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DIESEL/BIODIESEL SOOT OXIDATION WITH CeO_2 AND CeO_2-ZrO_2-MODIFIED CORDIERITES: A FACILE WAY OF ACCOUNTING FOR THEIR CATALYTIC ABILITY IN FUEL COMBUSTION PROCESSES

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CeO_2 and mixed CeO_2-ZrO_2 nanopowders were synthesized and efficiently deposited onto cordierite substrates, with the evaluation of their morphologic and structural properties through XRD, SEM, and FTIR. The modified substrates were employed as outer heterogeneous catalysts for reducing the soot originated from the diesel and diesel/biodiesel blends incomplete combustion. Their activity was evaluated in a diesel stationary motor, and a comparative analysis of the soot emission was carried out through diffuse reflectance spectroscopy. The analyses have shown that the catalyst-impregnated cordierite samples are very efficient for soot oxidation, being capable of reducing the soot emission in more than 60%.

Keywords: ceria-zirconia catalysts; diesel/biodiesel soot; automotive catalysis.

INTRODUCTION

Nowadays, a large number of urban centers suffer from the effects due to the air pollution, which results mainly from the fossil fuel burning, as in the case of mineral coal and petroleum derivatives (gasoline and diesel) combustion.[1] These two feedstocks are responsible for generating the energy that moves the electrical, industrial and transport sectors, which comprise a large part of the world economy. In particular, the current widespread use of diesel can be explained by its energetic efficiency compared with other fuels, durability of engines, and its relatively low cost in some countries.[2]

Nevertheless, the well-known environmental problems associated to non-renewable fuels has stimulated scientists around the world to substitute them and to develop sustainable technological processes. In this context, bio-fuels appear as a viable alternative to the substances commonly employed in the industry and in the transport sector, notably to diesel.[3,4] Thus, the partial or complete replacement of diesel by biodiesel means to deliver sustainability, once the biodiesel production is viable, its use is environmentally advantageous compared with diesel, it promotes the creation of new job vacancies, and leads to high energy yields.[4]

Even in the situations where biodiesel replaces large volumes of diesel in the fuel composition (percentages as high as 40% in some countries), some environmental effects still must be carefully evaluated. For example, it is well known that the particulate matter (PM) generated from diesel/biodiesel combustions is highly toxic and has been classified as probably carcinogenic to humans.[5,6] The large degree of soot generation is due to the fact that the defining feature of the diesel engine is the use of compression ignition to burn the fuel. So, a high level of incomplete diesel/biodiesel combustion occurs, thus producing undesirable byproducts such as nitrogen oxides, carbon monoxide, aromatic polycyclic hydrocarbons, as well as large amounts of PM.[7]

Due to the strictness of the laws regarding the reduction of soot emission by vehicles, there is a tendency for the technological update of more efficient engines, improvement of the fuel characteristics, and treatments aiming at reducing the emissions of air pollutants.[8,9] In this context, cerium compounds (mainly cerium(IV) oxide and its precursors) have gained importance since they participate in several catalytic reactions, especially those concerning the reduction of automobile exhaust emissions. The growing interest in cerium stems from its redox properties, its high oxygen mobility, and its ability to thermally stabilize the catalytic substrates,[10-13] which is applied, for example, in the widely diffused three-way catalysts (TWC).[14] The role of the catalytic converters is to eliminate the gases generated from the incomplete combustion of the fuel in explosion engines (alcohol or gasoline) or compression (diesel) by converting them into less aggressive substances.[15] In compression engines with an oscillating air/fuel ratio, CeO_2 favors the transformation of products arising from the incomplete fuel burning because it is capable of releasing and absorbing O_2 during these oscillations.[10,13,16,17]

Thus, aiming at the development of anti-pollution processes, two cerium-based catalysts in the oxide form (CeO_2 and CeO_2-ZrO_2) were synthesized and deposited onto ceramic substrates made of cordierite. These catalysts were then used to control the emission of PM formed during the burning of diesel and diesel/biodiesel blends in a stationary engine, and a subsequent comparative evaluation of the degree of soot emission through diffuse reflectance spectroscopy was performed.

EXPERIMENTAL

Catalyst preparation

Firstly, 0.10 mol L^{-1} $Ce(NO_3)_3$ and $ZrO(NO_3)_2$ stock solutions were prepared by dissolving appropriate amounts of cerium(IV) oxide (99.995%, Aldrich) and zirconium(IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$, >99.0% Riedel de Haën) in concentrated nitric acid under mild heating. In the case of the $Ce(NO_3)_3$ solution, hydrogen peroxide (30% v. solution) was eventually added in order to promote the Ce^{4+}/Ce^{3+} reduction. The pH of the solutions was adjusted to ~3.5 through evaporation of the excess acid.

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The mixed cerium(IV)-zirconium(IV) oxides were formed by adding appropriate volumes of the $Ce(NO_3)_3$ and $ZrO(NO_3)_2$ solutions (Ce^{3+}/ZrO^{2+}=1:1) to another solution containing ammonium hydroxide (25 wt.%), hydrogen peroxide (30 wt.%), and deionized water in a 4:1:4 (v/v) ratio. The mixture was kept under vigorous stirring at ambient conditions for 7 h. The resulting yellowish suspension was filtered and the solid was dried at 80 °C for 24 h. Finally, the obtained powder was post-annealed at 550 °C in air for 3 h to yield the final mixed catalyst.[18]

The cordierite ceramic substrates ($5SiO_2.2Al_2O_3.2MgO$, kindly provided by Umicore®, Brazil) were modified through CeO_2 and CeO_2-ZrO_2 deposition. For the catalytic tests, the substrates were cut so that cylindrical shapes measuring 3.5 cm in height and 2.5 cm in diameter were obtained. The deposition was performed by immersing the ceramic substrate into a 0.10 mol L^{-1} cerium(III) nitrate solution (or a mixture of cerium(III) and zirconyl nitrates, 0.10 mol L^{-1}, Ce^{3+}/ZrO^{2+}=1:1) at 50 °C for 5 min. Next, the substrate was heated at 550 ºC for 15 min; this procedure was repeated five times. The mass of catalyst adhered to the monolith after the impregnation procedure was gravimetrically determined for each preparation; for this, previously dried cordierite samples (in vacuum in a desicator over silica) were weighed before and after the impregnation procedure. The loaded amounts of catalyst varied around 10% in mass with relation to the initial mass of the substrate.

Catalyst characterization

The structural characterization of the catalysts (powder and modified cordierite) was accomplished by using a Siemens D5005 X-ray diffractometer (XRD) operating with a copper tube (Cu-K_α radiation, 1.541 Å) under a 40 kV voltage and 30 mA current. The scan speed was 2° min^{-1}, and the 2θ values ranged from 20° to 90°. The morphology and particle size of the formed materials were examined by scanning electron microscopy (SEM). The micrographs were acquired on a Zeiss EVO50 equipment, coupled to a 500 digital processing accessory (IXRF Systems) for the obtainment of the energy-dispersive X-ray (EDX) spectra. For the image acquisition, the samples were coated with a thin gold layer by means of a Bal-Tec SCD 050 sputter coater. Nitrogen adsorption data were obtained on a Quantachrome Nova 2200 analyzer, using a liquid nitrogen bath (77 K) and high purity nitrogen as adsorbate and applying the BET equation for the calculations. The samples were previously dried under vacuum at ~150 °C in an Abderhalden drying pistol.

The catalytic ability was evaluated through dynamic tests comprising diesel/biodiesel blend combustion in a Branco BD-5.0H diesel stationary motor coupled to a Branco B4T-2500 generator, operating under maximum acceleration at a 1500 W output level. The diesel used in all the experiments was provided by the Petrobras Petroleum Terminal of Ribeirão Preto, and the biodiesel used in the preparation of the blends (obtained through methanolic transesterification of soybean oil)[19] was provided by the Materials and Fuels Laboratory (Institute of Chemistry, University of Brasília). The B2, B5, B10, B20, and B50 fuels were then obtained by mixing biodiesel with diesel at biodiesel percentages of 2, 5, 10, 20, and 50% (vol./vol.), respectively, under constant stirring at room temperature for 1 h.

For the tests, impregnated cordierite substrates were held in an appropriated support placed on the base of the escape tube. For the filtering system to be assembled, an aluminum cylindrical tube (50 cm length, 8 cm internal diameter) was fixed to the escape tube. The emissions produced by the fuel burning in the engine were captured by employing quantitative papers (80 g m^{-2}, 3 cm diameter) as filters, which were held on the upper part of the cylindrical tube by a steel ring (Figure 1).

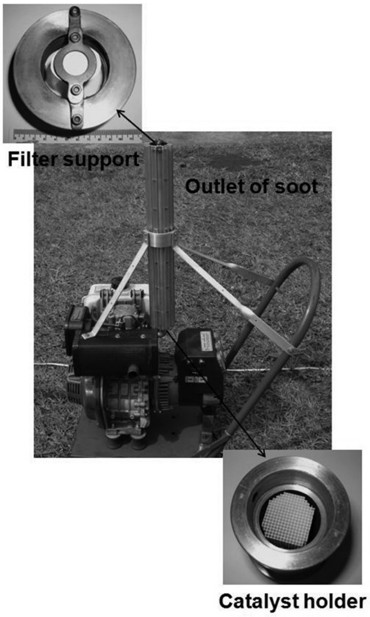

Figure 1. *Modified homemade diesel stationary motor*

The volume of fuel introduced in the engine reservoir was 0.5 L. After the engine was started, the filter papers were substituted in 10 min intervals, until complete triplicate samplings for each analysis were obtained. Impregnation into the filter papers was compared through diffuse reflectance (DR) spectroscopy.[10,20-24] The measurements were performed with an Ocean Optics USB4000 spectrometer, equipped with an R400-7-VIS/NIR reflection/backscattering probe (400 µm core diameter optical fiber) and with a LS-1 tungsten-halogen lamp as source. The DR spectra were recorded in the 400-800 nm range, with a 100 ms integration time and 0.5 cm of distance from the samples to the probe, which is kept at 90° in relation to the sample surface (backscattering geometry). Clean filters (without soot deposition) were used as internal standards of diffuse reflectance (i.e., blank samples, DR=100%) in all of the cases. The values of the integrated areas under the DR spectra in the visible range were taken for comparison of the soot emission in the presence of the cordierite samples.

RESULTS AND DISCUSSION

Figure 2 shows the obtained diffractograms of the dry filtered compound, resulting from the mixtures of the cerium(III) and zirconyl nitrates in basic medium, and the same compounds after the heat treatment at 550 °C. The diffractogram of the thermally treated compound displays the characteristic (111), (200), (220), (311), (400), (331), and (420) reflections of the face centered cubic fluorite-type structure ($Fm\overline{3}m$, O_h^5 space group) of CeO_2 (JCPDS 34-0394), as well as the (101), (110), (112), and (211) peaks related to the ZrO_2 tetragonal phase (JCPDS 79-1764, $P4_2/nmc$, D_{4h}^{15} space group). The diffractogram of the initial compound shows that both the oxide phases were already present before the heat treatment.[18,24] In this way, the ZrO_2 tetragonal structure, which is relatively unstable at ambient conditions due to a favorable conversion to the $P2_1/c$ monoclinic phase, can be obtained even with a low temperature annealing, as a result of the stabilizing action of the Ce^{4+} ions.[13] The occurrence of a stable tetragonal phase corroborates the coexistence of a cubic CeO_2 phase and a tetragonal $Zr_xCe_{1-x}O_2$ phase, thus enabling the presence of Ce-O-Zr bonds that increase the oxygen storage capacity of the solid.[13,25] The mean crystallite size for the synthesized powder was estimated through the Debye-Scherrer method by applying the $T= K\ \lambda\ (\beta_{1/2}\ \cos\theta)^{-1}$ relation, in which λ is the X-ray wavelength, θ is the considered Bragg diffraction peak, $\beta_{1/2}$ is the half-height peak width, and K is the shape parameter (considered to be equal to 0.9). Considering the peaks of the cubic phase as well as those of the tetragonal phase, the determined crystallite size for this sample was around 15-20 nm. This corresponds to the size of the ordered (crystalline) domains in the solid, which must be smaller or equal to the grain sizes that are observable by microscopy techniques, thus attesting for the nanostructural character of the synthesized catalyst. The CeO_2-ZrO_2 powder samples are built up of spherical particles, with grain diameters ranging from 50 to 100 nm. The particles show a very high degree of aggregation, which is a consequence of the annealing process to which the solid was submitted.

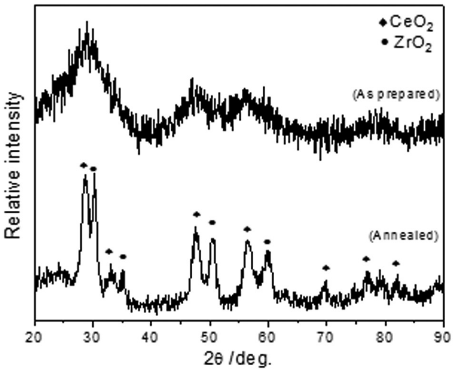

Figure 2. *X-ray diffraction patterns of the CeO_2-ZrO_2 after filtration/drying and after the heat treatment at 550 ºC*

In order to evaluate the morphological properties of the "native" cordierite substrate, SEM images of this solid were acquired. Figure 3, which depicts a photograph as well as four SEM micrographs of the cordierite substrate, attests that the material is very porous, although the specific area value estimated by the BET method is significantly low (4.4 $m^2\ g^{-1}$).

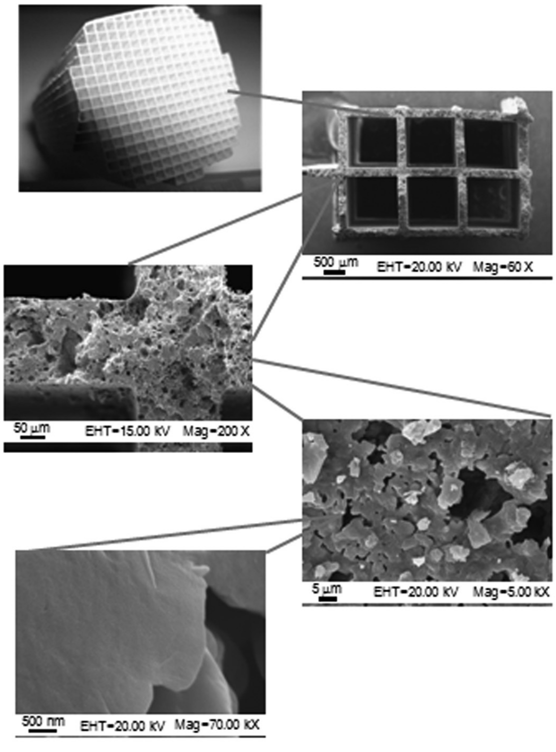

Figure 3. *Photograph and SEM images of the cordierite surface*

After the deposition of the oxide catalysts on the ceramic substrate, the SEM images obtained with different magnifications (Figure 4) reveal that the cordierite/CeO_2 surface becomes less porous, as well as the presence of cracks increases over the entire sample. In the case of the cordierite/CeO_2-ZrO_2 samples, the SEM images evidence a small amount of particles on the cordierite surface, which might be due to the migration of the oxide particles into the substrate bulk. Nevertheless, despite the SEM images show only few catalyst particles in the monolith surface, the impregnation of the catalyst in the cordierite structure in an appreciable extent is clearly attested by the X-ray diffractograms. Figure 5 depicts the XRD pattern of CeO_2- and CeO_2-ZrO_2-modified cordierites. In these cases, the Scherrer equation was not applied due to the superposition of diffraction peaks, so that the relation between the particle size and peak broadening is not straightforward. Moreover, for the CeO_2-ZrO_2-modified substrate, the peaks associated to the tetragonal phase are also present, thus indicating that the Ce^{4+} ions are incorporated in the ZrO_2 host as in the case of the pure mixed catalyst. In both modified samples, a high catalyst concentration in the cordierite (which is attested by the high relative intensities of CeO_2 or CeO_2-ZrO_2 characteristic

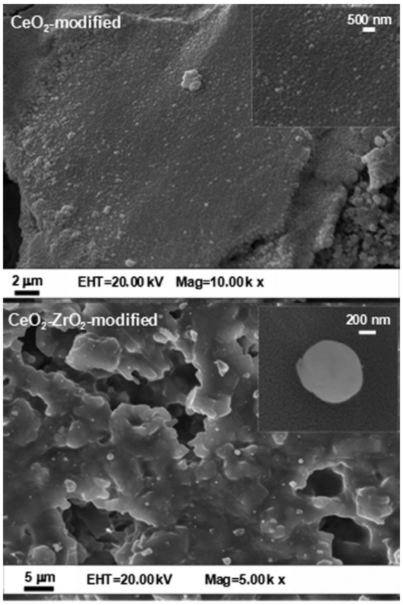

Figure 4. *SEM images of the cordierite/CeO_2 surface and cordierite/CeO_2-ZrO_2 surface*

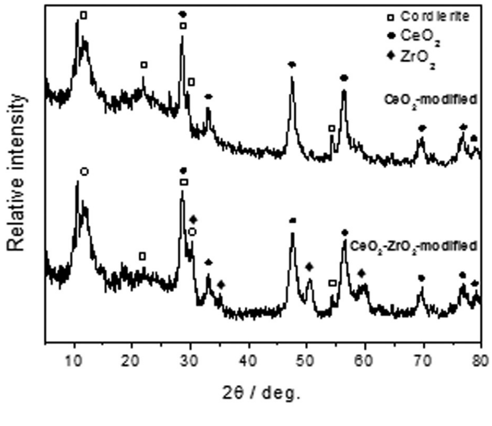

Figure 5. *X-ray diffractograms of the CeO_2-modified and CeO_2-ZrO_2-modified cordierites*

signals with regard to the cordierite signals in the XRD) is found, thus confirming that the simple immersion/annealing method leads to a very efficient impregnation.

The effective catalytic activity of the modified substrates on the reduction of diesel/biodiesel soot emissions was evaluated through diffuse reflectance experiments, which were carried out in order to compare unused filters with those containing soot produced in the operation of the stationary motor. This methodology, based in the principle of the Bosch method,[22] enables to by-pass the experimental difficulties of performing the usual gravimetric measurements since, after the proper soot collection, the comparative PM emission evaluation can be accomplished in few seconds, almost as in a spot-test. Once the amount of PM at the filter surface is proportional to its concentration in the effluents from the combustion of a fuel sample, the indirect measurement of its optical absorption (through DR, for example) provides a comparative way of determining its concentration in the effluents. Hence, by considering the clean filters as blanks, higher amounts of soot lead to higher absorbances and, consequently, to lower percentages of diffuse reflectance.[10,20-23] A typical DR spectra profile is depicted in Figure 6a, which corresponds to the DR spectrum of the filter exposed to the effluents of the combustion of B5 (after passing through the interior of the cordierite/CeO_2 substrate. A comparative analysis of the soot emitted by many samples can be accomplished by considering either fixed wavelengths (commonly 550 and 650 nm) or the integrated areas of the DR spectra. The last approach seems to be more adequate to the present cases, once, as the fuel composition is not constant, the soot composition can be slightly altered from one sample to another, thus leading to small fluctuations in the DR values; such effect can be eliminated by taking into account the integrated area values. Figure 6b illustrates the integrated area values obtained from the DR spectra (400-750 nm range) of the filters after combustion of diesel and the B2, B5, B10, B20 and B50 blends in the absence of cordierite, with a non-modified monolith, or in the presence of cordierite/CeO_2 or cordierite/CeO_2-ZrO_2. Smaller integrated areas correspond to lower diffuse reflectances, which can be interpreted as higher degrees of soot emission. The mean error in the application of the integrated area of the DR spectra in the 400-750 nm range for soot emission comparison was ~13%, which is coherent with the reported results.[10,23] In this sense, one can conclude that the soot emission decreases in the following order: absence of cordierite > cordierite/CeO_2-ZrO_2 > cordierite/CeO_2. The more effective action of the CeO_2-modified cordierite can be related to the higher level of exposition of the deposited ceria nanoparticles at the support surface, which results in a more effective contact of the fuel effluents with the catalyst oxide. In the CeO_2-ZrO_2 case, as already mentioned, the impregnation procedure leads to a particle migration into the substrate bulk, thus decreasing the effective contact of the catalyst with the emitted soot; this results in a lower catalytic efficiency for this material with regard to the CeO_2-modified cordierite. In summary, the presence of the cordierite/CeO_2 catalyst reduces soot emission in more than 60%. It is also noteworthy that this catalyst leads to effective soot reduction for all diesel/biodiesel blends.

CONCLUSIONS

The CeO_2-ZrO_2 mixed oxide synthesized in this work showed to have small particles with a mean size of 50 nm and well-defined diffraction patterns. Also, the two modified ceramics cordierite/CeO_2 and cordierite/CeO_2-ZrO_2 were successfully prepared and tested for the reduction of soot emission produced by the burning of diesel and diesel/biodiesel blends (B2, B5, B10, B20 e B50) in a stationary diesel motor. The best results were seen for the cordierite/CeO_2 substrate. Moreover, the simple system proposed here for collection and comparative measurement of soot from automotive emissions proved to be quite efficient.

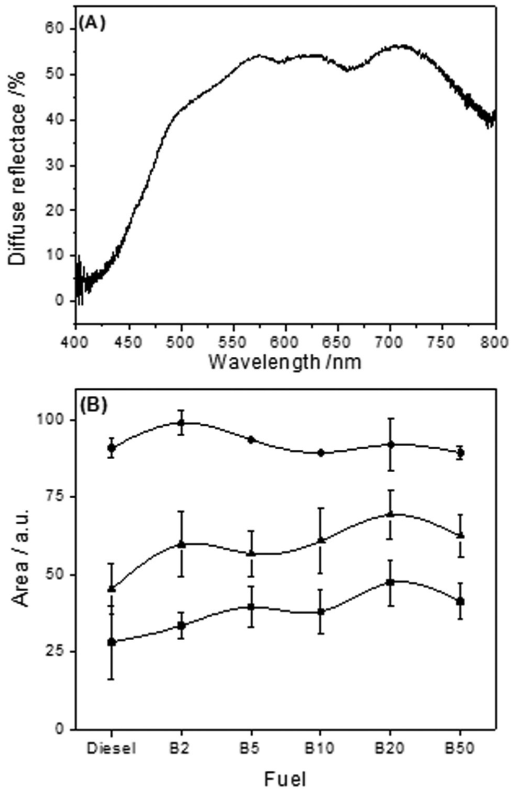

Figure 6. *(A) DR spectrum of the filter containing the emission products of the combustion of B5 (after passing through the cordierite/CeO_2 substrate). (B) integrated area values obtained from the DR spectra of the filters exposed to the combustions of diesel and the B2, B5, B10, B20 and B50 blends in the absence of cordierite (−■−), in the presence of cordierite/CeO_2-ZrO_2 (−▲−) and in the presence of cordierite/CeO_2 (−●−)*

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