pattern of $\text{CeO}_2\text{:ZnO}$ calcined at 650°C (**Fig. 3**) shows of the reflections in detail: the narrow lines perfectly match the indexed CeO_2 cubic system, unit cell, and cubic face centered space group $\text{Fm}\bar{3}\text{m}$ (225), as well as the ZnO hexagonal system, primitive unit cell, and space group $\text{P}63\text{mc}$ (186) (Lima et

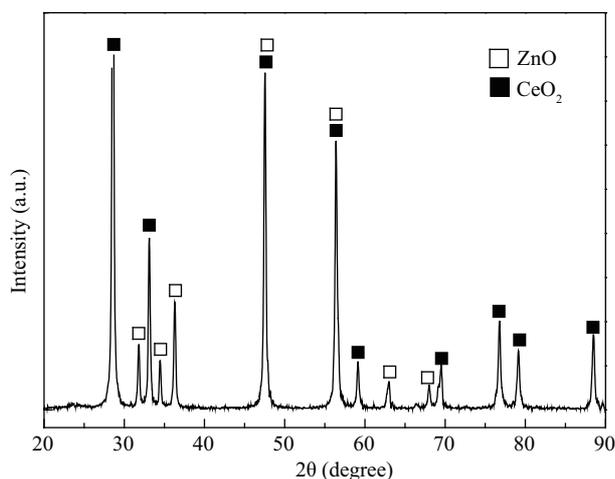


Fig. 3 X-ray diffractrogram of $\text{CeO}_2\text{:ZnO}$.

al., 2009). No peaks due to any other phases appear. Peaks associated with the hexagonal phase are also present, indicating that the ZnO host incorporated the Ce^{4+} ions.

The $\text{CeO}_2\text{:ZnO}$ particles display high aggregation degree, a consequence of the annealing process. The size of the ordered (crystalline) domains in the solid (27.9 nm) must be smaller than or equal to the grain sizes observed by electron microscopy, attesting to the nanostructure of the synthesized materials.

To evaluate the morphological properties of cordierite, we acquired SEM micrographs of this substrate. **Figure 4** depicts the SEM micrographs of the powder catalysts $\text{CeO}_2\text{:ZnO}$ (**Fig. 4a**) and $\text{CeO}_2\text{:ZnO}$ immobilized onto cordierite (**Fig. 4b**). We detected a large amount of monodisperse spherical particles on the surface of cordierite after we deposited $\text{CeO}_2\text{:ZnO}$ on the ceramic substrate (**Fig. 4b**). Moreover, the coated cordierite surface became less porous, and the entire sample surface was rougher.

The average diameter of the microspheres was $20\text{--}30 \text{ nm}$ for the $\text{CeO}_2\text{:ZnO}$ powder and $300\text{--}500 \text{ nm}$ for $\text{CeO}_2\text{:ZnO}$ anchored on cordierite. Higher magnification revealed that the spherical particles displayed rougher surface smaller crystallites bound together, to form the larger spheres. Therefore, according to crystallite size, each spherically shaped particle in the $\text{CeO}_2\text{:ZnO}$ system must consist of nanocrystallites measuring $20\text{--}30 \text{ nm}$. The particle size distribution was narrow.

UV-Vis diffuse reflectance spectroscopy (**Fig. 5**) helped estimate how the band gap energies of the $\text{CeO}_2\text{:ZnO}$ powder. Varied both samples presented low reflectance in the UV region, indicating high absorption; they also displayed high reflectance in the visible region, typical of lower absorption (**Fig. 5a**). To determine the band gap values, we plotted $(ah\nu)^2$ vs. $h\nu$ around the fundamental absorption region (**Fig. 5b**) (Santara et al., 2011). The high reflectance in the visible region and the low reflectance in the UV region clearly showed that the fundamental band gaps of both samples were fairly similar: 3.63 eV for $\text{CeO}_2\text{:ZnO}$. In the presence of increased carrier concentrations, the Fermi level shifts close to the conduction band, the energy transitions become unobstructed, and the band gap value decreases. This also agrees with the quantum confinement effect of the nanoparticles (Kumaran and Gopalakrishnan, 2012).

Raman spectroscopy of the $\text{CeO}_2\text{:ZnO}$ catalyst informed about crystallinity and structural defects (**Fig. 6**). The band at 460 cm^{-1} generally corresponds to the symmetric breathing mode F_{2g} of the oxygen atoms around Ce^{4+} ions, which resembles the active mode of the fluorite structure and corroborates that the synthesized materials have crystalline fluorite cubic structure. The low-intensity bands at ca. 250 and 588 cm^{-1} refer to oxygen vacancies (Laguna et al., 2011); the mode at 1180 cm^{-1} is due to LO phonon (**Fig. 6**, amplified). The ratio between the area of

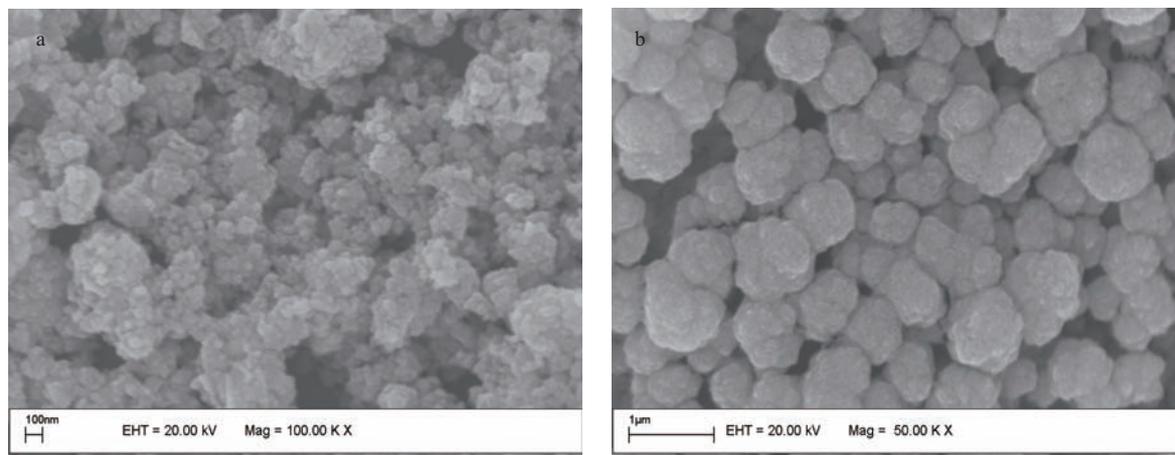


Fig. 4 SEM micrographs of the CeO₂:ZnO powder (a) and CeO₂:ZnO/cordierite (b).

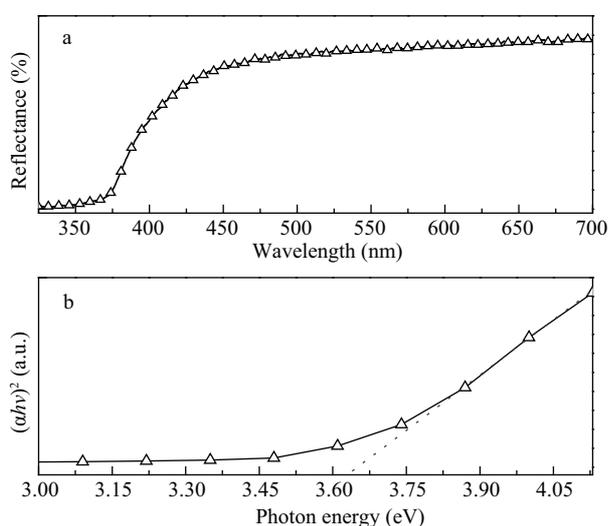


Fig. 5 (a) Reflectance UV-Vis spectra of the as-prepared CeO₂:ZnO, (b) band gap energy of the CeO₂:ZnO catalyst (powder).

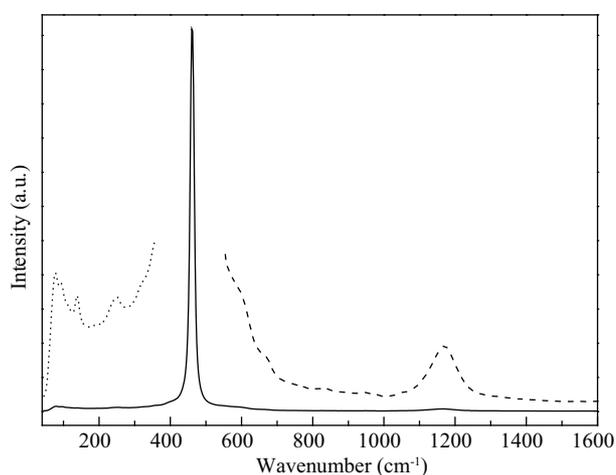


Fig. 6 Raman spectrum of CeO₂:ZnO (solid line) powder system and enlarged CeO₂:ZnO spectrum (dashed line).

the signal relative to the oxygen vacancies and the area of the F_{2g} signal is considered the most appropriate way to compare the population of oxygen vacancies in different solids (Hernández et al., 2009).

2.2 Catalytic activity

We investigated the catalytic combustion of soot over CeO₂:ZnO (Fig. 7) using Printex-U[®] as soot model in the loose contact conditions. The combustion temperature decreased to 430°C in the presence of CeO₂:ZnO; in the absence of this material, the process occurred at 620°C. And Table 1 summarizes the results from soot oxidation thermogravimetric analysis in the presence of CeO₂:ZnO.

The CeO₂:ZnO nanometric particles possess a special function in heterogeneous catalysis: only the outer surface can provide the active sites necessary for the catalytic reactions. The smaller the diameter of the surface particles on the catalyst surface, the larger the number of surface sites that the catalyst can provide, and the higher the

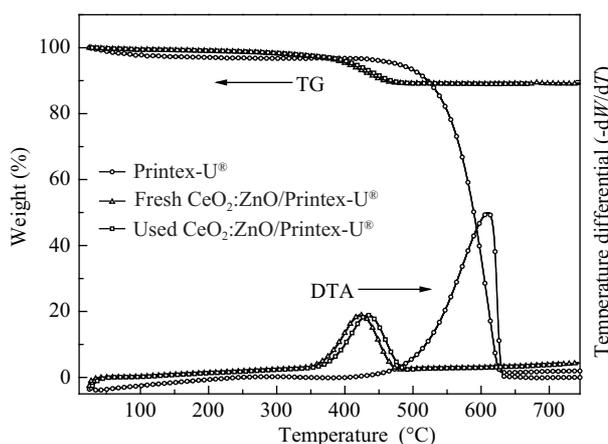


Fig. 7 TG/DTA of Printex-U[®], fresh CeO₂:ZnO/Printex-U[®], and used CeO₂:ZnO/Printex-U[®].

catalytic activity of the material. The well-dispersed Ru species on the surface of CeO₂:ZnO promote mobility of the active oxygen species, which are extremely reactive in oxidation reactions.

Table 1 CeO₂:ZnO catalytic performance in soot oxidation

Catalyst	T _i (°C)	T _c (°C)	T _f (°C)	ΔT (°C)
None ^a	480	610	640	160
CeO ₂ :ZnO (Fresh)	340	420	480	140
CeO ₂ :ZnO (Used)	345	434	486	141

^a Corresponding to Printex-U[®] oxidation without catalyst.

We assessed the catalytic performance of CeO₂:ZnO through dynamic tests comprising a diesel combustion stationary motor (Silva et al., 2011). This methodology is based on the principle of the Bosch method (Faiz et al., 1996). The exhausting gases and PM emission are directed to a filter paper, where the soot particles accumulate. The DRS of the paper is then read in an optical device such as a spectrometer. Once the amount of PM at the filter surface is proportional to its concentration in the effluent from the fuel combustion, the indirect measurement of its optical absorbance provides a comparative way of determining the soot concentration in the effluents. Hence, considering the clean filters as blank, larger amounts of soot should lead to higher absorbances and, consequently, to lower percentages of diffuse reflectance. **Figure 8** illustrates a typical DRS profile, which corresponds to the DRS of the filter exposed to the effluents of diesel combustion after passing through the interior of CeO₂:ZnO/cordierite.

The DRS of the filters impregnated with soot displayed the same profile, but CeO₂:ZnO reduced soot emission by about 70%. In other words, soot emission decreased in the following order: none > cordierite > CeO₂:ZnO.

Figure 9 represents a possible mechanism for soot oxidation over CeO₂:ZnO. First, gaseous O₂ is adsorbed on the surface of CeO₂ through a synergistic effect with the oxygen vacancies in ZnO:CeO₂, to form atomic oxygen species, the first active oxygen species (O*) to oxidize soot. These species migrate to the CeO₂:ZnO surface via

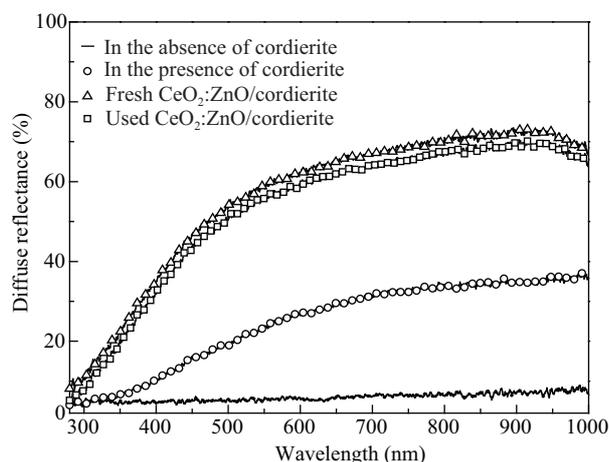


Fig. 8 DRS of the filters impregnated with soot upon combustion of diesel.

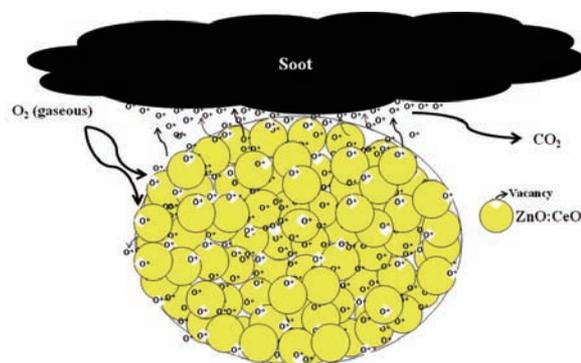


Fig. 9 Schematic soot oxidation by CeO₂:ZnO catalyst.

the interface, which is large and accelerates migration. The mobile active O* species on CeO₂:ZnO migrate to the surface of the soot particle through contact with the surface between the catalyst and the soot, oxidizing the latter to CO₂, which is finally released into the gas phase. The atomic oxygen species that are weakly adsorbed onto the CeO₂:ZnO surface desorb in the temperature range 300–400°C and function as active oxygen species for soot oxidation.

The presence, concentration, and mobility of lattice defects govern transport properties, such as oxygen diffusion (Yamazaki et al., 2011). The application of this type of materials, even in the nanometer range, will depend on these transport properties, which are also believed to play a key role in catalysis.

3 Conclusions

We synthesized CeO₂:ZnO nanopowder systems by a non-alkoxide sol-gel procedure and proved that they effectively diminish the soot combustion temperature. This simple inexpensive method provides ultrafine particles with the desirable characteristics. The resulting mixed oxide CeO₂:ZnO displays a bicrystalline phase consisting of wurtzite ZnO and cubic phase CeO₂. SEM analysis showed that the particles are spherical, with sizes ranging from 100 to 300 nm. The specific surface area and the redox properties of the solids affect the catalytic reactivity. Coexistence of Ce³⁺ and Ce⁴⁺ on the surface of the CeO₂:ZnO materials further contributes to the catalytic ability. The main advantage of the catalyst is that active oxygen can store both ceria, and the catalytic activity is related to the number of vacant oxygen lattice sites. Ceramics modified with CeO₂:ZnO can reduce soot emission during diesel burning in a stationary diesel motor.

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