Applied Catalysis B: Environmental 132–133 (2013) 479–486

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Catalytic coating synthesized onto cordierite monolith walls. Its application to diesel soot combustion

E.D. Banús, V.G. Milt, E.E. Miró, M.A. Ulla*

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form
10 December 2012
Accepted 14 December 2012
Available online 24 December 2012

Keywords:
Structured catalyst
Soot combustion
Cordierite monolith
Co,Ba,K/ZrO_2 coating

ABSTRACT

Co,Ba,K/ZrO_2 coating onto a cordierite monolith was produced using a sequential process. The first step involved the formation of a ZrO_2 layer using a colloidal suspension and the second, the incorporation of active metals. The coating morphology and its physicochemical properties were studied using different characterization techniques. The ZrO_2 colloidal suspension and the active ingredients, Co, Ba and K, penetrated through the macropores of the cordierite and their interconnections, both being retained inside the walls and on the external surface. After calcination, the active species were $BaCO_3$, KNO_3 and Co_3O_4.

The catalytic performance for diesel soot combustion was analyzed through the loose deposition of soot onto the structured catalyst and the TPO experiments showed a maximum in combustion rate at about 400 °C when NO (0.1%) was added.

Cordierite monoliths are well known as wall-flow type soot filters and the morphology of their walls provides an optimum substrate for the anchoring of a thin catalytic coating, thus achieving an excellent mechanical stability. Moreover, the catalytic layer also covers internal pores of the channel walls, where some of the soot particles are trapped, enhancing the catalytic activity and preserving most of the original cordierite monolith macroporosity. Therefore, coating cordierite walls with a Co,Ba,K/ZrO_2 catalyst constitutes a potential catalytic filter for soot combustion. As the textural properties indicated, no changes in the pore volume were observed after the incorporation of the catalytic coating, which favors the potential application of this type of monoliths.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The catalytic combustion of diesel soot particles has been the object of great research efforts in the last decade, and several review articles have been published [1–3]. Since it is foreseen that improvements in diesel engine designs will not be enough to meet the requirements of future legislation for soot emissions, a variety of aftertreatment technologies have been proposed, the combination of filters and combustion catalysts being among those most widely investigated.

Soot formation is related to incomplete diesel fuel oxidation and occurs in the high temperature, fuel-rich reaction zone around individual fuel droplets, where fuel hydrocarbons are oxidized under substoichiometric oxygen concentration [2]. The very small atomized droplets of fuel burn in hot compressed air leave an unburned core of fine carbon particles with adsorbed substances [3]. Diesel particulate matter (PM) consists of different components that form agglomerates of primary soot particles covered by a layer of adsorbed condensed hydrocarbons (SOF). The carbonaceous part of the diesel PM is constituted by an onion-like structure of graphene sheets [4].

Many options for the removal of particulates from diesel exhaust gases have been considered, but most of them use a filter. The most frequently used filters are wall-flow type monoliths that are formed from open (flow-through) monoliths into wall-flow type ones by plugging the channels alternatively which forces the incoming gases to pass through porous channel walls. Honeycomb ceramic filters possess high filtration efficiencies (more than 90%) as a result of the cake filtration mechanism that takes place after the filter saturates with soot [5]. Filter regeneration can be accomplished by burning the trapped particulate matter off. The ignition temperature of diesel particulate matter depends on the SOF content but it usually exceeds 550 °C, normally being between 600 and 625 °C whereas the temperature of the diesel exhaust is typically 200–400 °C under normal working conditions. When batch-wise oxidation of the accumulated soot is performed, temperatures of over 975 °C are reached, seriously damaging the filter. Hence, coating the filter walls with a catalyst is necessary to decrease the ignition temperature in order to continuously regenerate the trap during the engine operation [6,7]. The catalytic coating should have a good activity for the soot oxidation and a high adherence to endure both thermal and mechanical shocks [8–10]. Moreover, it is

* Corresponding author. Tel.: +54 342 4536861; fax: +54 342 4536861.
E-mail address: mulla@fiq.unl.edu.ar (M.A. Ulla).

0926-3373/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2012.12.020

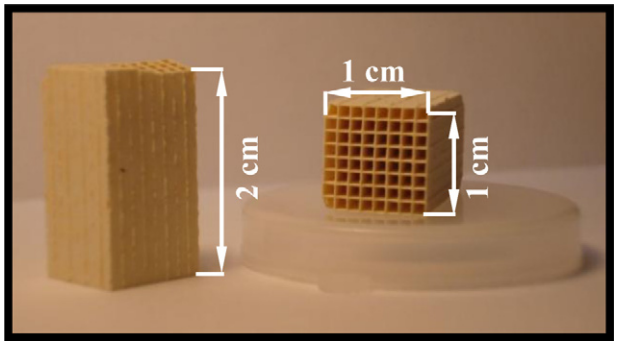


Fig. 1. Photograph of the original monolith used for the synthesis of the structured catalysts.

crucial to produce a thin catalytic layer, where the original ceramic filter macroporosity be maintained. In this way, the filter properties are preserved.

In the present work, we study the synthesis of a Co,Ba,K/ZrO_2 catalytic coating onto a cordierite monolith and its catalytic performance for the combustion of diesel soot. Cordierite is considered an excellent ceramic material due to its high melting point, high temperature and thermal shock resistance, as well as to its high chemical stability. On the other hand, the Co,Ba,K/ZrO_2 catalyst has proved to be an active material for soot combustion and can also act as a nitric oxide trap, thus simultaneously eliminating both diesel exhaust contaminants [11]. Thus, we used cordierite monoliths in order to evaluate the performance of the selected catalyst coated onto a structured support that presented higher filtration efficiencies. To this end, diesel soot combustion was carried out over Ba,Co,K/ZrO_2-cordierite catalysts under different conditions, i.e., with and without NO in the gaseous feed and with different soot-to-catalyst ratios, where soot was incorporated so as to achieve loose soot-to-catalyst contact. The structured catalysts were characterized before and after catalytic runs by Energy Dispersive X-ray Analysis (EDX) and Scanning Electron Microscopy (SEM) in order to analyze the changes in morphology and element distributions on the surface of the catalytic coatings. X-ray diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR) were also used as characterization tools to determine the active species present on the catalytic coatings. Mercury Intrusion Porosimetry was used to determine pore volumes.

2. Experimental

2.1. Synthesis of the structured catalysts

The cordierite monoliths used were provided by TENNECO® and had 64 cells per square centimeter. The average wall thickness and average cell width were 183 μm and 1120 μm, respectively.

The monoliths were cut into pieces of 1 cm^2 in section and 2 cm long (Fig. 1). As cleaning procedure, these pieces were washed in ultrasonic bath with water for 30 min and then in acetone for 30 min. Finally, the monolith pieces were dried in a stove at 130 °C overnight. After this stage, the monoliths were called structured substrates (Cor).

2.1.1. ZrO_2 coating of monoliths (ZrO_2-Cor)

The ZrO_2 coating was carried out using a colloidal ZrO_2 suspension (NYACOL® acetate stabilized, 20 wt.% ZrO_2) and a device as described by Banús et al. [12]. Previous to immersion, the structured substrates were wrapped with Teflon and heat-shrinkable rubber, where the former was used to avoid the deposition of ZrO_2 on the external monolith walls and the latter, to obtain a good adherence to the device. After immersion, the pieces were blown to remove the excess of slurry and dried at 130 °C overnight. The cycle immersion–blowing–drying was repeated four times. Finally, the Teflon and rubber heat-shrinkable covers were removed and the samples were calcined at 700 °C for 2 h. After this stage, the monoliths were called structured supports (ZrO_2-Cor).

2.1.2. Impregnation of active metals (Co,Ba,K/ZrO_2-Cor)

The active components were incorporated using cycles of immersion–blowing–drying–calcination, following the same procedure as described by Banús et al. [12]. In this case the structures were also wrapped with Teflon and heat-shrinkable rubber, using again the former to avoid the deposition of the metals on the external monolith walls and the latter, to obtain a good adherence to the device. An impregnation solution containing $Ba(Ac)_2$, $Co(Ac)_2$ and KNO_3 was used, where the atomic metal percentages were K: 35.9%, Co: 40.7% and Ba: 23.4%, and the $Ba(Ac)_2$ concentration was 0.05 M. After immersion during 1 min into the Co, Ba and K solution of the structured support (ZrO_2-Cor), the system was softly blown and dried at 130 °C for 12 h and then calcined at 500 °C for 2 h in air. This whole cycle, immersion–blowing–drying–calcination, was repeated several times in order to increase the amount of deposited metals. After this stage, the monoliths were called structured catalysts (Co,Ba,K/ZrO_2-Cor).

2.2. Characterization

X-ray diffraction (*XRD*): The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu Kα radiation at a scan rate of 1°/min, from $2\theta = 10$ to 80°. The monolith pieces were cut along the channels and held in a special holder for the XRD analysis. The software package of the equipment was used for the phase identification. *IR spectroscopy* (*FTIR*): A Shimadzu IR Prestige-21 spectrometer was used to obtain the infrared spectra. The IR wafers were prepared by mixing KBr powder with the particles obtained through scrapping the inner channels of the monolith pieces with a spatula (ca. 1% sample in KBr). All spectra were acquired at 4 cm^{-1} resolution, accumulating 80 scans. *Scanning electron microscopy* (*SEM*): A SEM Jeol JSM-35 C equipment was employed operated at 20 kV acceleration voltage. Pieces of the different samples (structured substrate, support and catalyst) were obtained to examine the inner channel walls and cross-sections. These portions were glued to the sample holder with Ag painting and then coated with a gold thin layer in order to improve the images obtained. *Energy-dispersive X-ray spectroscopy* (*EDX*): The elemental chemical analysis was performed using the energy-dispersive X-ray analysis (EDX) system attached to the SEM instrument. Semi quantitative results were obtained by the theoretical quantitative method (SEMIQ), which does not require standards. *Adherence test*: A Testlab TB04 equipment was used to study the weight loss caused when the different samples were exposed to an ultrasound bath. The samples were immersed into an acetone bath and subjected to ultrasound at 25 °C during 30 min. Two consecutive ultrasonic baths were performed; drying at 120 °C during 30 min between them. In order to check the thermal stability of the catalytic phase the Co,Ba,K/ZrO_2-Cor was calcined at 900 °C for 2 h. *Mercury intrusion porosimetry* (*MIP*): The pore volumes of the original cordierite monolith and the structured catalysts (Co,Ba,K/ZrO_2-Cor) were determined by means of mercury intrusion porosimetry (Pascal 440 porosimeter). The pressure range used was from 0.14 MPa to 200.41 MPa. The average pore volumes were 121.33 ± 12.45 mm^3/g and 112.7 ± 15.75 mm^3/g for the original cordierite monolith and the structured catalyst, respectively. These average values were calculated using the measurement of three sample pieces; each piece was constituted by one monolith channel. All the samples were previously dried at 120 °C.

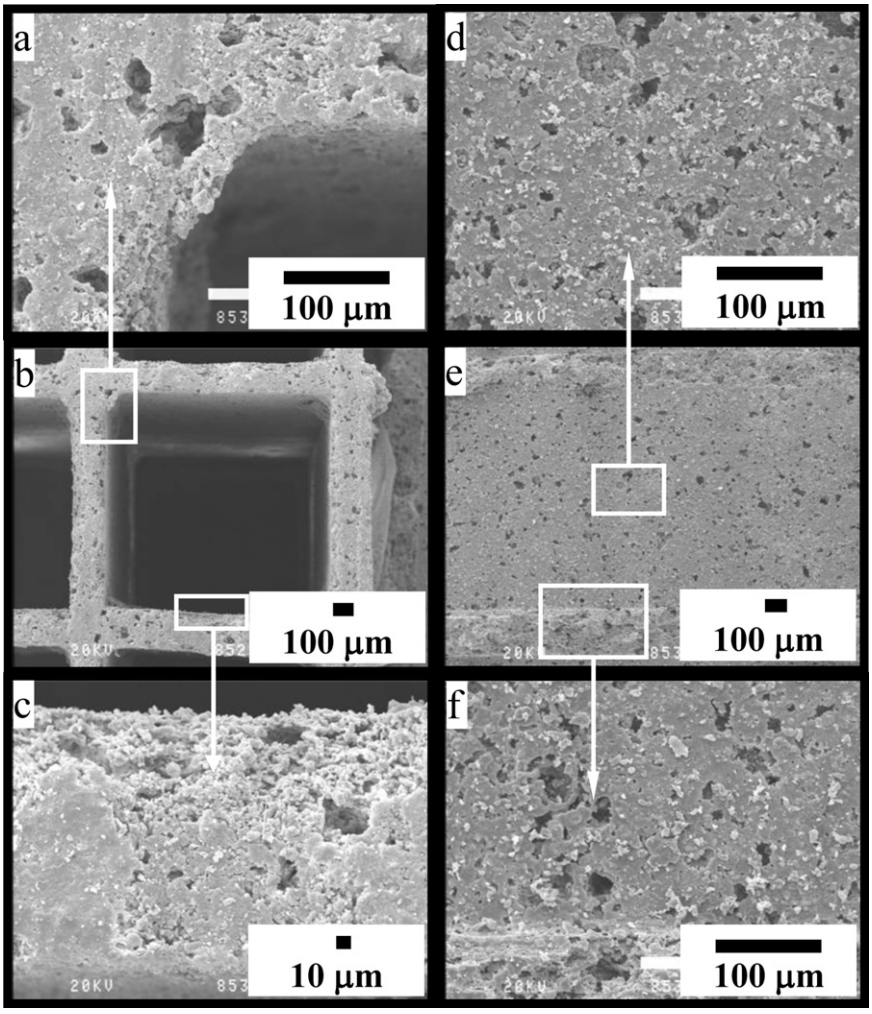


Fig. 2. Micrographs of the original monolith: (a) 320×, (b) 54×, (c) 540×, (d) 320×, (e) 60× and (f) 320×.

2.3. Catalytic soot combustion

Previous to the soot incorporation, the structured samples were wrapped with Teflon and heat-shrinkable rubber to avoid the soot deposition onto the outside walls, since those walls did not contain the catalytic coating. After that, the samples were immersed in soot-hexane suspensions of different concentrations (600, 3000 or 10,000 ppm) for 1 min, blown and dried at room temperature for 12 h.

The temperature-programmed oxidation (TPO) of soot was used to study the catalytic behavior of the structured catalysts [12]. After removing the Teflon and heat-shrinkable rubber, the structured sample was placed inside a quartz tubular reactor. In addition, the sample was surrounded with quartz wool to force the gas flow throughout the monolith channels. The soot containing structured samples was heated at $5\,^{\circ}C\,min^{-1}$ from room temperature up to 600 °C in O_2 (18%) diluted in helium, the total gas flow being $20\,ml\,min^{-1}$, corresponding to a space velocity of $940\,h^{-1}$. This is roughly a factor of 10–50 times lower than typical vehicle operation, but nevertheless suitable for demonstrating the relative effects of the various catalyst additives. The downstream gases were analyzed with a Shimadzu GC-2014 chromatograph (TCD detector), the CO concentration being negligible. The effect of the presence of 0.1% NO was studied by feeding O_2 (18%) +NO (0.1%) diluted in helium.

In order to study both the stability and reproducibility of the structured catalyst, two different pieces of Co,Ba,K/ZrO_2-Cor were treated as previously described at the beginning of the first paragraph of this section. After each TPO run, the structured catalyst was extracted from the reactor, soot was loaded again and the structured catalyst was again put into the reactor and evaluated. This procedure was repeated four times for each Co,Ba,K/ZrO_2-Cor piece.

3. Results and discussion

3.1. Synthesis of the structured catalyst

Cross-section observations of the original monolith (Fig. 2a–c) indicate that this structured substrate has a high internal porosity with some connections among the pores. As measured by mercury Intrusion Porosimetry, cordierite monoliths have a pore volume value of $121.33 \pm 12.45\,mm^3/g$. The channel walls present well-distributed macropores, having a diameter in the 5–20 μm range, as observed in Fig. 2d–f. Besides, the X-ray diffractogram of the monolith has the characteristic diffraction peaks of the cordierite structure ($Mg_2Al_4Si_5O_{18}$) (Fig. 3a).

3.1.1. Deposition of the ZrO_2 layer

The weight gains of six pieces of structured substrates after four immersion–blowing–drying cycles are shown in Fig. 4, the average gain being 21.84 ± 2.79 wt.%. The calcination treatment caused a weight decrease, as observed in Fig. 4, due to both the burning of the stabilizing agent of the ZrO_2 colloidal suspension and the

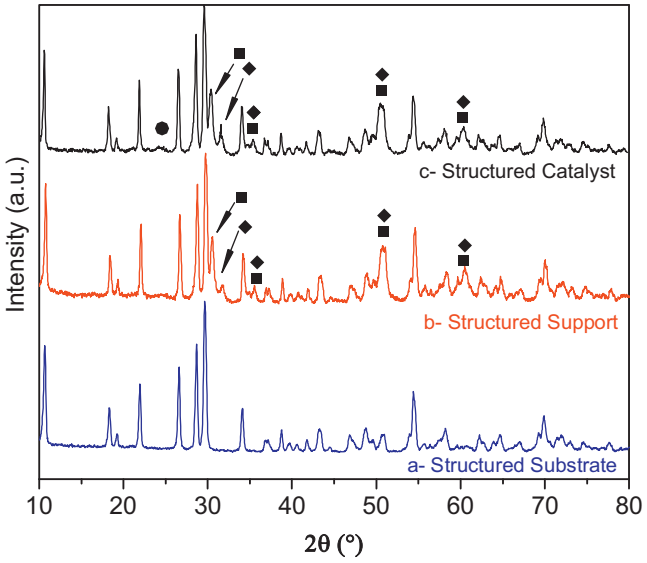


Fig. 3. XRD of the different stages of the synthesis process of the structured catalyst. (♦) ZrO_2 (monoclinic), (■) ZrO_2 (tetragonal) and (●) $BaCO_3$.

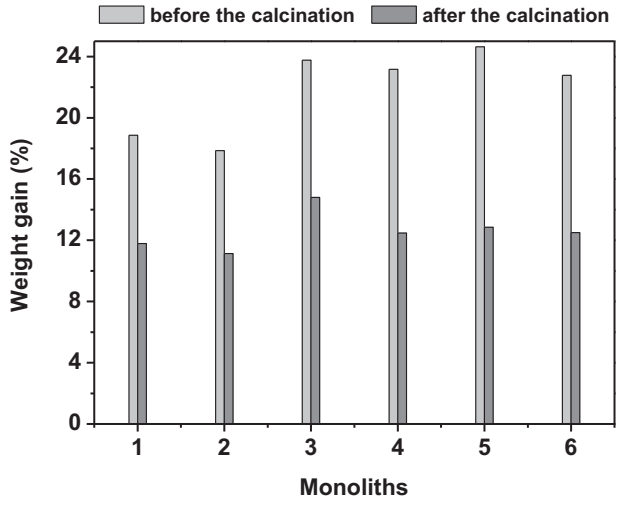


Fig. 4. Weight changes for six monoliths before and after calcination, after four cycles for the deposition of the ZrO_2 layer.

coating dehydroxilation. Therefore, the final weight gain average after calcination was 12.69 ± 1.21 wt.%. Comparing the weight gaining values for the six structured support pieces, it is confirmed that this procedure of obtaining a ZrO_2 coating had a good reproducibility.

Fig. 3b presents the structured support XRD pattern. The ZrO_2 signals for both the monoclinic and the tetragonal structures are detected along with the cordierite signals. In addition to the peaks corresponding to ZrO_2, signals of this oxide overlapping with others of cordierite also appear at $2\theta = 28^\circ$ and $2\theta = 30^\circ$.

The ZrO_2 coating morphology is shown in Fig. 5. The micrographs of the channel walls (Fig. 5d–f) point out that a very thin ZrO_2 layer with rather interconnected surface cracks was produced and part of the small original pores of the walls were covered (compare Fig. 2d–f and Fig. 5a–c). The cracks would be generated during the drying step as observed in our previous work [13,14]. Additionally, the layer thickness is not homogeneous, being thicker at the corners of the square cells (Fig. 5d-f). This difference in thickness is caused by the fluid dynamic phenomena during the blowing step of the ZrO_2 deposition procedure [15]. Even though after the ZrO_2 coating, the weight gain was close to 13 wt.%, the layer so obtained was fairly thin. This result suggests that the ZrO_2 colloidal suspension penetrated through the macropores and their interconnections during the immersion step. Therefore, the ZrO_2 particles would be retained inside the walls during the blowing and drying steps but also on the wall surface without blocking the wall pores.

The EDX analysis confirmed the presence of the Zr element in the monolith walls. This analysis was performed in different wall regions, the relative average atomic ratios being Mg: 8, Al: 22, Si: 31 and Zr: 39 for the center and insides of the wall and Mg: 7, Al: 15, Si: 17 and Zr: 61 and for the cell corner. The latter was richer in Zr than the center and insides of the wall, as expected owing to the difference in thickness of the ZrO_2 layer. The identification of the cordierite components was consistent with the formation of a very thin ZrO_2 coating. Besides, the presence of Zr inside the walls confirmed the diffusion of colloidal suspension through the wall macropores and their interconnections.

3.1.2. Impregnation of active metals

Fig. 6 shows the weight gain percentages after each cycle of active component impregnation for four structured support samples. As it can be observed, the weight gaining evolutions are constant and reproducible and twelve cycles

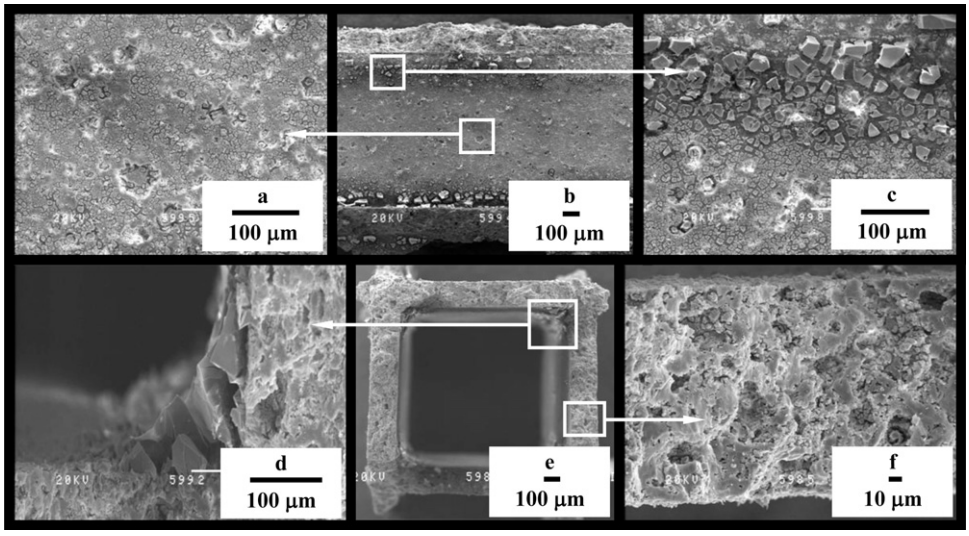


Fig. 5. Micrographs of the structured support (ZrO_2 layer): (a) 320×, (b) 54×, (c) 400×, (d) 320×, (e) 60× and (f) 320×.

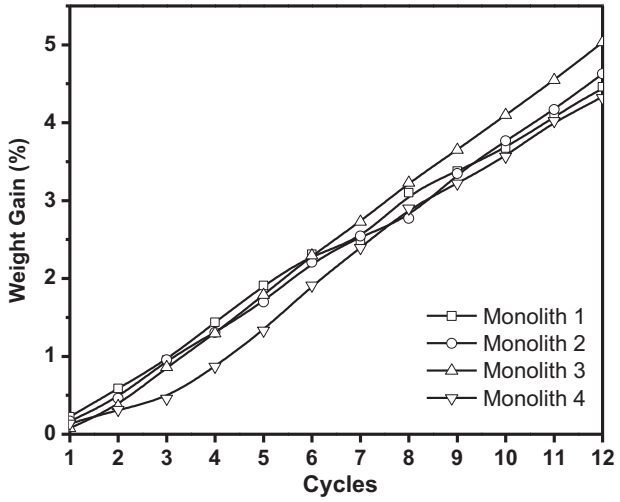


Fig. 6. Evolution of the percentages of weight gain during the addition of metals (Co, Ba and K) to the structured support on four samples.

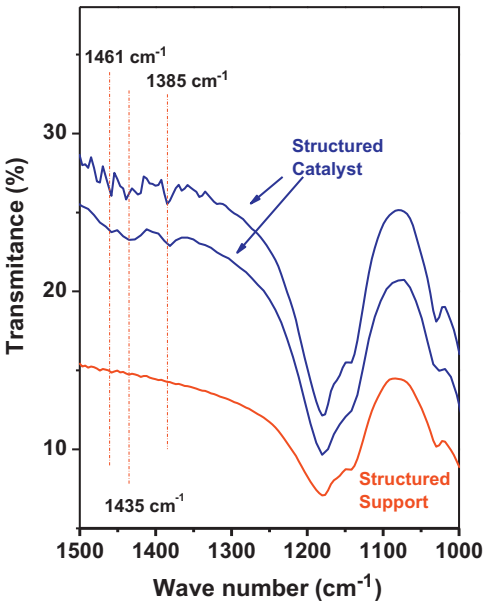


Fig. 7. FTIR Spectra of the structured support and the structured catalyst (two different pieces).

(immersion–blowing–drying–calcination) were needed to achieve a weight gain close to 5 wt.%.

In order to determine the different component species present in the catalytic coating, FTIR and XRD analysis were carried out. Fig. 7 shows the IR spectrum of the structured support and the IR spectra of two structured catalysts. It is evident that the last two spectra contain extra signals at 1461, 1435 and 1385 cm^{-1}. The first two are characteristic of $BaCO_3$ and the latter corresponds to the νNO_3^- stretching, which is probably related to KNO_3, as it was the salt used during the catalyst preparation The XRD pattern of the structured catalyst is in line with the presence of $BaCO_3$, as shown in Fig. 3c from the insinuation of a diffraction line near $2\theta = 25^\circ$, attributed to $BaCO_3$.

The comparison of the SEM pictures of the structured catalyst (Fig. 8) and the structured support (Fig. 5) indicates that although the catalytic components are introduced into the structured support pores, no significant modifications in morphology are produced on the coating because of the active metals impregnation. Moreover, the pore volume determined by MIP was $112.7 \pm 15.75\ mm^3/g$ is quite similar to that of the base cordierite, and the appearance of the catalyst changes from brownish to black due to the characteristic color of the Co_3O_4 spinel formed after the structured catalyst calcination.

The results of the EDX analysis in different zones of the Co,Ba,K/ZrO_2-Cor are shown in Table 1. The Co, Ba and K were deposited on the channel surfaces (zones 1–3) as well as inside the walls (zones 4–8). The enrichment in Zr near the cell corner (zones 2 and 4) was preserved after the impregnation process. The average atomic ratios of Si/Al and Mg/Al calculated from Table 1

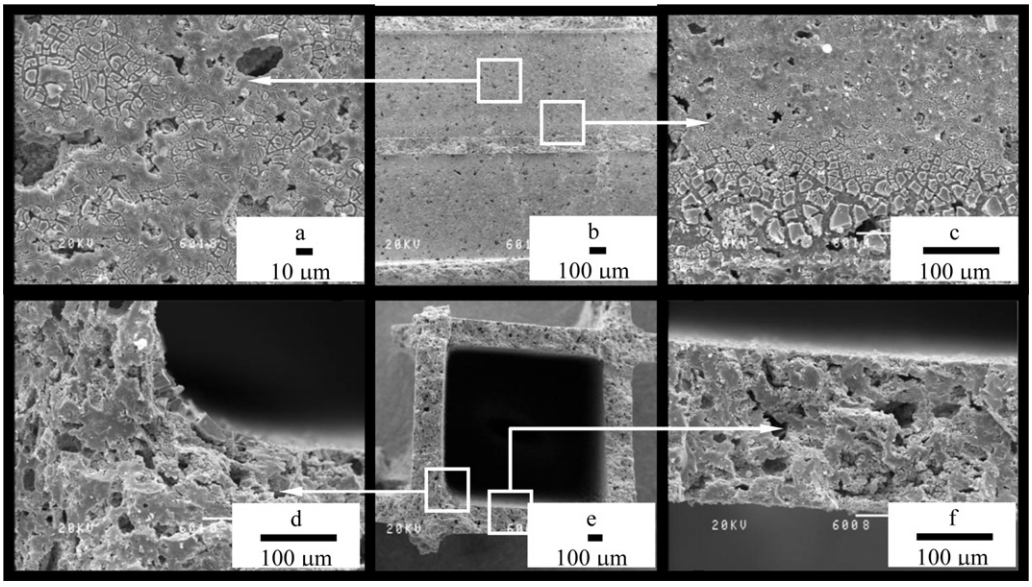
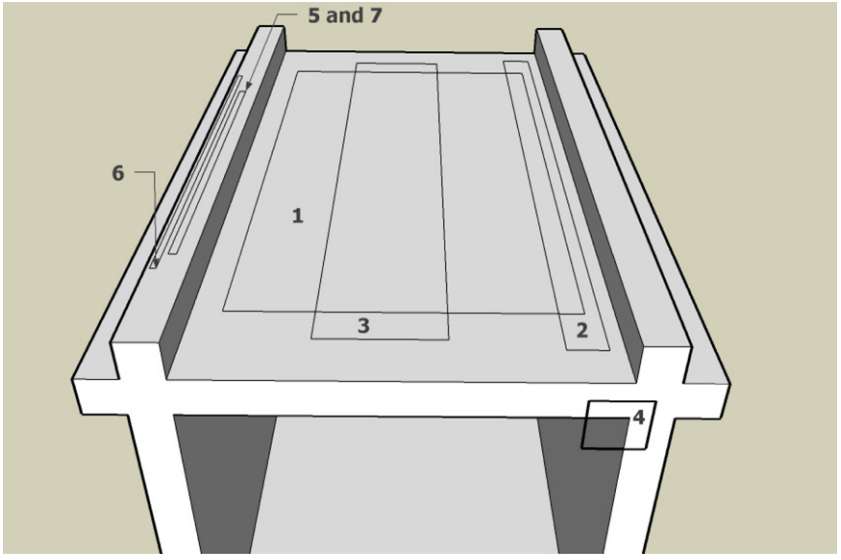


Fig. 8. Structured catalyst morphology. View of the channel surface: (a) 300×, (b) 40×, (c) 300× and view of the channel cross-section: (d) 300×, (e) 54× and (f) 300×.

Table 1
Distribution of elements in different regions in the structured catalysts.

Relative atomic ratio (%)							Analyzed zone
Mg	Al	Si	Zr	Co	Ba	K	
10.5	33.0	48.6	4.9	1.6	0.7	0.8	Channel Surface (1)
18.7	20.6	19.8	35.5	2.6	1.5	1.3	Channel border (2)
10.0	31.6	39.0	13.8	3.4	1.2	1.0	Channel center (3)
16.0	25.6	29.2	24.2	2.9	0.9	1.1	Cell corner (4)
8.7	32.5	47.4	8.8	1.2	0.5	0.9	Inside of the wall (center) (5)
11.1	31.3	46.9	8.2	1.2	0.5	0.9	Inside of the wall (border) (6)
12.0	29.8	42.9	10.4	3.1	0.8	0.9	Inside of the wall (center) (7)
12.4	29.2	39.1	15.1	2.3	0.9	1.0	Average
3.6	4.5	10.8	10.9	1.0	0.4	0.2	Standard deviation



are 1.25 and 0.38, respectively and the theoretical ratios obtained from the cordierite formula are 1.30 and 0.45, which implies that no significant changes were observed. These results indicate that no preferential leaching from the substrate to the ZrO_2 layer would take place during the different processes performed to obtain the catalytic coating.

The comparison between the active metal atomic percentage obtained by EDX analysis and the theoretical percentage corresponding to the impregnation solution are shown in Table 2. According to this chemical analysis, Ba and K were deposited in a smaller proportion than it was expected, while Co did so in greater proportion. The most marked differences are given for Co and K; therefore, cobalt preferentially deposits on the ZrO_2 coating. Taking into account that K is mostly present as KNO_3, the lower concentration of this element in the coating could be attributed to the dissolution of the salt during the successive cycles of impregnation. This behavior was already observed during the preparation of other structured catalysts supported on foams [12–14]. Nevertheless, the K percentages corresponding to the Co,Ba,K/ZrO_2 coating onto ceramic and metallic foams were lower than those of the structured catalyst in this work. This difference can be explained since K was incorporated into the monolith substrate not only on the channel surface but also inside the walls, where it would be more difficult for potassium to be dissolved.

3.2. Catalytic performance

In order to study the structured catalyst performance for the soot combustion, temperature-programmed oxidation experiments were carried out under streams containing NO and O_2. Soot was deposited onto the structured catalyst using suspensions of different concentration (600, 3000 and 10,000 ppm), as described in the experimental section. TPO profiles are shown in Fig. 9. The amounts of soot retained using either the 600 or the 3000 ppm soot suspensions were quite small (Table 3), hence the corresponding TPO profiles were wide and in the former case, without a well-defined maximum (Fig. 9a, Table 3). On the other hand, the TPO profiles obtained using the 10,000 ppm soot suspension are reproducible and present a maximum (Fig. 9, Table 3). Therefore, the 10,000 ppm-soot suspension was chosen for the subsequent TPO experiments.

In order to study the positive effect of the active metal incorporation to the ZrO_2 layer, the TPO profile for the structured catalyst (Co,Ba,K/ZrO_2-Cor) is compared to that of the structured support (ZrO_2-Cor) for both stream feedings, O_2 + He and NO + O_2 + He. These results are shown in Fig. 10, where it is pointed out that the presence of the active components significantly decreased the temperature at which the CO_2 production rate was maximum, from 550 °C to 400 °C under NO + O_2 atmosphere and from 550 °C to 490 °C under O_2 atmosphere. As it is well known, NO_2 is a more powerful oxidant than O_2, and decreases the temperature of the maximum combustion rate in 150 °C, which is in agreement with our previous work [12,14].

The reproducibility of the TPO experiment was also studied testing two structured catalyst pieces and performing four TPO runs for each one, as explained in the experimental section (Fig. 11a and b). It is clear that the temperature of maximum combustion rate is reproducible both for each experiment using the same monolith and between the experiments carried out using the different pieces

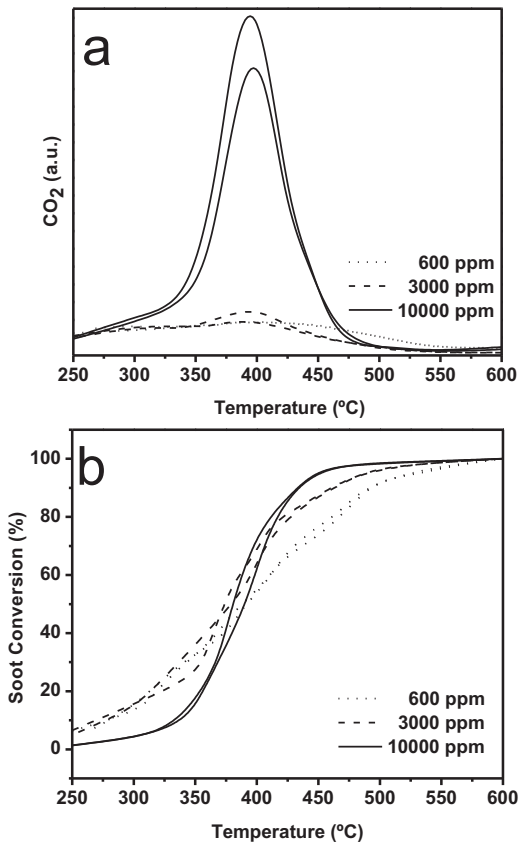


Fig. 9. Effect of soot loading on the structured catalysts performance for the catalytic soot combustion. Reactor Feed: 18% O_2 + 0.1% NO + 81.9% He. (a) CO_2 evolution and (b) Soot conversion.

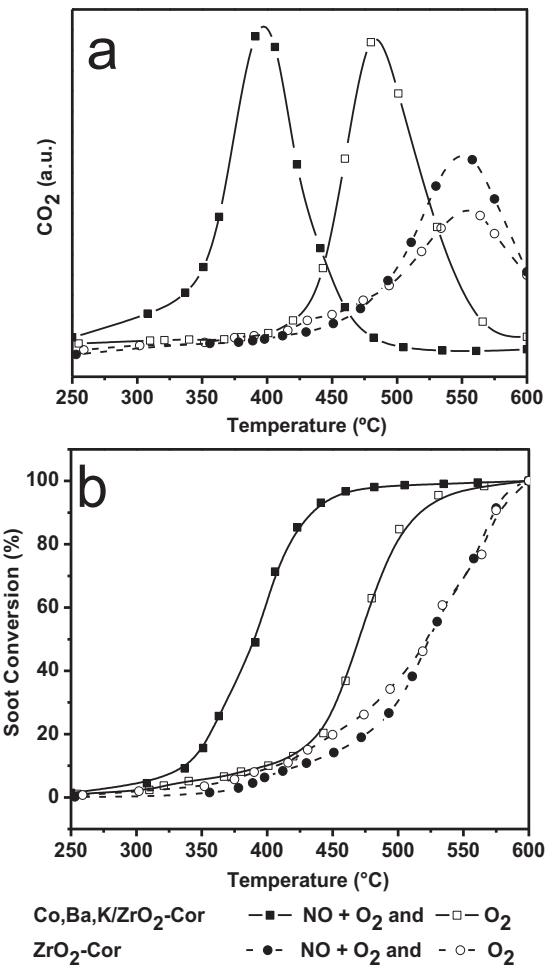


Fig. 10. Effect of the catalytic coating and the presence of NO on the structured catalyst performance for the catalytic soot combustion. Concentration of soot suspension: 10,000 ppm. Full symbols: 18% O_2 + 0.1% NO (Helium balance), empty symbols: 18% O_2 (Helium balance). (a) CO_2 evolution and (b) Soot conversion.

of monoliths. Besides, the average amount of loaded soot for one of the monoliths (Fig. 11a) is 44.47 mg with a standard deviation of 5 mg, and for the other monolith (Fig. 11b), the area under the curve corresponds to an average mass of soot of 50.55 mg, with a standard deviation of 9 mg, which indicates that the method for soot addition is quite reproducible.

Having the loaded amount of soot and the catalytic coating weight for each TPO experiment, it is possible to estimate the soot:catalytst coating ratios. The ratio range using the 10,000 ppm-soot suspension was between 1/4 and 1/3, whereas ratio values of 1/11 and 1/13 were calculated using soot suspensions of 600 ppm and 3000 ppm.

3.3. Mechanical and thermal stability

This catalytic structure is proposed to be used in exhaust pipes; consequently, it is essential to have a good mechanical resistance. In order to analyze this resistance, two consecutive ultrasonic baths were performed and no weight loss was detected. The excellent coating adherence can be associated with the wall high porosity of the cordierite monolith, which offers many sites for the catalytic coating anchoring. Furthermore, the thermal stability is confirmed comparing the XRD patterns of the Co,Ba,K/ZrO_2-Cor as-synthesized (Fig. 12a), after being tested in soot combustion 12 times (Fig. 12b) and after being treated in air flow at 900 °C for 2 h (Fig. 12c). No significant changes were found except for the expected transformation of the tetragonal ZrO_2 to the monoclinic one due to the high temperature treatment.

Table 2
Atomic ratios of active metals in the structured catalyst.

Metal	Theoretical atomic ratio (impregnation solution)	Average atomic ratio (EDX)
Co	40.8	53.6
Ba	23.3	20.8
K	35.9	25.6

Table 3
Loaded soot and temperature of maximum combustion rate (data obtained from Fig. 9).

Concentration of the soot suspension	Mass of loaded soot (mg)[a]	T_{max}(°C)[b]
600 ppm	18.3	–[c]
3000 ppm	15.7	386
10,000 ppm	58.8	398

[a] Average of two TPO experiments.
[b] Temperature of maximum combustion rate.
[c] Very broad signal where a maximum cannot be defined.

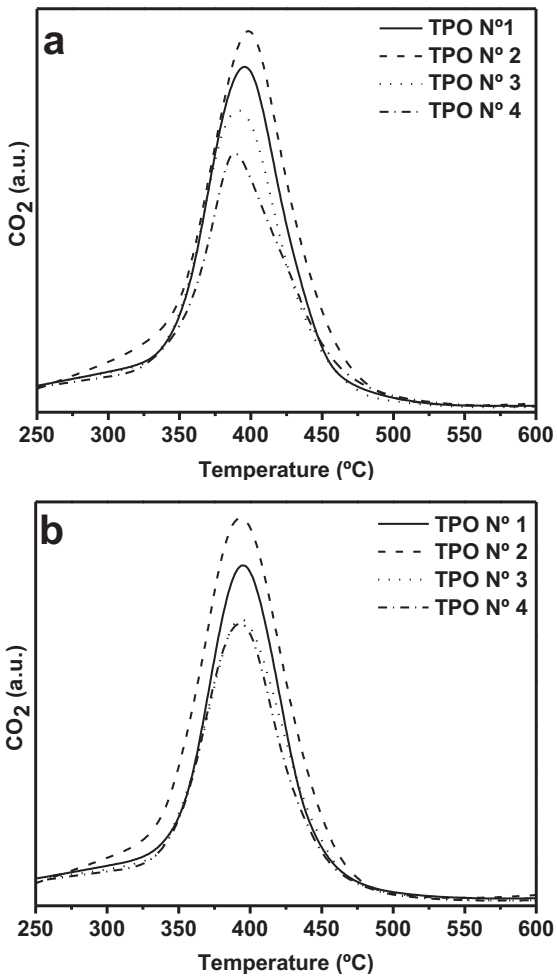


Fig. 11. Study of the TPO experiment reproducibility made with two different structured catalyst pieces (a and b, respectively). Reactor feed: 18% O_2 + 0.1% NO. Concentration of the suspension of soot: 10,000 ppm.

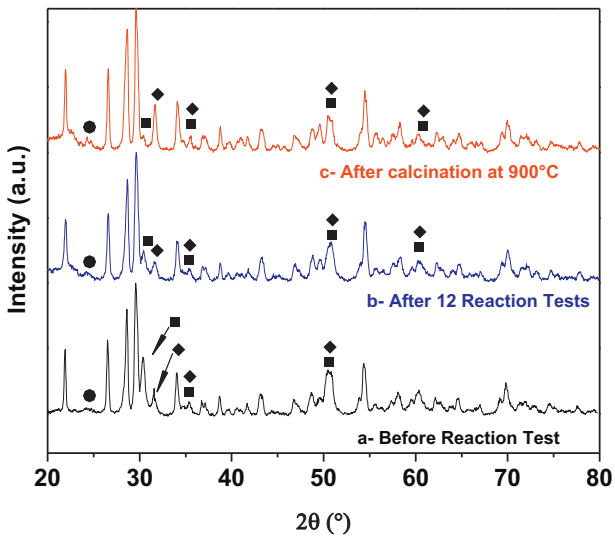


Fig. 12. XRD of the Co,Ba,K/ZrO_2-Cor (a) before reaction test, (b) after 12 reaction test and (c) After of calcination at 900 °C. (♦) ZrO_2 (monoclinic), (■) ZrO_2 (tetragonal) and (●) $BaCO_3$.

4. Conclusions

The Co,Ba,K/ZrO_2 catalyst was deposited on a cordierite monolith for use in the combustion of diesel soot particles. The preparation was performed in sequential steps, the first one being the washcoating of the monoliths with a suspension of colloidal circonia that penetrated through the macropores and their interconnections during the immersion step. Small ZrO_2 particles were retained inside the walls during the blowing and drying steps and also on the external surface, obtaining ca. 13 wt.% of zirconia. The active ingredients, Co, Ba and K, were then impregnated obtaining reproducible weight gaining evolutions, and twelve cycles were needed to achieve a weight gain close to 5 wt.%. The Co, Ba and K were deposited on the channel surfaces as well as inside the walls. FTIR and XRD characterizations indicate that barium is present as $BaCO_3$ and K as KNO_3 whereas the Co_3O_4 spinel is formed after the structured catalyst calcination. Another important feature of the catalysts prepared is the excellent coating adherence, associated with the wall high porosity of the cordierite monolith, which is preserved after the catalytic coating is obtained.

The soot was loosely deposited onto the structured catalyst using soot suspensions (10,000 ppm), and TPO experiments showed a maximum in combustion rate at about 400 °C, when NO (0.1%) was included in the feed. The method employed provides a reproducible way to evaluate monolithic pieces, as our results show. The temperatures for the maximum rate of soot combustion are somewhat higher for the cordierite monoliths when compared with other substrates also studied (ceramic and metallic foams). Notwithstanding this lower activity, the cordierite monolith offers an excellent material for soot filtration, and the Co,Ba,K/ZrO_2 is a potential candidate for the continuous regeneration of the filter. Moreover, considering the possibility of heating diesel exhaust gases, as in fact it occurs with diesel vehicles that possess particulate filters.

Acknowledgments

The authors wish to acknowledge the financial support received from ANPCyT, CONICET and UNL. Thanks are also given to JICA for the donation of the XRD and FTIR equipment and to Elsa Grimaldi for the English language editing.

References

[1] D. Fino, Science and Technology of Advanced Materials 8 (2007) 93–100.
[2] B.A.A.L. Van Setten, M. Makkee, J.A. Moulijn, Catalysis Reviews: Science and Engineering 43 (2001) 489–564.
[3] M.V. Twigg, Applied Catalysis B: Environmental 70 (2007) 2–15.
[4] B. Azambre, S. Collura, J.M. Trichard, J.V. Weber, Applied Surface Science 253 (2006) 2296–2303.
[5] A. Mayer, U. Matter, G. Scheidegger, J. Czerwinsky, M. Wyser, D. Kieser, J. Weidhofer, SAE paper (1999), 1999-01-0116.
[6] M.E. Gálvez, S. Ascaso, R. Moliner, M.J. Lázaro, Chemical Engineering Science 87 (2013) 75–90.
[7] M.E. Gálvez, S. Ascaso, I. Tobías, R. Moliner, M.J. Lázaro, Catalysis Today 191 (2012) 96–105.
[8] S. Bensaid, N. Russo, Catalysis Today 176 (2011) 417–423.
[9] D. Mescia, J.C. Caroca, N. Russo, N. Labhsetwar, D. Fino, G. Saracco, V. Specchia, Catalysis Today 137 (2008) 300–305.
[10] P.A. Kumar, M.D. Tanwar, S. Bensaid, N. Russo, D. Fino, Chemical Engineering Journal 207–208 (2012) 258–266.
[11] V.G. Milt, E.D. Banus, M.A. Ulla, E.E. Miro, Catalysis Today 133–135 (2008) 435–440.
[12] E.D. Banús, V.G. Milt, E.E. Miró, M.A. Ulla, Applied Catalysis A: General 379 (2010) 95–104.
[13] E.D. Banús, V.G. Milt, E.E. Miró, M.A. Ulla, Applied Catalysis A: General 362 (2009) 129–138.
[14] E.D. Banús, M.A. Ulla, E.E. Miró, V.G. Milt, Applied Catalysis A: General 393 (2) (2011) 9–16.
[15] J.M. Zamaro, M.A. Ulla, E.E. Miró, Chemical Engineering Journal 106 (2005) 25–33.