



Potassium-promoted $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ monolithic catalysts for diesel soot combustion



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HIGHLIGHTS

- Diesel soot combustion over $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ catalysts is reported.
- $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ deactivation was observed after ten cycles of soot combustion.
- XRD diffractograms of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ determined the Zr insertion into CeO_2 structure.
- Domains enriched in Ce or Zr were determined in $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ by SEM/EPMA/Raman.
- Number of Ce surface atoms could be as important as the Zr presence for soot oxidation.

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ABSTRACT

This work presents a comparative study of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ and CeO_2 catalysts supported on cordierite for soot combustion, and the effect of potassium on the catalytic performance. The catalysts were prepared by sequential impregnation over the monolith. The activity in the soot combustion by O_2 was studied by successive temperature programmed oxidation cycles, using a loose-contact mode between the soot and the catalyst. A deactivation was observed after ten cycles of combustion for potassium catalysts. This deactivation was attributed to potassium loss at high temperatures. On the other hand, the catalysts without K showed activation after the ten soot combustions. When catalysts with the same cerium molar loading were compared, an improvement in the activity of the mixed oxide compared with the pure ceria was observed. The soot combustion was improved for $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ and $\text{K}/\text{CeO}_2/\text{cordierite}$ with NO/O_2 presence. However, the catalyst $\text{K}/\text{CeO}_2/\text{cordierite}$ was still more active. By X-ray diffraction analyses, it was found that insertion of zirconium into the CeO_2 structure took place during preparation. However, a Raman and SEM/EPMA studies indicated heterogeneity in $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$. Domains of cerium–zirconium inside the cordierite channel with a ratio different from the nominal value were observed by scanning electron microscopy analyses. This heterogeneity could decrease the catalytic activity of the cerium–zirconium oxide mixture. The catalytic activity in supported catalysts strongly depends on the effect of Zr, the number of $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox surface sites, the BET area and the structural changes induced by high temperatures.

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1. Introduction

Different alternatives have been studied in order to reduce particulate emissions from diesel engines and reach the maximum limits of established regulations [1–5]. Among the proposed alternatives, the entrapment of soot from exhaust gases by a diesel particulate filter (DPF) is the one most extensively studied. The problem of trapped soot is that the onset temperature for combustion is very high (above 500 °C). Due to the fact that the

temperature of diesel exhaust gases is generally between 150 and 400 °C, a spontaneous DPF regeneration cannot occur without a catalyst. This catalyst must be efficient and thermally stable in order to regenerate the filter continuously, thus avoiding an increment in the pressure drop that could lead to an engine failure. A large number of catalytic formulations have been tested for the combustion of diesel soot, such as perovskites, base metal oxides (V, Cu, Mn, Cr, Fe, Mo, etc.) and noble metals [6–10]. In our research group, the K/CeO_2 powder catalyst has been extensively analyzed [11–16]. Potassium acts as a molten salt with the ability of improving catalyst–soot contact by increasing surface mobility, in this way favoring the contact with soot and increasing the surface mobility

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of oxygen species formed in the K compounds [11,12,16,17]. However, the poor thermal stability of potassium restricts its application, since evaporation temperature is low and this might lead to K loss at high temperatures. The catalyst based on cerium oxide improves soot combustion due to its high availability of surface oxygen and high surface reducibility ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$) [11,16,18]. It has been reported that the catalytic reaction involves a redox mechanism where oxygen from the catalyst surface is transferred to the soot by contact points in a typical reduction/oxidation mechanism, with a partial reduction of catalyst. The resulting oxygen defects of the catalyst surface are refilled either by surface migration and final re-oxidation by gas-phase oxygen, respectively, or by diffusing bulk oxygen. The oxygen deficiency of the lattice is balanced by migration of oxygen from the surface or sub-surface to the bulk of the catalyst [18,19]. The incorporation of elements like Zr^{4+} into the CeO_2 lattice strongly affects the redox properties of ceria by increasing its oxygen storage capacity, increasing the movement of bulk oxygen [20,21]. Zirconium also improves the thermal stability of CeO_2 [18,21]. In the $\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ powder oxides, the highest activity for soot combustion has been obtained with cerium-rich mixtures [20,23–25]. In these samples, the surface redox cycle $\text{Ce}^{4+}/\text{Ce}^{3+}$ occurs at low temperature faster than in the case of ceria and consequently, these solid solutions have a better ability to donate oxygen for soot oxidation. On the other hand, ZrO_2 is reported to show moderate catalytic activity for soot combustion [20,23–25]. The $\text{K}/\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ powder catalyst was studied for soot combustion by Wu et al. [26]. These authors determined a synergetic effect between ceria–zirconia oxide and potassium nitrate in 7 wt.% $\text{K}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, which decreased the combustion temperature compared to K/CeO_2 and K/ZrO_2 catalysts, in tight and loose contact. This improved activity was also observed even in a sample aged at 800 °C for 24 h. According to these results, it seems that potassium stabilizes on the $\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ support. It is important to consider that according to literature [23], the preparation method of $\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ leads to oxides with different physicochemical properties and structure that could affect the catalytic activity. Likewise, the different experimental conditions used in the soot combustion reaction lead to different results; therefore, the activity of catalysts in the soot combustion reaction is difficult to be compared.

On the other hand, the contact between the catalyst and soot markedly influences the reaction kinetics [6]. Although the loose contact between catalyst and soot presents higher combustion temperatures than the tight contact, the first one can simulate real conditions of filter traps in diesel engines.

In the specialized literature, there are few publications related to the activity of K/CeO_2 supported on a porous filter [27], but none about the supported $\text{K}/\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ catalyst. However, a few patents related to catalytic filters for soot oxidation, containing cerium–zirconium mixed oxide and/or potassium have been reported [28–30].

The aim of the present work was to study the $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ catalyst supported on a cordierite monolith. Cordierite is considered a good support due to its high melting point, high temperature and thermal shock resistance, as well as to its high chemical stability. Although this support does not have the same configuration as the DPF (wall flow), it is useful to compare the activity of different supported catalysts under loose contact with soot [27]. The activity for soot combustion of $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ was compared with a $\text{K}/\text{CeO}_2/\text{cordierite}$ catalyst with similar potassium and oxide loadings. The potassium was added using KNO_3 . This work reports the effect of several cycles of soot oxidation carried out with O_2 over the supported catalysts. Since the real diesel engine could reach very high temperatures during operation, the activity of the samples in soot combustion with O_2 was also studied after ageing treatments at 800 °C. Besides, the soot combustion activity was studied

with a gas mixture containing NO. It is known that the presence of NO_x presence favours the combustion activity at much lower temperatures than molecular oxygen. According to Southward and Basso [31], the NO_2 initiates the soot oxidation and there is a competition with the direct catalytic soot oxidation. In this work, the comparison of the activity of different samples in the absence and presence of NO was carried out.

The structured catalysts were characterized by X-ray diffraction (XRD), BET area analysis, optical microscopy (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Besides, the mixed oxide powder was characterized by BET area analysis, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

2. Experimental

2.1. Structured catalysts preparation

A cordierite ($2\text{MgO}:2\text{Al}_2\text{O}_3:5\text{SiO}_2$) honeycomb monolith (Corning), with 400 cps and 0.17 mm average wall thickness, was used as structured support. The apparent monolith density and its geometric surface were 0.42 g/cm^3 and $27.4 \text{ cm}^2/\text{cm}^3$, respectively. Portions of cordierite containing 12 channels were cut with a stainless steel cutter and used as support monoliths in the preparation, with dimensions of $0.45 \text{ cm} \times 0.6 \text{ cm}$ of section and length of 1.2 cm. Before use, the monoliths were washed 3 times with ethanol and calcined at 500 °C for 2 h.

The cerium–zirconia mixed oxide was prepared by the sol–gel modified method, by adding an aqueous solution of $\text{Ce}(\text{NO}_3)_3$ to a solution of $\text{Zr}(\text{OC}_3\text{H}_7)_4$ (70% in propanol) in 20 ml of isopropyl alcohol [32]. This mixture was dried at 120 °C overnight and finally calcined during 3 h at 700 °C. According to the precursor concentrations, the nominal composition of the mixed oxide was $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$. One monolithic sample was divided in various portions and they were impregnated with the slurry, showing reproducible activity results.

The cerium and cerium–zirconium oxides were fixed to the ceramic support by successive immersions of cordierite monoliths in aqueous suspensions of CeO_2 (Aldrich) or $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$, containing 0.13 g/ml and 0.12 g/ml, respectively. The immersions were done at ambient temperature while stirring the suspension. After each immersion, the solution excess contained in the channels was blown with N_2 , and then the samples were calcined at 700 °C for 1 h. Successive impregnations were done to obtain oxide loadings of 0.01 g.

The mechanical stability of the oxide film deposited on the monolith, as described in Section 2.2, was performed to all the CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ catalysts. After this test, some samples were impregnated with potassium by immersion in aqueous solutions of 0.02 g/ml KNO_3 (Anedra, analytic reagent) at ambient temperature under stirring. The solution excess was blown with N_2 and dried in a stove. At the final potassium concentration, the samples were calcined at 400 °C for 2 h.

During the CeO_2 , $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ and K impregnation on the cordierite monoliths, the loadings were determined by gravimetric difference.

2.2. Coating adherence test

The adherence of ceria and ceria–zirconia coating on monoliths was evaluated by exposing the samples to ultrasonic waves at ambient temperature [33,34]. The coated monoliths were immersed in acetone inside a glass vessel, which was placed in an ultrasonic bath (Testlab TB04, 40 kHz and 160 W) for 1 h. After this treatment, the samples were dried overnight at 120 °C. The

measurement of the weight loss indicates the adherence to the cordierite support of the CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ coating.

2.3. Soot catalytic combustion measurements

The soot was obtained by burning a sample of diesel fuel in a glass vessel by Bunsen burner. After being collected from the vessel walls, the soot was dried in a stove at approximately 120 °C during 24 h and milled in a mortar. A soluble organic fraction of soot (SOF) was obtained by two methods: (i) heating 20.8 mg of sample at 500 °C in N_2 and weighing the remaining material [35] and (ii) by analyzing 122 mg by Soxhlet method with toluene as solvent [36]. Also, the ash of soot was determined after calcination of 0.723 g of sample at 750 °C. In this way, an average of 9.2 wt.% of SOF and 0.13 wt.% of ash were determined, being the remaining solid composed mostly by dry soot.

The structured catalysts were impregnated with soot by immersion during a second into a methanol suspension of 7 g/L, under vigorous stirring. After each impregnation, the loading of soot was gravimetrically determined. The average soot loading, over a monolith catalyst that weighed approximately 0.15 g, was 1.22 mg (0.85 wt.% of total weight), with a maximum difference of 20%. A loose contact was obtained with this impregnation method [6].

2.3.1. Soot catalytic combustion by O_2

The activity of the structured samples for the soot combustion was studied by temperature-programmed oxidation (TPO) tests, using a gas mixture of 4% O_2 in N_2 , and a heating rate of 12 °C/min. A modified TPO technique was used [13,37]. The gases coming out from the reactor were introduced into a methanation reactor, where the CO , CO_2 and the hydrocarbons formed during the reaction were totally transformed to CH_4 by a Ni catalyst at 400 °C. The CH_4 was continuously measured by a FID detector. After the TPO analysis, the samples were impregnated with soot and a new cycle was performed. Several cycles of TPO were studied for each catalyst. The weight changes were determined after each impregnation and the final TPO.

The activities of CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powders (unsupported catalysts) were also analyzed in the soot oxidation reaction by TPO. The powder catalysts were mixed in loose and tight contact with soot, with a catalyst:soot mass ratio of 20:1. In the loose contact, the weighted solids were mixed in a vessel and shaken during 4 min. In the catalyst–soot tight contact, the mixture was placed in a mortar and was mechanically mixed for 6 min. The amount of sample loaded into the TPO reactor was 10 mg.

As reference, the combustion of 2.2 mg of soot without catalyst was studied in the same condition as catalytic reaction.

2.3.2. Soot catalytic combustion by NO/O_2

The activity of the structured samples was studied for the soot combustion with NO/O_2 and O_2 by temperature-programmed oxidation (TPO) with an oxygen concentration similar to that of the motor exhaust gases. For this purpose, the catalysts were heated at 5 °C min^{-1} from room temperature up to 600 °C in O_2 (18%) diluted in He balance (total flow 20 ml min^{-1}) in a flow equipment designed for this purpose. The effect of the NO presence was studied by feeding O_2 (18%) and NO (0.1%) diluted in He (total flow 20 ml min^{-1}) under the same test conditions. The exhaust gases were analyzed with a Shimadzu GC-2014 chromatograph with TCD detector.

2.4. Thermal stability test

The thermal stability was studied for two catalysts, $\text{K/CeO}_2/\text{cordierite}$ and $\text{K/Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$. The catalysts used in ten

TPO cycles were then exposed to an ageing treatment by calcination at 800 °C for 24 h, in an air stream at 12.2 mL/min . In all cases, the activity of the aged samples of $\text{K/CeO}_2/\text{cordierite}$ and $\text{K/Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ was analyzed by TPO analysis with O_2 , under the same conditions detailed in Section 2.3.1. After the thermal stability test, the final K concentration was determined by ICP.

2.5. Characterization

2.5.1. BET area

The surface area was determined with a Micromeritics Accusorb 2100 sorptometer using N_2 . The samples were previously degassed during 3 h at 300 °C.

2.5.2. X-ray diffraction (XRD)

The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with a monochromator using $\text{Cu K}\alpha$ radiation at a scan rate of 1°/min, with 2θ from 20° to 80°. For the XRD analysis of the supported catalysts, the monoliths were supported on the edge of an aluminum sample holder window. The powders used for the impregnation of cordierite were also studied using a conventional holder. The crystal sizes of the latter samples were determined by Scherrer's equation using the peak obtained at 2θ of 28°, with the wavelength of the radiation used (λ) of 0.154178 nm for $\text{Cu K}\alpha$ and a particle shape factor (K) of 0.94.

2.5.3. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA)

The sample morphology of the coatings over the cordierite support was examined by SEM with a Jeol JSM-35C scanning electron microscope operated at accelerating voltages of 20–25 kV. Samples were glued to the sample holder with Ag paint. Then, the CeO_2 sample was coated with a thin layer of Au in order to improve the quality of the images. For the sample containing zirconium, the coating was performed with C to avoid the interference between zirconium and gold peaks. The distribution of the chemical elements in the coating was analyzed by EPMA with X-ray spectra and EDAX software. Semiquantitative results were obtained with the theoretical quantitative method (SEMIQ), which does not require standards. X-ray spectra were obtained with an acceleration of 20 kV.

2.5.4. X-ray photoelectron spectroscopy (XPS)

The XPS analyses were performed in a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a monochromated Al $\text{K}\alpha$ X-ray source (300 W and 14 kV) with a pass-energy of 30 eV. The working pressure in the analyzing chamber was less than 5×10^{-10} kPa. The spectral Ce4d, Zr3d, O1s and C1s were recorded for the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder sample. The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions in a 70/30 ratio. For the quantification of the elements, we used the sensitivity factors provided by the manufacturer.

2.5.5. Laser Raman spectroscopy (LRS)

The Raman spectra of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder was recorded using a LabRam spectrometer (Horiba–Jobin–Yvon) coupled to an Olympus confocal microscope (a 100× objective lens was used for simultaneous illumination and collection), equipped with a CCD detector cooled to about –73 °C using the Peltier effect. The excitation wavelength was in all cases 532 nm (Spectra Physics diode pump solid state laser). The laser power was set at 30 mW.

2.5.6. Optical microscopy (OM)

The surface morphology of monolith catalysts was studied with a Leica S8 APO stereo-microscope equipped with a Leica LC3 digital camera and LAS EZ software.

3. Results and discussion

3.1. Catalysts composition

The nominal concentrations of the oxides CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$, and the mass ratio K/oxide of the prepared samples are presented in Table 1. The initial potassium, cerium and zirconium concentrations were not determined. It has to be kept in mind that in order to determine the concentrations by analytical tools, the supported catalysts should be destroyed.

The composition of the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder for the cordierite coating was studied by XPS. The atomic relative concentrations obtained by XPS were Ce4d 15.32, Zr3d 6.56, C1s 38.48 and O1s 39.65. The Ce/Zr surface ratio was calculated with Ce4d and Zr3d ratio because these peaks correspond to comparable photoionization energy and thus comparable analysis depth [38]. The Ce4d/Zr3d was 2.3 corresponding to $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$, while the nominal value for the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ oxide was 1.86. According to the literature, the surface XPS study could give a Ce/Zr ratio higher than the bulk [39,40].

3.2. Mechanical stability

After the CeO_2 or $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ fixation over the cordierite support, the coating adherences were studied by measuring the weight loss after 1 h of treatment in an ultrasonic bath. Considering all the samples of CeO_2 /cordierite and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ /cordierite, the average losses of the total weight were 4% and 20%, respectively. This indicates that CeO_2 has a higher adherence than the mixed oxide. The final concentrations of CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ over cordierite after coating adherence analyses are shown in Table 1. The adherence tests were useful for both measuring the mechanical stability and detaching the loosely adhered portions of catalyst.

3.3. Potassium promoted catalysts

After the adherence study of the oxide coating over CeO_2 /cordierite and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ /cordierite samples, KNO_3 was impregnated. Considering that in a previous work it was observed that the activity had a smooth maximum as a function of the K content, being around 7 wt.% for the K/ CeO_2 powder catalyst [12], the samples of K/ CeO_2 /cordierite and K/ $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ /cordierite were prepared with a K/oxide mass ratio of approximately 0.07. The potassium nominal concentrations were expressed as K/oxide mass ratio

Table 1

Catalysts compositions: nominal concentrations of ceria, ceria–zirconia oxide and potassium.

Catalyst	Oxide coating	Oxide loading (g)	K/oxide (wt/wt)
M1	$\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$	0.0134	0.092
M2	$\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$	0.0137	0.63
M3	CeO_2	0.0153	0.05
M4	$\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$	0.0111	–
M5	CeO_2	0.0154	–
M6	CeO_2	0.0108	0.074
M7	CeO_2	0.0085	–
M8	$\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$	0.0103	0.084
M9	CeO_2	0.0221	0.061
CeZr	Powder	–	–
CeO_2	Powder	–	–
Mc	–	–	–

(Table 1). The adherence of potassium was not studied by ultrasonic bath since in a previous work it was determined that the weight loss was very small [27].

3.4. BET area

The BET area was determined for powder oxides, bare cordierite and supported cordierite catalysts. The surface area determined for the CeO_2 and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder catalysts were 2 and 47.3 m^2/g . The surface area for cordierite was 0.5 m^2/g . However, the supported catalysts had a very low surface that could not be determined due to the lack of sensitivity of the equipment for the very low mass of catalyst contained on the monolith sample. These results indicated that the catalysts supported on the monolith had a lower surface area than the powder samples.

3.5. Catalytic activity in soot combustion by O_2

The activity behavior in soot combustion was studied by TPO analysis. The particulate matter obtained by diesel combustion consists mainly in soluble organic fraction (SOF), soot, ashes, sulfates and adsorbed water. The target materials to be catalytically removed are soot and SOF. The oxidation of soot is influenced by the coexisting SOF [41]. The SOF content was determined by Soxhlet method [36] and heating in N_2 at 500 °C [35]. The obtained results were 9.8% and 8.7%, respectively. The low SOF percentage assures that the main activity results correspond of soot. As mentioned in Section 2.3, the ashes content of soot was only 0.13%.

The structured catalysts were impregnated with soot by immersion in a soot-methanol suspension under vigorous stirring. With this procedure, the soot loading in loose contact with the structured catalysts was approximately 1 mg for all samples. We determined that this loading favors a combustion reaction in a kinetically controlled regime. This was verified by loading different amounts of soot, following the procedure described by Peralta et al. [15]. On the other hand, the soot loading method over the supported catalysts assures to be reproducible, avoiding different activity by different loading [31]. The performance of the catalysts was evaluated by taking the temperature corresponding to the maximum of the peak (T_{max}) and the temperatures for 50% of soot conversion ($T_{50\%}$) for the temperature programmed oxidation experiments.

Table 2

Maximum and half soot conversion temperatures (T_{max} and $T_{50\%}$ respectively) obtained during soot combustion by temperature programmed oxidation (TPO).

Samples	T_{max} (°C)		$T_{50\%}$ (°C)		Weight loss (%)
	1st TPO	10th TPO	1st TPO	10th TPO	
M1	440	535	435	493	2.0
M2	445	422	436	414	4.9
M3	436	499	448	472	1.9
M4	580	543	546	515	1.5
M5	550	519	521	483	0.2
M6	436	569	425	531	0.6
M7	579	566	556	543	0.1
M8	510	–	501	–	0.5
M9	512	–	487	–	0.4
CeZr	418 _{TC} /604 _{LC}	–	416 _{TC} /588 _{LC}	–	–
CeO_2	531 _{TC} /602 _{LC}	–	529 _{TC} /601 _{LC}	–	–
Mc	540	543	517	507	–
M1 aged	553	–	555	–	0.3 ^a
M3 aged	575	–	545	–	1.5 ^a
Soot	591	–	601	–	–

TC: soot-catalyst in tight contact; LC: soot-catalyst in loose contact.

^a Weight loss after ageing treatment of used catalysts.

The results of combustion by O₂ are shown in Table 2. The activity in soot combustion of samples of K/Ce_{0.65}Zr_{0.35}O₂/cordierite and K/CeO₂/cordierite were compared with their respective catalysts without potassium. The TPO profiles of the supported catalysts with Ce_{0.65}Zr_{0.35}O₂ and CeO₂ are shown in Figs. 1 and 2, respectively, for the first and tenth cycle of soot combustion. These results are reported in Table 2 along with the total weight loss of the catalysts after ten TPOs.

The soot combustion without catalyst was also analyzed. The T_{\max} and $T_{50\%}$ were 591 and 601 °C, respectively. These results are presented in Fig. 3 and Table 2, together with the soot combustion over cordierite (Mc).

3.5.1. Effect of potassium

In order to study the potassium loading effect on the activity of the K/Ce_{0.65}Zr_{0.35}O₂/cordierite catalyst, samples M1 and M2 were compared. These samples have a similar content of Ce_{0.65}Zr_{0.35}O₂ (0.0134 and 0.0137 g, respectively) and different potassium loading (K/Ce_{0.65}Zr_{0.35}O₂ mass ratio of 0.092 and 0.63, respectively). In other words, the concentration of potassium in the M2 sample was much higher than in M1. Table 2 shows that catalysts M1 and M2 had the same catalytic activity for T_{\max} in the first TPO analysis (440 and 445 °C, respectively). This behavior was also noticed for $T_{50\%}$ with 435 and 436 °C for catalysts M1 and M2. Fig. 1A shows the soot conversion as a function of temperature in the first cycle, obtained from the TPO profile. It can be observed that the curves corresponding to M1 and M2 are very similar. The

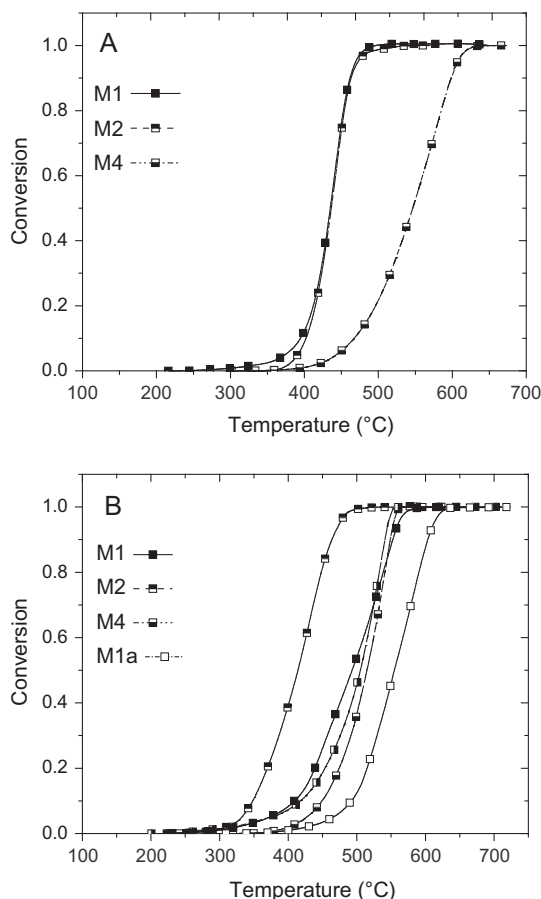


Fig. 1. Conversion profiles of soot combustion for K/Ce_{0.65}Zr_{0.35}O₂/cordierite (M1 and M2) and Ce_{0.65}Zr_{0.35}O₂/cordierite (M4) catalysts: (A) fresh catalysts and (B) catalysts after ten cycles of TPO; M1a: TPO of M1 catalyst after the ageing treatment.

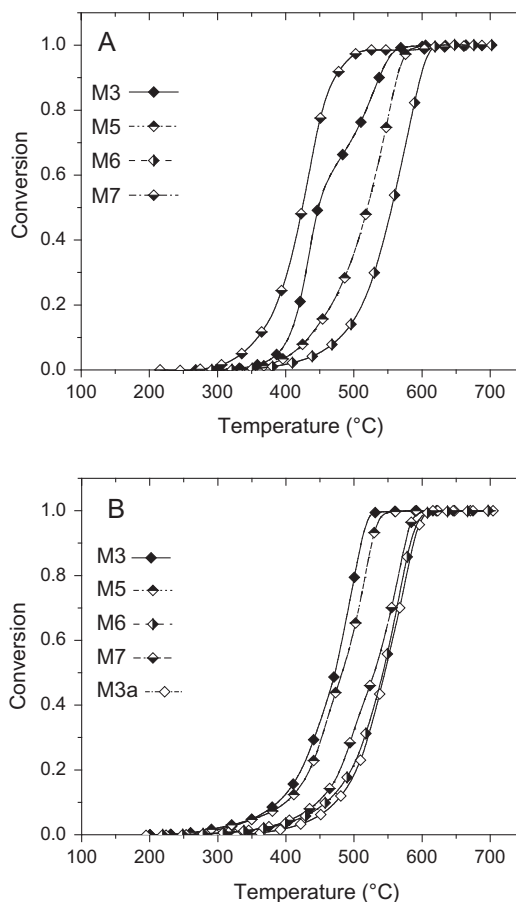


Fig. 2. Conversion profiles of soot combustion for K/CeO₂/cordierite (M3) and CeO₂/cordierite (M5, M6 and M7) catalysts: (A) fresh catalysts and (B) catalysts after ten cycles of TPO; M3a: TPO of M3 catalyst after the ageing treatment.

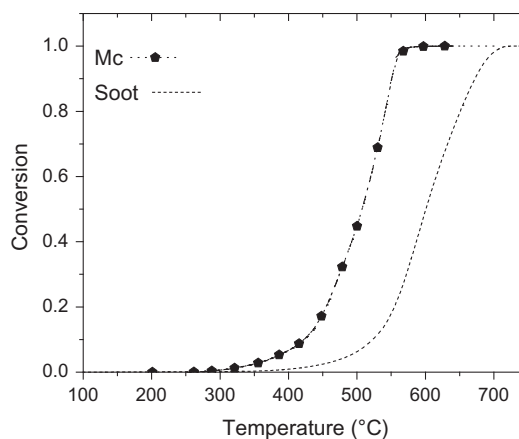


Fig. 3. Conversion profiles of uncatalyzed soot combustion and soot combustion over cordierite sample (Mc).

potassium concentration of M1 would be enough to produce a good contact between soot and the active sites in the first combustion since it burnt the soot at lower temperature than both M4 (Ce_{0.65}Zr_{0.35}O₂/cordierite catalyst without potassium) and the cordierite (Mc) (Table 2). After ten TPO cycles, a difference in the soot combustion activity was observed between the M1 and M2 samples (Table 2 and Fig. 1B). The T_{\max} for M1 was 535 °C while for M2 it was 422 °C. Besides, the $T_{50\%}$ for these catalysts were 493

and 414 °C, respectively. The difference between T_{\max} and $T_{50\%}$ obtained with sample M1 after ten TPO cycles indicates that the peak became broader as compared to the first TPO. According to the results, after ten TPO cycles, the M1 catalyst suffered a deactivation compared to the M2 sample. It can be deduced that a loss of potassium was produced in the M1 catalyst after several cycles of TPO combustion, mainly due to the high temperature used in these analysis, which was approximately 700 °C. The M2 catalyst could suffer a similar loss of potassium as M1, but due to its higher initial concentration, the activity was maintained for longer times. In other words, if a change in potassium loading was produced in the M2 sample, it did not affect the activity. However, it has to be considered that the potassium concentration in the M2 catalyst was very high. It is interesting to note that after several cycles of soot combustion, the M2 catalyst became a little more active ($T_{50\%}$ and T_{\max} in Table 2). This result suggests that a potassium concentration lower than the initial one, obtained after ten reaction cycles, could produce a more active catalyst. However, in powder catalysts, Peralta et al. [12] determined an optimum K/oxide mass ratio for K/CeO₂ samples of 0.07. In consequence, the optimum ratio could be different for structured catalysts.

All catalysts were calcined at 400 °C after potassium deposition. The treatment at 700 °C in the first TPO produces activation of M2 due to loss of potassium and a new distribution in the catalysts. This result was observed for samples M8 and M9, treated at 700 °C after KNO₃ impregnation, whose T_{\max} and $T_{50\%}$ for the first TPO were higher than the temperatures for M1 and M3 (Table 2). According with this result, the first TPO produce a decrease in K loading. The benefit of using 400 °C as the first catalyst treatment after KNO₃ impregnation is that the loading of potassium in the first TPO is similar to the nominal concentration.

In spite of a potassium loss produced at high temperatures, the potassium concentration in M2 was still in excess. In the M1 sample, the loss produced at high temperature was not compensated by the activation of the rest of potassium present in the catalyst. According to Table 2, the total weight loss of the catalysts after ten TPO was 2% in M1 while in M2 it was 4.9%. These values could represent the total K loading in both catalysts. However, taking into account that the catalytic activity of these samples after ten TPO cycles was still higher than the catalyst without potassium, the total loss of this promoter could be discarded.

3.5.2. Effect of mixed oxide

In order to analyze the possible improving effect in the soot catalytic combustion of ceria–zirconia oxide as coating, the M1 catalyst (K/Ce_{0.65}Zr_{0.35}O₂/cordierite) was compared with the M3 sample (K/CeO₂/cordierite), with similar oxide loading and K/oxide ratio. Similar T_{\max} temperatures were observed for both catalysts for the first TPO (440 and 436 °C for M1 and M3, respectively). On the other hand, the $T_{50\%}$ indicated that the conversion of half the soot loading was produced at higher temperature for M3 than for M1 (448 vs. 435 °C). After ten cycles of TPO, the T_{\max} and $T_{50\%}$ of the M1 sample were higher than in M3 (535 and 493 °C for M1 vs. 499 and 472 °C for M3). Considering the T_{\max} of the first TPO, the results are in agreement with the activity reported by Wu et al. [26] who found that K/Ce_{0.65}Zr_{0.35}O₂ powder catalyst had the same T_{\max} of K/CeO₂ for loose contact of soot-catalyst and samples previously calcined at 600 °C. Notably, the M3 sample was a little more active than M1 after several cycles of soot combustion. According to the final temperature of TPO experience, the results indicate that a loss of potassium during reaction cycles occurred in the K/oxide/cordierite samples, and that the M1 sample could lose more potassium than M3 after ten TPO cycles up to 700 °C. However, the total weight changes shown in Table 2 indicate that both catalysts (M3 and M1) had similar weight losses. These weight losses were 2% and 1.9% of the total weight for catalysts

M1 and M3, respectively. These values represented more than the total potassium loading. In consequence, the weight loss was due to both K sublimation and catalyst loss due to a mechanical failure during the manipulation. On the other hand, the lower activity of M1 compared with M3 after ten cycles could not be totally attributed to a potassium loss.

In the samples M4 and M5 (Ce_{0.65}Zr_{0.35}O₂/cordierite and CeO₂/cordierite, respectively) without K, the activity difference was observed from the first TPO. The T_{\max} was 580 and 550 °C for the first TPO and 543 and 519 °C for the tenth TPO of M4 and M5, respectively. A similar behavior was observed for $T_{50\%}$. The half soot conversion was obtained at 546 and 521 °C for the first TPO and 515 and 483 °C for the last TPO with the M4 and M5 samples, respectively (Table 2). These results are different from what was expected, taking into account the effect of the Zr addition to ceria, as discussed in Section 1. However, there are references in literature that determined similar or low activity for the mixed oxide. Aneggi et al. [20,25] observed a similar behavior for fresh powder samples of Ce_{0.75}Zr_{0.25}O₂ and CeO₂ in soot combustion in tight contact. In the work of Guillén-Hurtado et al. [42], it can be observed a higher activity for CeO₂ than the cerium–zirconium oxide at low surface area. Considering that the BET areas in our supported catalysts are low (Section 3.4), the results found in this study seems to have the same behavior as those reported by other authors [20,25,42]. It is interesting to note that catalysts M4 and M5 had $T_{50\%}$ and T_{\max} higher than Mc (cordierite) for the first TPO. This behavior indicates that the components of cordierite are active for soot combustion [43].

The results obtained with M4 and M5 showed a higher activity difference between the catalysts than in the case of the M1 and M3 samples. The lower difference in the latter catalysts was due to the potassium presence. It is interesting to note that the catalysts containing K (M1 and M3) deactivated after several cycles, while those without K (M4 and M5) activated. This activation could be due to a positive restructuring of oxide coatings. After ten cycles of soot oxidation, the catalysts containing CeO₂ were the most active one. On the other hand, catalysts M4 and M5 also had weight losses.

The weight loss values presented in Table 2 were different from those previously reported for K/CeO₂/cordierite catalysts [27], in which the loading difference was only attributed to monolith breaking. It is important to point out that in the latter publication, the TPO for soot combustion was carried out up to 600 °C during six cycles. In the present study, the final temperature was approximately 700 °C with ten cycles. In consequence, the weight difference in this case could be related to monolith breaking and the loss of potassium loading due to sublimation.

In order to study the catalytic effect of zirconium incorporated to CeO₂ in the mixed oxide, the samples M1 and M4 were compared with M6 and M7 (see Figs. 1 and 2, and Table 2). The latter samples were prepared by CeO₂ coating in order to have a similar number of cerium atoms and K/oxide ratio than M1 and M4. Comparing the K/oxide/cordierite samples, it can be observed that M1 and M6 had similar T_{\max} and $T_{50\%}$ for the first TPO. The T_{\max} for catalysts M1 and M6 were 440 and 436 °C while the $T_{50\%}$ were 435 and 425 °C, respectively. After ten soot combustion cycles, the catalysts deactivated. The T_{\max} of the samples M1 and M6 were 535 and 569 °C, and the $T_{50\%}$ were 493 and 531 °C, respectively. The deactivation in both samples could be attributed to potassium loss. However, the sample containing the mixed oxide (M1) had a lower deactivation than the K/CeO₂ (M6). These results indicate that the initial presence of K, which is a promoter in soot combustion, was the reason that the mixed oxide and the ceria catalysts had similar activities. As the K concentration decreased with consecutive cycles at high temperatures, the presence of Zr in the mixed oxide improved the activity compared with the pure ceria. The mixed oxide is more stable upon high temperature treatments, and it

maintains a higher concentration of active oxygen than in the pure ceria.

Catalysts M4 and M7 showed similar T_{\max} and $T_{50\%}$ for the first TPO. The T_{\max} were 580 and 579 °C, while the $T_{50\%}$ were 546 and 556 °C for the M4 and M7 samples respectively. After ten cycles of reaction, samples M4 and M7 showed a better activity. The T_{\max} decreased to 543 and 566 °C and the $T_{50\%}$ to 515 and 543 °C, respectively. It is important to note that M7 sample had a lower activation than the M4 sample. In these catalysts, the structural change of the coating during reaction could be the reason for the activation.

According to these results, it can be concluded that the lower deactivation of M1 compared with M6 and the higher activation of M4 compared with M7 was produced by the improvement in the active oxygen concentration due to the zirconium atoms present in the cerium oxide matrix. It is important to emphasize those catalysts M1, M4, M6 and M7 had the same number of cerium atoms and the difference was produced by the presence of zirconium. In consequence, it could be deduced that the better activity of M1 and M4 compared with that of M6 and M7 was only produced by the presence of zirconium.

3.6. Powder oxides activity

As mentioned above, the activity results of supported ceria–zirconia oxide catalysts are different from those reported in the literature for soot combustion over powder oxide. In several studies, a better activity in soot combustion of ceria–zirconia oxide powder than in ceria was reported, due to a higher oxygen capacity [22–26]. The activity improvement of $Ce_xZr_{1-x}O_2$ was higher in tight contact as compared to the loose-contact mode. In order to test the activity of the $Ce_{0.65}Zr_{0.35}O_2$ powder used for coating, this mixed oxide was studied in soot catalytic combustion and compared with the CeO_2 powder at different soot-catalyst contacts. Results are shown in Fig. 4 and Table 2. The tight contact, where the soot and catalyst are mechanically mixed in a mortar, led to a T_{\max} of 531 and 418 °C for CeO_2 and $Ce_{0.65}Zr_{0.35}O_2$, respectively. In the case of the loose-contact mode, where the soot and catalysts were mixed by shaking in a vessel, the combustions of soot were produced at higher T_{\max} : 602 °C for CeO_2 and 604 °C for $Ce_{0.65}Zr_{0.35}O_2$. In all cases, the $T_{50\%}$ temperatures are similar to T_{\max} (Table 2). In tight contact, the obtained results corroborate the greater oxygen capacity of $Ce_{0.65}Zr_{0.35}O_2$. In soot-catalyst low contact, the combustions are similar to the uncatalyzed soot (Table 2 and Figs. 3 and 4). This result indicates that this contact was not enough to produce catalytic reaction. Atribak et al. [22] determined that the activity

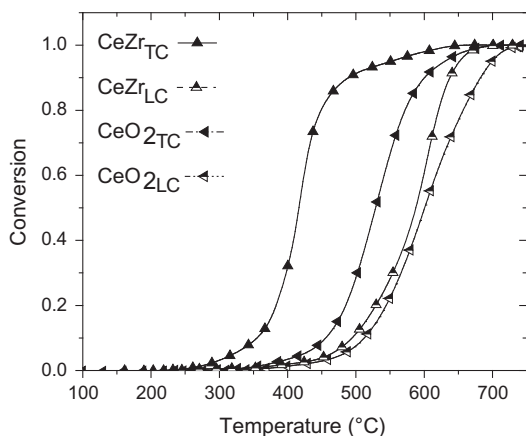


Fig. 4. Conversion profiles of soot combustion for $Ce_{0.65}Zr_{0.35}O_2$ and CeO_2 powder samples with different soot-catalyst contacts: TC – tight contact, LC – loose contact.

of the $Ce_{0.69}Zr_{0.31}O_2$ catalyst decreased dramatically in loose soot-catalyst contact, but it was still a better catalyst than the bare oxides although with a small difference.

It is interesting to note that the temperatures of the $Ce_{0.65}Zr_{0.35}O_2$ and CeO_2 powders in the reaction with loose contact are higher than those presented by supported powders (M4 and M5) in $T_{50\%}$ and T_{\max} . This result could be related to an intermediate contact between soot and catalysts that were obtained by impregnation of supported catalysts with a soot suspension.

Interestingly, it can be observed that the powder catalysts without potassium and using loose contact, yield values similar to those of the non-catalyzed soot combustion. This fact indicates that the presence of potassium is highly necessary to improve the activity under these conditions.

The obtained results for powder samples are not in total accordance with the results of supported catalysts with the same oxide loading. However, Guillén-Hurtado et al. [42], determined that the activity of these oxides depend on the surface area, the homogeneity, the composition and the cerium precursor. The Ce^{4+} precursor produce a more homogeneous oxide than Ce^{3+} . Although our sample was prepared with Ce^{3+} , the higher surface area of the mixed oxide than CeO_2 could be the reason for the better activity of $Ce_{0.65}Zr_{0.35}O_2$ as powder.

To understand the activity of $Ce_{0.65}Zr_{0.35}O_2$, the characterization of supported catalysts and powder oxide is important.

3.7. XRD analysis

To determine if there were changes in the bulk structure of these catalysts during reaction, XRD analyses were performed for the used supported catalysts in soot combustion by O_2 and compared with diffractograms of the fresh powder CeO_2 and $Ce_{0.65}Zr_{0.35}O_2$ for 2θ between 20° and 80° (Fig. 5). The diffractogram of the CeO_2 fresh powder presents the main reflections typical of a fluorite-structured material (face centered cubic unit) at approximately 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.6° and 79° [22]. The fresh powder of $Ce_{0.65}Zr_{0.35}O_2$ presents similar but broader peaks, indicating the zirconium incorporation into the cubic structure of CeO_2 . Also, the $Ce_{0.65}Zr_{0.35}O_2$ diffractogram shows a small shoulder at 30.3° over the fluorite peak of 28.5° that could be attributed to the coexistence of a small fraction of tetragonal phase with the main cubic phase [22]. As observed by Aneghi et al. [44] and Wu et al. [45], the composition, sample preparation and thermal treatment could be responsible for the change in symmetry, and the appearance of a tetragonal phase characteristic of zirconium rich content. No peaks of pure ZrO_2 were observed in the

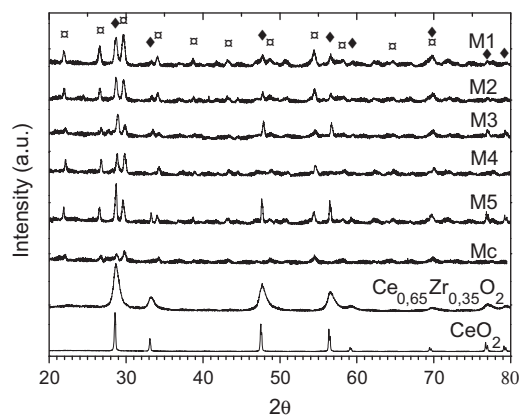


Fig. 5. XRD diffractograms of Mc, M1 to M5 catalysts after ten cycles of TPO and fresh $Ce_{0.65}Zr_{0.35}O_2$ and CeO_2 powder samples (♦ Peaks of CeO_2).

powder $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ diffractogram. In consequence, the XRD study confirmed the formation of the cerium–zirconium mixed oxide with the coexistence of a small fraction of zirconium rich phase. With the Scherrer equation and the peak at 28.5° , the apparent crystal size was calculated for powder samples. The results revealed a lower apparent crystal size for the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder (10 nm) than for CeO_2 (45 nm). The diffractograms of the supported catalysts, $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ (M1 and M2) and $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ (M4), after ten cycles of TPO, presented the sum of the peaks corresponding to the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder plus cordierite. In a similar way, the $\text{K}/\text{CeO}_2/\text{cordierite}$ (M3) and the $\text{CeO}_2/\text{cordierite}$ (M5) have the same peaks as the CeO_2 powder and cordierite, both in similar intensity. Therefore, all the supported samples display peaks corresponding to the coating oxides plus cordierite. The cordierite (Mc) pattern was also included to show the peaks that correspond to the support, as reference. The cordierite peaks have a similar intensity as the coating oxides peaks due to the low loading of the coating oxides (approximately 0.013 g). In all the $\text{K}/\text{CeO}_2/\text{cordierite}$ or $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ catalysts, potassium species peaks were not detected by XRD because of their extremely low content. On the other hand, the masking of the potassium peaks by cordierite should not be discarded. On the basis of XRD results, it can be deduced that the observed lower activity of $\text{K}/\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ compared with $\text{K}/\text{CeO}_2/\text{cordierite}$ could not be related to a change in the bulk of the mixed oxide after ten soot combustion cycles.

3.8. Raman analysis

The aim of the Raman spectra analysis was to investigate the homogeneity of the mixed oxide $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ to explain the activity results. The ZrO_2 presents six Raman active modes for tetragonal phase while fluorite lattice only one, around 490 cm^{-1} [46,47]. For CeO_2 , the fluorite cubic phase shows a sharp peak around $463\text{--}465\text{ cm}^{-1}$ [46–50]. In Fig. 6, the Raman spectra of the prepared $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ shows a peak at 466 cm^{-1} and weak peaks at around $115, 264, 311, 584$ and 605 cm^{-1} . The low shift of the main peak at 466 cm^{-1} of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ with respect to CeO_2 , suggests a poor insertion of Zr in the structure [49,50]. According to Letichevsky et al. [49] and Guillén-Hurtado et al. [50], a higher shift was observed for mixed oxides solution prepared with Ce^{4+} precursor with a tetragonal (t'') phase, indicating a more homogeneous mixed oxide. However, a low shift was observed when a Ce^{3+} precursor was used. This latter result is similar to our spectrum [50]. On the other hand, the peaks at $115, 264, 311, 584$ and 605 cm^{-1} can be assigned to the zirconium tetragonal phase ($t\text{-ZrO}_2$) [47,49,50]. It is important to mention that for $t\text{-ZrO}_2$ a peak at

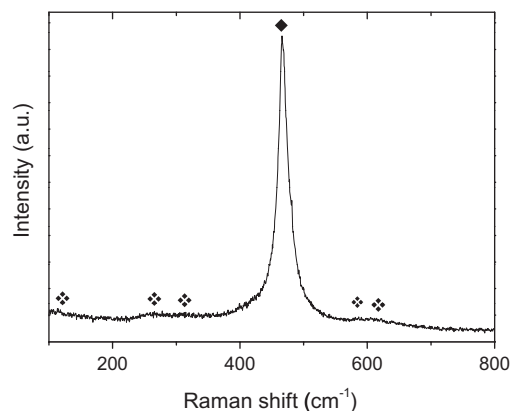


Fig. 6. Raman spectroscopy study of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder sample: (◆) $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ peak, (◆) zirconium tetragonal phase ($t\text{-ZrO}_2$) peaks.

464 is also present; however it overlaps with CeO_2 peak in Fig. 6. The peak at 466 cm^{-1} could not be assigned only to $t\text{-ZrO}_2$ because it is usually weaker than the peak at 311 cm^{-1} [51]. The presence of ZrO_2 in a tetragonal phase could indicate that cerium act as dopant because monoclinic phase is more stable phase for pure zirconium oxide. Therefore, a heterogeneous mixed oxide composition could also be present. For example, Zhang and Chen [51] also observed similar weak peaks for zirconium concentration above 50%. Moreover, these authors explained that the Raman band at 600 cm^{-1} range can be attributed to defects and oxygen displacements that distort the cubic structure, breaking the cubic symmetry. Therefore, the peak at 605 cm^{-1} obtained in Fig. 6 for $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ could be assigned to lattice distortions and defects. On the other hand, the peak at 311 cm^{-1} could be associated with the appearance of distorted tetragonal phase (t'') in addition to cubic phase [51]. This led us to conclude that a heterogeneous mixed oxide could be present.

3.9. Microscopy analyses

The catalysts were also analyzed by optical microscopy before and after soot combustion by O_2 . The images of catalysts M1, M2 and M3 can be observed in Fig. 7. A significant concentration of crystals in the channel front was observed for the fresh M2 sample calcined at 400°C after KNO_3 impregnation. These crystals were not observed for the fresh M1 and M3 catalysts, which had lower potassium concentration. Evidently, these crystals belong to potassium species. After ten soot combustions carried out heating up to 700°C , these crystals were not observed in the same amount for M2. However, the activity of this used sample was almost the same of the fresh one. Therefore, the optical microscopy indicated that there was a redistribution of the catalytic components inside the cordierite due to the treatment at high temperatures. This fact was not observed for catalysts M1 and M3 due to the low potassium concentration, even though it is not discarded.

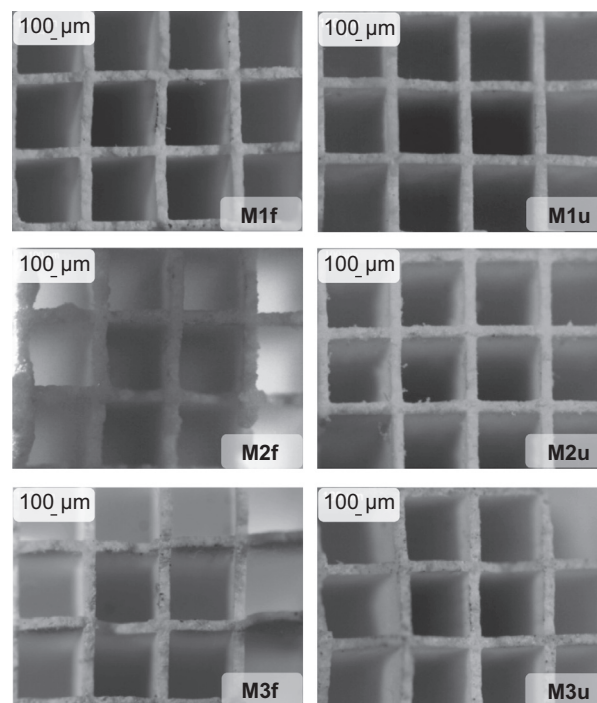


Fig. 7. Microscopic optical images of samples M1, M2 and M3, fresh and used after ten TPO reactions, respectively.

It is possible that the low activity observed for $\text{K/Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ in catalyst M1 can be attributed to a low contact of the active sites with the soot due to the insertion of the mixed oxide into the cordierite porous wall during coating. This is likely to be due to the low apparent crystallite size of the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ powder determined by XRD (Section 3.7). In order to obtain more information regarding the distribution of the active phase over the cordierite support, the catalysts were studied by coupling SEM observation with EPMA. Fig. 8 shows the SEM results obtained with fresh samples of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2/\text{cordierite}$ (M4) and $\text{CeO}_2/\text{cordierite}$ (M5). Cordierite support (Mc) is also shown as reference. The relative concentrations at different points studied by microprobe analysis (EPMA) are presented in Table 3. In the M4 sample, two subsequent sections of 10 μm on the surface were studied (A and B in Table 3). Both sections have a Ce/Zr molar ratio of approximately 5. This means a greater concentration of Ce with respect to Zr. A similar behavior was observed for points D and E. On the other hand, point C on the surface has a Ce/Zr molar ratio of 3.3, more similar to the result obtained by XPS (Section 3.1). In the M5 catalyst, the insertion of the coating oxide (CeO_2) inside the porous of cordierite can also be seen in Table 3. Point H on the surface has a higher cerium concentration than points I and J located inside the wall (Fig. 8, Table 3). A similar concentration to point H was observed at point K, which is near the opposite surface. The study by EPMA–SEM inside the support walls showed that the suspensions of catalysts wet the channels walls and diffuse into the pores by capillary action depositing the catalysts inside the pores. In other words, both oxides, $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ and CeO_2 , were deposited inside the walls of cordierite. According to EPMA results, the activity difference between the catalysts could not be attributed to the low soot–catalysts contact due to the insertion of catalyst inside the support, because in both cases a similar incorporation of active components in the monolith wall was observed.

The different Ce/Zr ratios determined by EPMA for the M4 sample in the cross section of the cordierite channels are related with a not perfect mixture of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ (XRD and Raman analysis). A

similar result was obtained by Mamontov et al. [52] analyzing a $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample with neutron diffraction. These authors determined that small domains enriched in ceria or zirconia inside the sample may be present. These domains are undetectable by conventional diffraction analysis.

Fig. 9 shows SEM surface images of oxide coatings near the cordierite channel surface. The relative concentrations of the crystals determined by EPMA are present in Table 3 as L and M points for $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ and CeO_2 , respectively. Point L corresponds to the surface of M4, the Ce/Zr ratio being 1.6, which is the nearest value to XPS analysis (Section 3.1). The SEM images also show that the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ over cordierite presented a different crystal morphology from CeO_2 . On the M4 catalyst surface, agglomerates of very small crystals of cerium–zirconium mixed oxide were observed. On the other hand, in the M5 sample, more compact aggregates of CeO_2 were observed. This morphology could be related to the coating adherence test reported above (Section 3.2). According to Zamaro et al. [53], a higher adhesion to the support is obtained with lower sizes and stable aggregates. In consequence, the low adherence of the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ oxide over the cordierite could not be attributed to the size but is produced by the low intrinsic stability of aggregates. It is important to remember that the catalysts were obtained by multiple depositions that affect the morphology of deposited oxide.

3.10. Activity comparison in soot combustion by O_2

The higher activity of supported CeO_2 with respect to $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ in catalysts with similar loadings (M1 and M4 vs. M3 and M5) could be related to the work of Aneggi et al. [20,25]. These authors determined a similar activity in soot combustion for fresh powder samples of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and CeO_2 in tight contact, with a T_{max} of 389 and 387 $^{\circ}\text{C}$, respectively. Although these latter temperatures were much lower than the obtained temperatures for supported catalysts due to the soot–catalyst contact and higher surface area, the same behavior was observed with respect to our supported catalysts. According to literature, the soot was oxidized by surface active oxygen. However, two mechanisms for surface oxygen replacement were indicated. The surface oxygen defect created by oxidation could be refilled by gaseous oxygen and/or by bulk oxygen. The role of ceria is expected to provide surface oxygen species for the soot combustion while the redox reaction $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ is produced [20,25]. The gas O_2 refills the oxygen vacancies [19,18]. In this work, contradictory results were found when samples were compared according to the same loading or according to the same mole number. When the number of cerium atoms in the loading oxide is the same, there is a similar amount of redox reaction $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ sites for soot combustion in the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ and CeO_2 catalysts. However, the M1 and M4 showed better activity than M6 and M7 catalysts. In consequence, there is an increased mobility of oxygen by presence of zirconium along that affects cerium redox behavior. According to Guillén-Hurtado et al. [42], the homogeneity of the mixed oxide improves the soot combustion. However, the $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ characterization indicated a not homogeneous mixed oxide, an improvement of the efficiency of cerium redox sites was observed by the zirconium presence.

When catalysts with the same oxide loading were compared (M1 and M4 vs. M3 and M5), a higher activity of supported CeO_2 with respect to $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ in catalysts was observed. There are references in literature that determined similar or low activity for the mixed oxide. For example, Aneggi et al. [20,25] observed a similar behavior for fresh powder samples of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and CeO_2 in soot combustion in tight contact, with a T_{max} of 389 and 387 $^{\circ}\text{C}$, respectively. In the work of Guillén-Hurtado et al. [42], it can be observed a higher activity of CeO_2 than the cerium–zirconium oxide at the lowest surface area. Considering that the

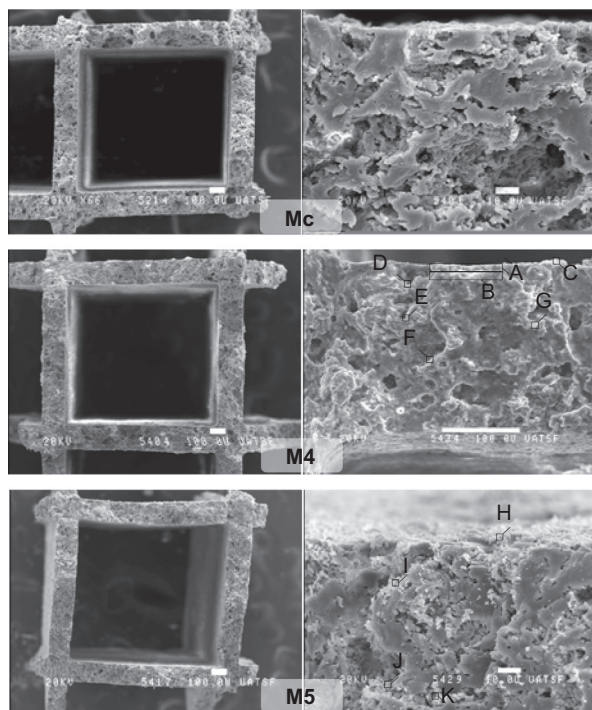
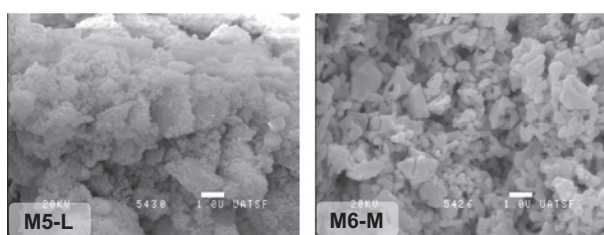


Fig. 8. SEM images of cross section of monolith channels of Mc, M4 and M5 fresh samples and EPMA determination of different points described in Table 3.

Table 3

Relative concentrations at different positions of M4 and M5 samples during microprobe analysis (EPMA).

Point	Relative Concentrations (wt.%)						Ce/Zr weight ratio	Ce/Zr mole ratio
	Ce	Zr	Mg	Al	Si			
A	32.8	4.3	8.5	26.9	27.6		7.7	5.0
B	14.1	1.7	10.3	30.7	43.3		8.5	5.6
C	77.4	15.2	0.4	4.1	2.8		5.1	3.3
D	49.0	3.2	7.8	19.3	20.7		15.5	10.1
E	21.8	0.3	9.9	28.4	39.6		75.3	49
F	6.4	–	10.7	30.2	52.7		–	–
G	23.3	2.6	9.8	26.9	37.4		8.9	5.8
H	60.8	–	6.3	16.3	16.6		–	–
I	49.4	–	6.9	20.9	22.8		–	–
J	28.5	–	9.4	27.4	34.9		–	–
K	67.4	–	4.7	13.6	14.3		–	–
L	38.3	15.6	6.8	18.9	20.4		2.5	1.6
M	90.4	–	1.7	4.2	3.7		–	–

**Fig. 9.** SEM images of cross section of surface of monolith catalysts for CeO₂ and Ce_{0.65}Zr_{0.35}O₂ for fresh M4 and M5 samples and EPMA determination described in Table 3.

BET areas in our catalysts are low (Section 3.4), the result seems to have the same tendency. In our work, the higher activity of K/CeO₂/cordierite (M3) and CeO₂/cordierite (M5) samples compared with K/Ce_{0.65}Zr_{0.35}O₂/cordierite (M1) and Ce_{0.65}Zr_{0.35}O₂/cordierite (M4), after several TPO cycles, could be ascribed to the higher concentration of ceria atoms in catalysts with CeO₂ that produce more surface active oxygen. The difference between the catalysts with the same oxide loading is that the number of cerium atoms decrease in the mixed oxide (replaced by Zr). Although the presence of zirconium enhances the oxygen mobility [18,22–25,45], the soot combustion by the redox reaction sites Ce⁴⁺ ↔ Ce³⁺ decreases. This could explain the activity difference between catalysts M1 and M3. According to these results, the number of cerium atoms on the surface could be as important as the zirconium presence.

The obtained results not allowed the determination of the type of oxygen involved in the soot combustion, surface or bulk. According to Aneghi et al. [25] and Guillén-Hurtado et al. [42], under loose contact situation, the regeneration of surface oxygen could be determined by sub-surface and bulk oxygen affected by Zr atoms. This could be the behavior of supported catalysts activity, where the surface area is low. In the supported catalysts, the coating of oxides on the cordierite leads to BET areas similar to those of the support (Section 3.4). On the other hand, these authors [25,42] mentioned that under tight contact, the combustion is determined by cerium surface sites and not affected zirconium atoms. In this case, the area has a greater effect. In consequence, this area effect could be the reason of the higher activity of a Ce_{0.65}Zr_{0.35}O₂ powder sample with respect to CeO₂. The difference in the activity of powder samples with respect to supported catalysts could also be attributed to the contact type.

3.11. Catalytic activity in soot combustion by NO/O₂

Samples M4, M8, M9, Mc and soot were analyzed under similar conditions to those present in the diesel exhaust gases: O₂ (18%) and NO (0.1%) in He flow. Under these conditions, NO is

catalytically transformed into NO₂, which is active for soot oxidation, thus decreasing the soot combustion temperature as compared to that obtained in the presence of oxygen. Both O₂ and NO_x are active oxidants to convert the soot into CO₂ [31,42]. Table 4 and Fig. 10 show the results obtained in the activity tests carried out in the presence of NO. It can be observed that the activity in the combustions of uncatalyzed soot and soot over cordierite (Mc) did not significantly change in the presence of NO as compared to the presence of O₂ only. The T_{max} were 520 and 460 °C for uncatalyzed soot and Mc respectively, with or without NO. The T_{50%} showed a difference smaller than 15 °C in both cases between the different gas mixtures (O₂ and NO/O₂) (Table 4). These results suggest that without catalysts there was not a significant amount of NO₂ formed in the reactor. On the other hand, catalysts M8 and M9 showed a T_{max} difference of approximately 40 °C between the reactions with and without NO. The M8 catalysts presented the T_{max} in soot combustion with and without NO at 420 and 460 °C, while M9 showed temperatures of 403 and 445 °C, respectively. Similar differences were observed in the T_{50%}. The better activity observed in the presence of NO with the catalysts M8 and M9 strongly suggests that there was a substantial amount of NO₂ formed during the reaction with both catalysts. However, the similar T_{max} difference indicates that the presence of the mixed oxide cerium–zirconium in M8 did not improve the NO₂ formation. A high NO₂ formation by NO oxidation was observed by Atribak et al. [39,42] for CeO₂ and mixed oxide with cerium rich content, indicating that the cerium-rich surface improved the NO₂ formation.

Sample M9 (K/CeO₂/cordierite) showed a better activity than M8 (K/CeZr/cordierite) following the same trend as in the case of the combustion with O₂ (Section 3.5). In consequence, the presence of Zr in ceria did not lead to an improvement in the activity, either in oxygen or in oxygen–nitrogen monoxide. Nevertheless, the soot combustion temperatures obtained with the mixed oxide catalysts are similar to those obtained in the diesel exhaust gases.

Table 4Maximum and half soot conversion temperatures (T_{max} and T_{50%} respectively) obtained during soot combustion by temperature programmed oxidation (TPO) with O₂ and NO/O₂.

Samples	T _{max} (°C)		T _{50%} (°C)	
	O ₂	NO/O ₂	O ₂	NO/O ₂
M4	502	440	450	426
M8	460	420	444	398
M9	445	403	405	373
Mc	460	460	431	416
Soot	520	521	493	485

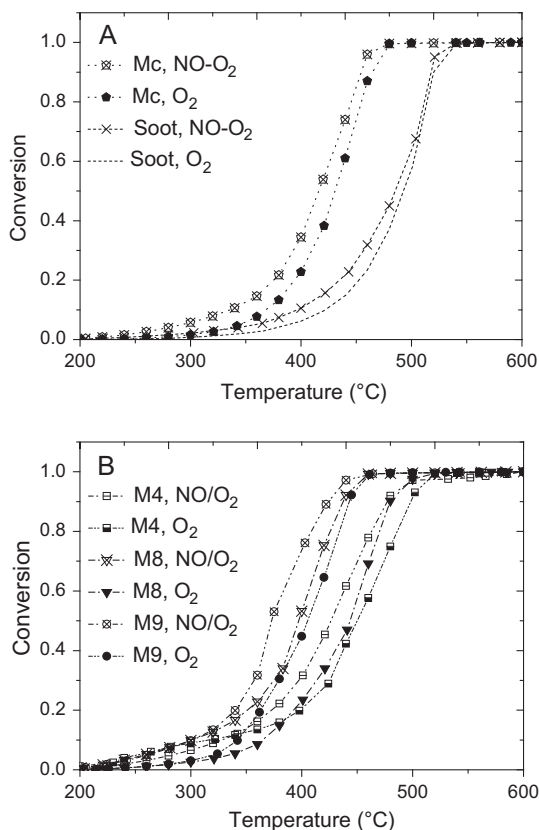


Fig. 10. Conversion profiles of soot combustion with O₂ and NO/O₂ for different samples: (A) TPO for uncatalyzed soot and Mc and (B) TPO for M4, M8 and M9.

The potassium effect was studied with the CeZr/cordierite samples in the presence of NO, comparing samples M8 and M4 (Table 4). A difference of 40 °C was observed for the sample containing potassium both in combustions with and without NO. In consequence, the presence of K favors the combustion of soot, regardless of the gas phase composition. The results obtained with M8 compared to Mc are interesting. In this case, the NO_x formation due to the presence of the cerium catalyst, increased the activity of M8 when NO was present in the gas phase.

3.12. Stability at high temperature

Since it was observed that the stability of potassium is poor at high temperatures due to evaporation [26,54], the catalysts stability under severe conditions was studied. The activity of used samples M1 and M3 was tested in soot combustion after treatment at 800 °C during 24 h in oxygen flow. The temperatures for soot combustion of the aged samples are shown in Table 2 and Figs. 1B and 2B. After ageing, a marked deactivation was observed. The T_{max} of M1 and M3 shifted from 535 to 553 °C and from 499 to 575 °C, respectively. A similar shift was observed for $T_{50\%}$ from 472 to 545 °C in M3 and from 493 to 555 °C in M1. This clearly shows that the catalysts were deactivated after the severe ageing treatment. The observed behavior could imply that the potassium volatility is the reason for the deactivation. The total weight losses of used catalysts after the ageing treatment were 0.3% and 1.5% for M1 and M3, respectively. According to the ICP analysis, potassium was not detected in catalysts M1 and M3 after the high temperature treatment. This result is not in agreement with the results of Wu et al. [26] that observed activity for soot combustion by powder K/Ce_xZr_(1-x)O₂ catalyst after ageing at 800 °C for 24 h. However, it is important to recall that according to the preparation method, the Ce_xZr_(1-x)O₂ oxide could have different physicochemical

properties and structure that could affect the catalytic activity [23]. On the other hand, the T_{max} obtained for aged M1 and M3 were even higher than those obtained with Mc, M4 and M5. This result could be ascribed not only to potassium loss but also to a detrimental structural change induced by K at high temperatures, as already suggested in other supports [55]. In order to probe this point, an XRD was measured for the aged catalysts M1 and M3 and was compared with the diffractograms obtained for samples after ten TPO cycles (figure not shown). The same main peaks of Ce_{0.65}Zr_{0.35}O₂ and CeO₂ oxides were observed in the aged samples M1 and M3. Notably, the XRD analyses did not show any modifications of the crystalline phases. Besides, the XRD analysis did not indicate the presence of additional crystalline phase beyond the cubic structure. In consequence, the low activity of the aged samples M1 and M3 could be attributed to the loss of potassium concentration and a surface modification not observed by the DRX technique. Although it is well known that the zirconium presence increases ceria stability at high temperature treatments [22,24,45], a deactivation was observed in M1.

4. Conclusions

The activity of K/Ce_{0.65}Zr_{0.35}O₂/cordierite and K/CeO₂/cordierite catalysts supported on cordierite was studied for soot combustion and compared with catalysts without potassium. In this work, contradictory results were found when samples were compared according to the same oxide loading or according to the same mole number of cerium, in soot combustion by O₂. The potassium presence decreases the differences between the oxides. However, after several soot combustion cycles the gradual loss of potassium determined that the effect of oxides were more clear and produced the differences. In catalysts with Ce_{0.65}Zr_{0.35}O₂ with the same loading of CeO₂ a low activity was observed for the mixed oxide sample. The sample with CeO₂/cordierite could be more active due to higher redox sites for soot combustion. However, when catalysts with the same number of cerium mole sites are compared, the zirconium effect in combustion is observed. In consequence, the catalysts with Ce_{0.65}Zr_{0.35}O₂ were better than CeO₂. It is important to consider the low surface area obtained for all supported sample. In consequence, the intrinsic activity of redox sites determined the combustion reaction. On the other hand, the activity of the powder Ce_{0.65}Zr_{0.35}O₂ was better than that of CeO₂ only in tight-contact mode. This result was attributed to the higher surface area of the mixed oxide ant contact type. It is important to mentioned, that the heterogeneity, determined to Ce_{0.65}Zr_{0.35}O₂ by Raman and SEM/EPMA characterization, limited the beneficial effects. According to X-ray diffraction analysis, the catalysts did not present structural changes after use if they were compared with oxide powder samples.

The presence of NO in the reactive gas mixture improves the combustion temperature. Although the activity of K/Ce_{0.65}Zr_{0.35}O₂/cordierite with NO/O₂ is still lower than K/CeO₂/cordierite in this work, the temperatures reached are of practical significance.

According to these results, the activity of K/Ce_{0.65}Zr_{0.35}O₂/cordierite catalyst, with loose catalyst-soot contact, could be determined by the number of redox sites and the improvement effect of zirconium by a homogeneous mixed oxide. In consequence, the comparison of catalytic activity of CeO₂ and mixed oxide cerium-zirconium should be taken with care.

Since a real diesel engine could reach extreme temperatures during operation, the activity of the aged catalyst of K/Ce_{0.65}Zr_{0.35}O₂/cordierite and K/CeO₂/cordierite was studied. It was determined that the catalytic behavior of these samples became lower than that of catalysts without potassium after treatments at high temperatures.

The difference in the catalytic behavior between the supported mixed oxide and the powder form of the catalyst shows the importance of addressing the study of these catalysts in a configuration as similar to the real application as possible.

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