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Ultrasound-Assisted Deposition of Co−CeO_2 onto Ceramic Microfibers to Conform Catalytic Papers: Their Application in Engine Exhaust Treatment

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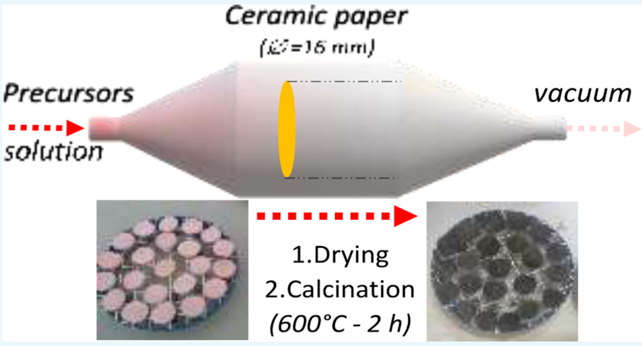

ABSTRACT: The combination of the selective catalytic reduction technology with catalytic filters constitutes one of the most efficient ways for diesel engine exhaust treatment. In this paper, the development of catalytic ceramic papers as structured systems for the abatement of diesel soot particles is addressed. Ceramic papers were prepared by the dual-polyelectrolyte papermaking method, which is based on the conventional papermaking technique used for cellulosic papers, in which a portion of cellulosic fibers is replaced by ceramic ones. The deposition of Co and Ce as catalytic materials by the wet spray method on ceramic papers was studied for the development of structured catalysts using an ultrasonic nebulizer and different solvents. The use of alcohol−water solutions for the impregnation of cobalt generated smaller particles and a high dispersion of them on the ceramic fibers, greater than that obtained when pure water was employed. Temperature programmed oxidation (TPO) assays showed that the best catalytic performance was acquired with the catalysts generated with alcohol solvents, showing a maximum rate for soot combustion at a temperature close to 400 °C. The adequate soot combustion performance and the high thermal and catalytic stability make catalytic ceramic papers impregnated by the wet spray method, promising systems for their application as diesel particulate filters.

1. INTRODUCTION

Fibrous structures offer high surface to volume ratio and high void fractions that make them attractive for catalytic applications. Besides, they are cheaper, can be adapted to various geometries, and have better coatability compared to microreactors.[1] Different materials can be used to synthesize fibers, which in turn can be conformed in a variety of cellular structures. For example, metallic fibers can be easily fabricated as wire mesh structures, which can be easily stacked inside cylindrical cartridges.[2] Fibers made of carbon or glass can be structured in the form of felts and they have been successfully applied to the treatment of drinking water.[3]

Another possible arrangement consists in a paper-like structure, which could be made of ceramic fibers instead of cellulosic ones. Ceramic papers constitute a fibrous inter-connected matrix with pore-type spaces that benefits gas diffusion.[4] The employment of ceramic and cellulosic fibers during the papermaking process produces ceramic papers resistant to severe thermal conditions after calcination (temperatures above 900 °C).[5]

The development of ceramic paper has two important challenging aspects: the mechanical strength, which can be achieved through the incorporation of binder agents during paper manufacturing,[6] and the deposition of the catalytic material, which should be homogeneously dispersed and firmly anchored to the fibers. Catalytic ceramic papers have been reported to be efficient for a variety of gas-phase reactions with industrial and environmental concern. Among them, reforming reactions,[7−12] hydrocarbon dehydrogenation,[13,14] nitric oxide reduction,[4,15] and CO oxidation[5] have been studied.

The oxidation of diesel soot is an application with significant environmental interest, which involves a solid reactant (soot particles) and gas-phase compounds (oxygen and nitric oxide). Diesel engines are widely employed both in light and heavy vehicles because of their durability, reliability, and fuel economy. Today, between 40 and 50% of the vehicles sold in Europe are powered by diesel engines, and they are also extensively used all over the world. However, the exhaust gases emitted by these engines have high concentrations of the particulate material (soot) and nitrogen oxides that are harmful to human health and environment.

So far, the most adequate treatment to abate particulate matter consists in employing filters capable of retaining the soot particles. To tolerate adequately the operation conditions, these filters should be chemically, thermally, and mechanically resistant, especially during the regeneration step that could

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originate high-temperature spots. Besides, they should have high retention capacity to trap efficiently the soot particles present in the exhaust gases. Thus, an attractive application of catalytic papers is the development of a structure that may act simultaneously as a particulate filter as well as a catalyst with the possibility of self-regeneration (passive regeneration).[16−19]

With focus on the above-mentioned challenge, this contribution presents a new method for the deposition of Co and Ce onto ceramic papers, which consists in the ultrasound-assisted formation of micrometric droplets of the catalyst precursors. The use of different solvents to prepare the precursor solutions of active phases and its effect on the active-phase dispersion and the catalytic performance is analyzed. As a matter of fact, Khmelev reported that the properties of the solvents (viscosity and surface tension) define the diameter of drops formed by nebulization.[20] After calcination, a system applicable for the soot combustion reaction was conformed, for which we present a thorough characterization. Activity and stability experiments on diesel soot combustion are also discussed.

2. RESULTS AND DISCUSSION

2.1. Catalytic Coating: Morphology and Physical Chemistry Properties.

The average weight of the active phase incorporated onto the substrates is summarized in Table 1. The weight increments correspond to a set of three papers used in the catalytic tests, referred to the same bare ceramic papers. A more significant weight gain can be observed when the papers were impregnated with the most concentrated solutions (0.3 M), when using water as a solvent. Because of the higher molecular weight of cerium, the higher the Ce−Co proportion is, the higher weight percent gained. On the other hand, the amount of active phase deposited can be increased by modifying the solvent. Indeed, solvents with lower surface tension favor the amount of catalyst deposited, being the order of weight increment: isopropyl alcohol > ethanol > polyvinyl alcohol ≅ water. This result is in agreement with scanning electron microscopy (SEM) micrographs that will be discussed below.

Table 1. Percentage of Catalytic Loading Referred to the Bare Ceramic Paper

Co*X*Ce*Y* (*Z* − *S*) catalysts[a]	wt gain (%)
Co100Ce0 (0.05 − *W*)	0.6
Co100Ce0 (0.15 − *W*)	2.3
Co100Ce0 (0.30 − *W*)	7.2
Co75Ce25 (0.30 − *W*)	8.2
Co50Ce50 (0.30 − *W*)	8.8
Co25Ce75 (0.30 − *W*)	10.7
Co0Ce100 (0.30 − *W*)	11.1
Co100Ce0 (0.15 − *E*)	6.7
Co100Ce0 (0.15 − *I*)	14.6
Co100Ce0 (0.15 − *P*)	3.6

[a] *X* and *Y* are the relative molar percentages of Co and Ce, respectively. *Z* is the molar concentration of the (Ce + Co) solution and S is the solvent: water (W), ethanol (E), isopropyl alcohol (I), and poly vinyl alcohol (P). See text (section 2.2).

Figure 1 shows the SEM micrographs of catalytic ceramic papers impregnated with cobalt nitrate aqueous solutions (*W*) with different concentrations: 0.05, 0.15, and 0.30 M. The lowest concentration leads to a scarce cobalt deposition onto the ceramic fibers (Figure 1A), whereas the 0.15 M solution (Figure 1B) allows the deposition of more significant amounts of cobalt, both onto the ceramic fibers and onto the cerium oxide.

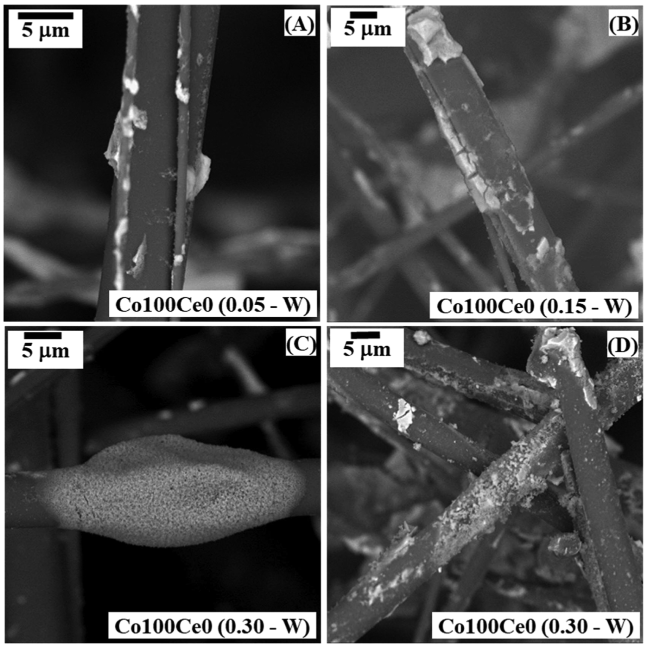

Figure 1. SEM micrographs of the catalytic ceramic papers [Co100Ce0 (*Z* − *W*)], prepared from aqueous solutions (*W*) with different concentrations (*Z*): 0.05 (A), 0.15 (B), and 0.30 M (C,D).

The morphology of the catalytic material deposited from a 0.30 M solution was variable. Two different forms were observed: (i) droplets of an average size 30 × 15 μm (Figure 1C) and (ii) small particles of an average 2 μm with a random dispersion (Figure 1D). However, the first one was the predominant morphology.

The effect of the solvent in the active-phase morphology and distribution can be observed in Figure 2. A better distribution and smaller particle sizes than those obtained with aqueous solution were observed in all cases. Figure 2A shows that the use of poly(vinyl alcohol) (PVA) produced small particles and well dispersed over the ceramic fibers. Impregnation with isopropyl alcohol also shows a homogeneous deposition of the active material on the ceramic fibers (Figure 2B), with particle shape and distribution similar to that obtained with PVA. Figure 2C,D shows the catalytic ceramic paper obtained by impregnation with the ethanol-based solution. A similar morphology to that obtained by impregnation with isopropyl alcohol is observed. In addition, the deposition of the active phase occurred over the whole ceramic paper (Figure 2D).

Table 2 lists the surface tension values of the solutions used for the impregnation by spray method. The better distribution of the active phase onto the ceramic fibers obtained with the alcohol-based solutions compared to those obtained with water could be related to the decrease in the surface tension, which favors the wetting of fibers since causes lower contact angles.

In order to investigate the element dispersion, energy-dispersive X-ray (EDX) mapping of catalytic ceramic papers is shown in Figures 3 and 4. As expected, constituent elements of the ceramic fibers (aluminum and silicon) are present throughout the fiber analyzed. Cobalt (Co) and cerium (Ce) are also found homogeneously distributed on the surface of the

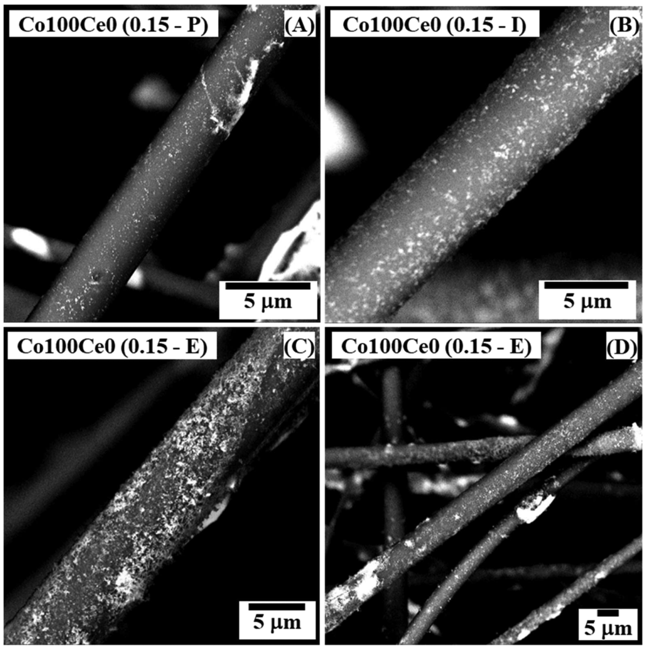

Figure 2. SEM images of the catalytic ceramic papers [Co100Ce0 (0.15 − *S*)] prepared with different solvents (*S*): polyvinyl alcohol (A), isopropyl alcohol (B), and ethanol (C,D).

Table 2. Surface Tension Values of the Impregnation Solutions

solution	surface tension (mN m^{-1})
water	70
ethanol (40% v/v)	32
isopropyl alcohol (60% v/v)	24
polyvinyl alcohol (0.5% w/v)	62
$Co(NO_3)_2$ 0.15 M in water	70
$Co(NO_3)_2$ 0.15 M in ethanol (40% v/v)	32
$Co(NO_3)_2$ 0.15 M in isopropyl alcohol (60% v/v)	24
$Co(NO_3)_2$ 0.15 M in polyvinyl alcohol (0.5% w/v)	64

fiber. The first one is deposited both on cerium oxide binder and on the fiber surface. The distribution of active phase over the fibers is improved with the PVA-based solution (Figure 4). This behavior could also be observed when the other organic solvents were used. In summary, the results indicate that the wet spray deposition method is suitable for obtaining a good active-phase distribution onto the ceramic substrate. Moreover, the dispersion is enhanced by controlling some features of the impregnation solution, that is, surface tension.

Crystalline phases corresponding to the fluorite-like cubic structure of CeO_2 and cobalt oxide spinel were identified in the X-ray diffractograms (Figure 5). Characteristic signals of cobalt oxide are identified at 2θ (°) = 31.3, 36.9, 38.6, 44.8, 55.7, 59.4, 65.3, 68.7, 74.2, 77.4, and 78.5, corresponding to the crystalline planes 111, 220, 311, 222, 400, 422, 511, 440, 531, 620, 533, and 622, respectively (JCPDS 421467). At 2θ (°) = 28.6, 33.1, 47.5, 76.8, and 79.1, the characteristic signals of cerium oxide (JCPDS 340394), corresponding to the crystalline planes 111, 200, 220, 331, and 420, respectively, are observed. The signals corresponding to the planes 311, 222, and 400 of the cerium oxide, overlap with that of the planes 422, 511, and 531 of cobalt oxide.

The estimated sizes of the CeO_2 and Co_3O_4 crystallites raised by spraying were calculated by the Scherrer equation. The planes used for the calculation of the crystal size were (111) and (220), respectively. The crystallite size of CeO_2 resulted between 7 and 9 nm for all the catalysts [Co*X*Ce*Y* (0.30 − *W*)], whereas the crystallite sizes of Co_3O_4 obtained were 14 nm for Co100Ce0 (0.15 − *W*) and 16 nm for Co100Ce0 (0.30 − *W*). For the catalysts with lower Co amounts, the crystallite sizes are not reported because of the low intensity in the X-ray diffraction signals, which provokes higher errors in their determination.

Raman spectra of different samples (Figure 6) show the five active vibration modes associated with CO_3O_4. The modes A_{1g} (691 cm^{-1}), F_{2g} (191, 521 and 681 cm^{-1}), and E_g (488 cm^{-1}) can be clearly differentiated. At 465 cm^{-1}, the characteristic signal of the crystal structure cubic of CeO_2 (fluorite) is also observed. This is the only allowed mode, T_{2g}, coming from the symmetric vibration Ce−O−Ce.[21]

2.2. Catalytic Activity and Stability.

Figures 7 and 8 show soot conversions obtained from temperature pro-

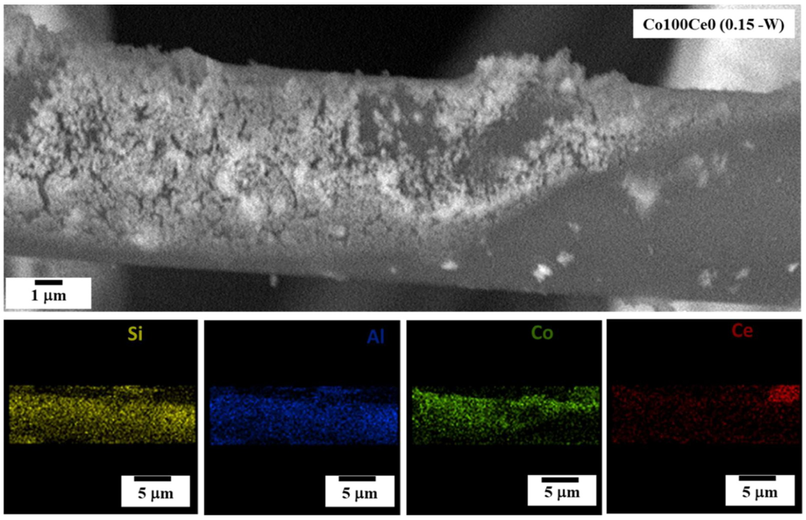

Figure 3. Elemental mapping analysis of the Co100Ce0 (0.15 − *W*) paper.

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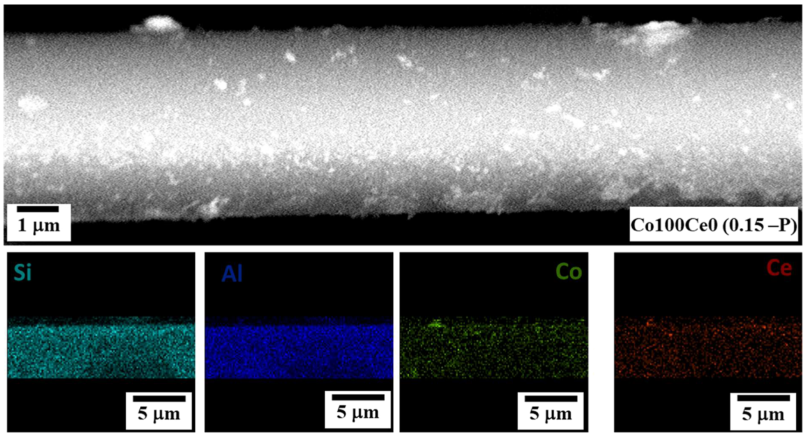

Figure 4. EDX mapping analysis of catalytic ceramic paper Co100Ce0 (0.15 − *P*).

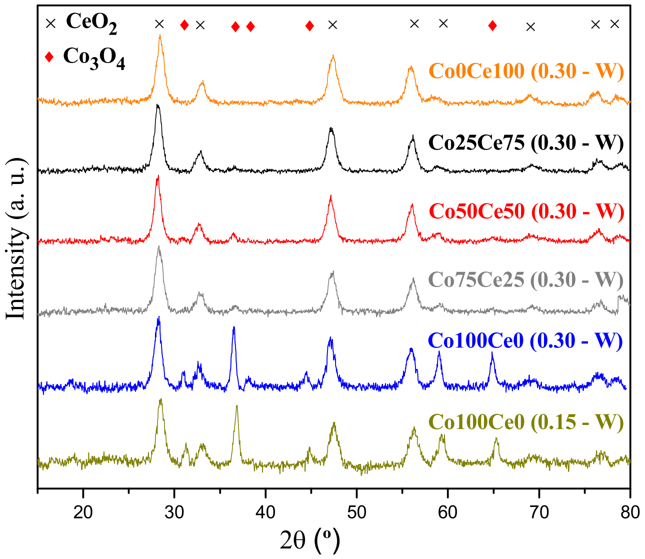

Figure 5. Crystalline phases of the synthesized catalytic ceramic papers.

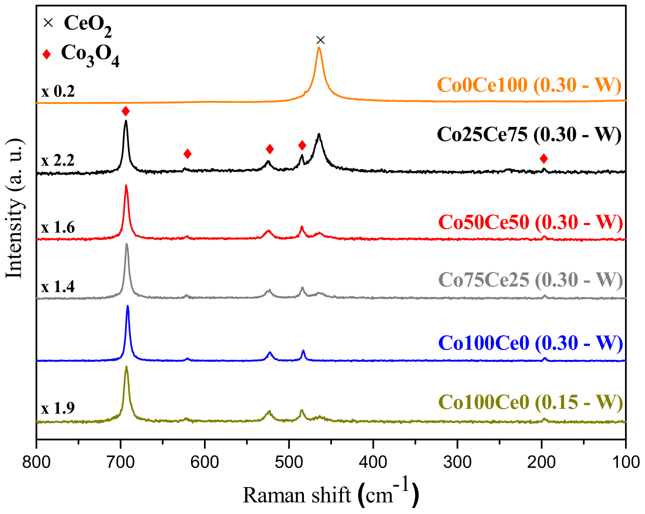

Figure 6. Raman spectra of the catalytic ceramic papers.

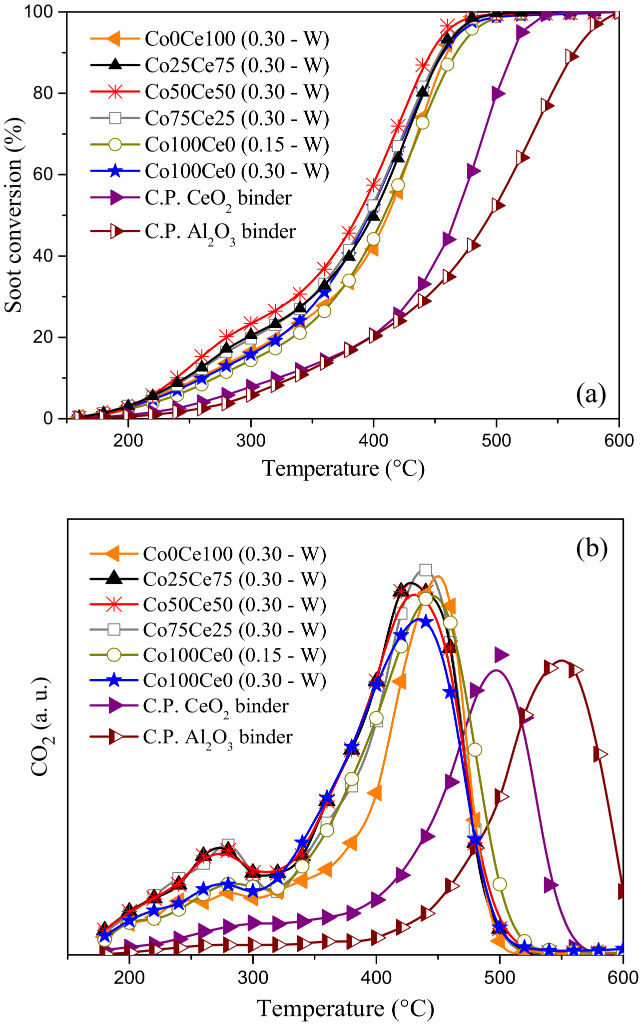

Figure 7. Catalytic behavior on soot conversion for the prepared ceramic papers. Reactor feed: 20 mL/min (18% O_2 + 0.1% NO, helium balance). Soot was loaded from a suspension of soot in hexane (600 ppm), being the amount loaded approximately 1 mg. (a) Soot conversion as a function of the reaction temperature. (b) TPO profiles (normalized with carbon content).

grammed oxidation (TPO) experiments for different catalytic papers and the corresponding TPO profiles. The activity of ceramic papers prepared using Al_2O_3 Nyacol as a binder is also shown as a blank. The change of cobalt concentration from 0.15 to 0.30 M or cerium incorporation to the solution leads to a slight shift of maximum conversion temperature toward

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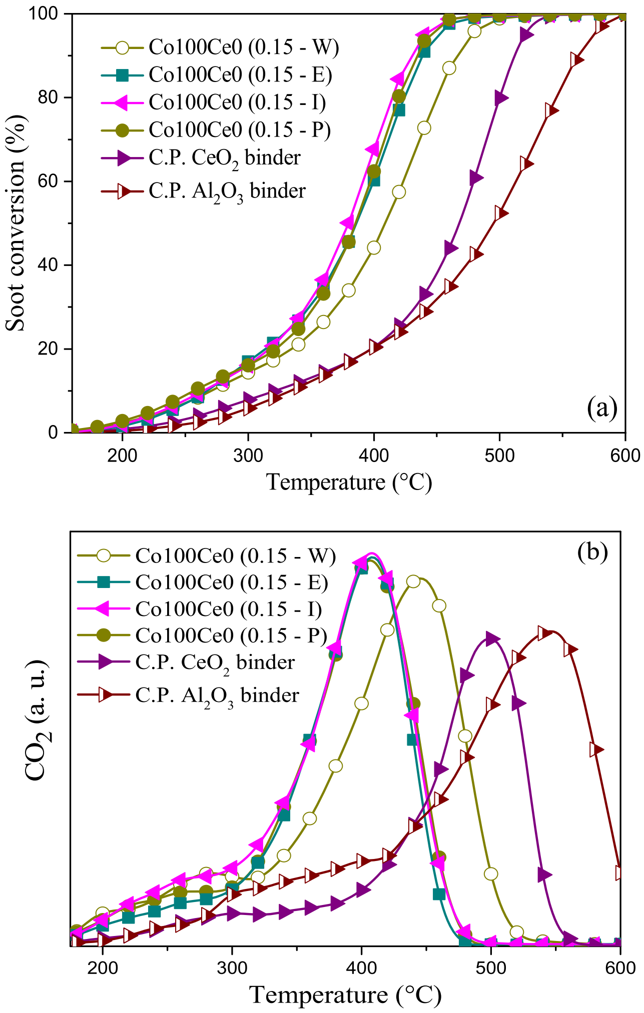

Figure 8. Catalytic behavior of ceramic papers impregnated with 0.15 M Co solutions. Cobalt nitrate was dissolved in different solvents: water (W), ethanol (E), isopropanol (I), and polyvinyl alcohol (P). Reactor feed: 20 mL/min (18% O_2 + 0.1% NO, helium balance). Soot loaded from a 600 ppm soot suspension in hexane. (a) Soot conversion as a function of the combustion temperature. (b) TPO profiles.

lower values, thus indicating a promoter effect on the catalytic activity. If the ceramic papers (C.P.) are analyzed, a catalytic effect of cerium oxide used as a binder is also observed. The catalytic activity of cerium oxide is related to its oxygen storage capacity and the formation of superoxides on the surface, which would react with the neighboring carbons or recombine to form O_2.[22]

The temperature of the noncatalytic combustion of soot is above 550 °C, which is close to that obtained when an alumina binder is used (C.P. Al_2O_3 binder, Figure 7). The use of ceria Nyacol as a binder decreases this maximum combustion rate temperature in about 50 °C. The catalytic activity is further enhanced after the incorporation of either Co and/or Ce nitrate solutions. Like cerium oxide, cobalt oxide presents variable oxidation states (Co^{3+}/Co^{2+}), which improve the storage—release of O_2 of the catalytic system. Also, Co species contributes to the oxygen availability of the catalyst.[23]

The differences in catalytic activity among the catalytic ceramic papers loaded with Co using different concentrations of the impregnation solutions are not significant. However, SEM and EDX analysis showed that the best distribution of the catalyst is achieved with the 0.15 M solution. Furthermore, the use of alcoholic solvents instead of water is beneficial to some extent for the catalytic activity. This effect would be related to a better soot−catalyst contact because of an improved catalyst distribution onto the fibers, also observed from SEM micrographs.

Despite the catalytic effect of CeO_2 incorporated as a binder was verified, the incorporation of cerium in the precursor solutions significantly improved the performance of the catalytic papers, as well as the addition of cobalt solution did. Nevertheless, the increase in the cobalt concentration from 0.15 to 0.30 M did not significantly modify the catalytic behavior. For this reason, Co100Ce0 (0.15 − *W*) was selected among the catalysts prepared using water as a solvent, as a representative sample for the subsequent analysis of the catalytic performance.

Figure 8 depicts the effect of the use of different solvents for the 0.15 M solutions used for the impregnation of ceramic papers. It can be observed that the use of alcohol solutions enhances the performance of ceramic papers as compared with those prepared with water solutions. This behavior is in agreement with characterization results that indicated a better distribution of cobalt in the ceramic matrix.

Stability tests were performed for Co100Ce0 (0.15 − *W*). Figure 9 shows the temperatures at 10, 50, and 90% of soot conversion (T_{10}, T_{50}, and T_{90}) for 15 consecutive tests. The analysis was also performed for the catalytic papers impregnated with the different solvents. Table 3 summarizes temperature T_{10}, T_{50}, and T_{90} values for the catalytic papers impregnated with water and solvent mixtures.

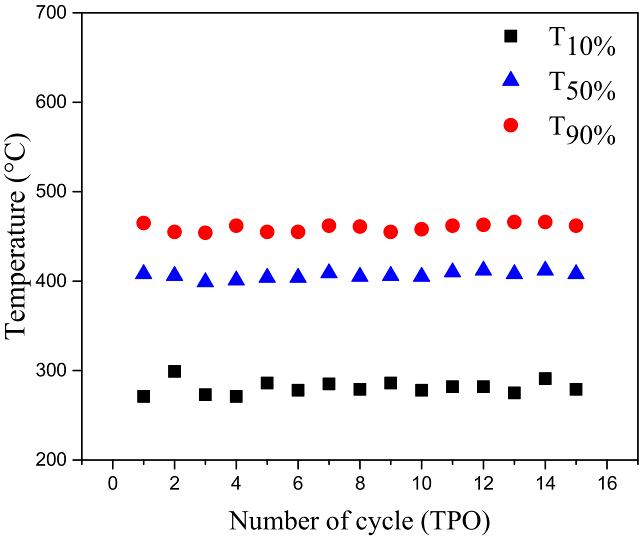

Figure 9. Catalytic stability of Co100Ce0 (0.15 − *W*) during 15 consecutive cycles of soot combustion: temperature at 10, 50, and 90% of soot conversion. Reactor feed: Q_t = 20 mL/min (18% O_2 + 0.1% NO, helium balance). Soot loaded from a 600 ppm soot suspension in hexane.

The catalytic ceramic papers prepared by the wet spray method showed a high catalytic stability after 15 TPO cycles under the same conditions, even when the maximum temperature of the tests is high (600 °C). This behavior provides promising results for future developments. It should be noted that after the cycles of reusing, the papers showed no

Table 3. Temperature Values for 10, 50, and 90% of Soot Conversion Obtained with Co100Ce0 (0.15 − *S*) papers Prepared from Different Solvents

catalyst	test number	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)
Co100Ce0 (0.15 − *W*)	1[a]	271	408	465
	5[a]	286	404	455
	10[a]	278	405	458
	15[a]	279	408	463
Co100Ce0 (0.15 − *E*)	1	288	405	455
	5	287	369	413
	10	295	387	449
	15	293	398	446
Co100Ce0 (0.15 − *I*)	1	271	381	451
	5	321	405	453
	10	285	384	433
	15	293	402	450
Co100Ce0 (0.15 − *P*)	1	329	414	459
	5	285	393	440
	10	307	416	461
	15	325	390	446

[a] Values extracted from Figure 9.

mechanical wear that would hinder their handling or lead to their rupture.

In order to evaluate the performance of these structures in soot combustion with different soot−catalyst ratios, four consecutive TPO tests were carried out with different soot loadings (600, 1200, 1800, and 2400 ppm) on the same sample (Co100Ce0 (0.15 M − *W*)). After 16 successive TPO runs, these samples were evaluated again with the 600 ppm soot suspension, designated as 600 ppm (b), Figure 10. Table 4 summarizes the average soot load produced by each soot suspension and the soot/catalyst ratio used.

Table 4. Soot Loading and Soot/Catalyst Ratio for Co100CeO (0.15 − *W*) Corresponding to the Stability Tests (Figure 10)

soot suspension concentration (ppm)	soot load (mg)	soot/catalyst ratio (wt/wt)
600	1.48	0.15
1200	2.46	0.24
1800	5.00	0.50
2400	6.73	0.67
600 (b)	1.48	0.15

Figure 10 shows the temperatures for the maximum rate of combustion for the evaluated samples. No significant changes were observed in the activity of the catalytic papers when exposing them to different types of interactions with the diesel soot. This would indicate a high stability of the systems against different interactions with the particulate material.

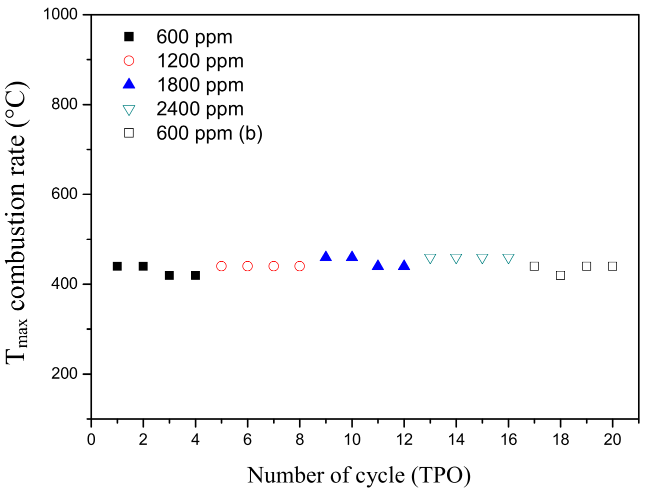

Figure 10. Catalytic stability of Co100Ce0 (0.15 − *W*) impregnated with different amounts of soot from suspensions with 600, 1200, 1800, and 2400 ppm. "b" indicates that the suspension of 600 ppm was used in two series of nonconsecutive runs (cycles 1−4 and 17−20). Reactor feed: 20 mL/min (18% O_2 + 0.1% NO, diluted in helium).

It is well-known the oxidizing character of NO and its contribution to the combustion of soot. In order to evaluate the Co100Ce0 (0.15 − *W*) catalytic papers under poorer oxidation conditions, four TPO tests were carried out using 600 and 2400 ppm soot suspensions without NO in the feed. The results were compared with TPO tests for ceramic papers with 600 and 2400 ppm carried out with 0.1% NO and 0% NO. Figure 11 shows the maximum combustion rate temperature of these tests. A high stability of the catalytic systems can be observed with different soot concentrations under poor oxidizing conditions. Moreover, no significant differences were observed comparing the performance for catalytic ceramic papers under the absence of NO or presence of NO. It should be noted that nitrogen oxides are present in the exhaust gases of diesel engines.

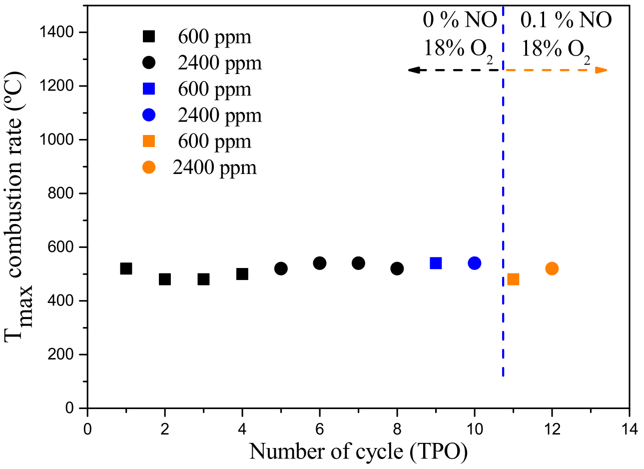

Figure 11. Effect of NO and soot amount on soot combustion. Temperature of maximum combustion rate for soot oxidation using Co100Ce0 (0.15 M − *W*) impregnated with different soot loadings. Reactor feed: 20 mL/min (18% O_2 + 0 or 0.1% NO, helium balance).

In order to subject the structure to extreme temperature conditions, similar to those that can be generated during filter operation, a set of Co100Ce0 (0.15 − *W*) papers was calcined at 900 °C for three different times (1, 30, and 120 min). Figure 12 shows the soot conversion of Co100Ce0 (0.15 − *W*) calcined at 600 and 900 °C for 1, 30, and 120 min and the corresponding TPO curves. A slight increase in the temperature of the maximum burning rate about 40 °C is observed, when the samples are submitted by 2 h at 900 °C, thus evidencing the high thermal stability of these structured systems.

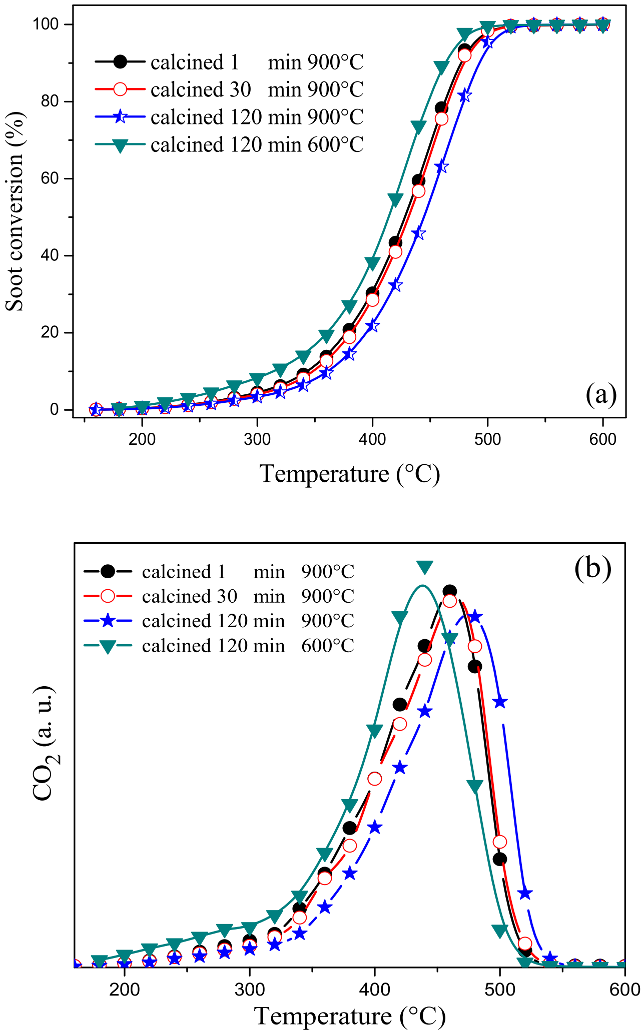

Figure 12. Thermal stability runs. Soot conversion for Co100Ce0 (0.15 − *W*) catalyst (calcined 120 min 600 °C) and the same calcined at 900 °C during different time range and the corresponding soot combustion profiles. Soot conversion curves (A) and the corresponding TPO profiles (B).

3. CONCLUSIONS

The wet spray method developed showed to be convenient to achieve a homogeneous deposition of the Ce and Co oxide precursors onto ceramic fibers. Active and stable structured catalysts were obtained.

The decrease in the surface tension of the precursor solutions resulted in a better distribution of the active phases onto the ceramic fibers, thus increasing the soot−catalyst contact and improving the catalytic activity.

TPO experiments showed that cerium and cobalt oxides act as active centers in the catalytic combustion of diesel soot. Although no significant differences were observed between the Co*X*Ce*Y* (*Z* − *W*) catalysts, the best performance was obtained for the catalyst with the equimolar mixture of cobalt and cerium.

Synthesized catalysts showed excellent thermal and chemical stability, even when they were submitted to high temperatures (900 °C). Despite the different soot loadings, the activity was maintained. This fact corroborates the correct distribution of the active phases onto ceramic fibers, thus making the wet spray method a useful tool for the preparation of structured catalysts.

4. EXPERIMENTAL SECTION

4.1. Ceramic Papers Preparation. A papermaking technique with a dual-polyelectrolyte retention system was used to prepare ceramic papers.[7−15] CeO_2 nanoparticles and polyelectrolytes were added in order to give mechanical resistance and favor the formation of flocs, respectively.

First, 10 g of ceramic fibers (50 wt % SiO_2, 48 wt % Al_2O_3), purified by elutriation and washing, was dispersed into a 1000 mL NaCl (0.01 M) aqueous solution under continuous stirring. Then, specific reagents were added in the following proportions and order: 66 g of cationic polyelectrolyte polyvinyl amine (Luredur PR 8095), 5 g of CeO_2 nanoparticle colloidal suspension (20% wt %, Nyacol), and 23 g of anionic polyelectrolyte polyacrylamide (A-PAM Aquatec, molecular weight 10^4 to 10^5 g/mol). After that, 1.5 g of cellulosic fibers was added to the mixture.

Finally, a sheet of 16 cm of diameter was formed by applying pressure (350 kPa) for 5 min and then again for 2 min. Then, the sheet was dried under controlled atmosphere (23 °C, 50% RH) for 24 h and then calcined in air at 600 °C for 2 h.

4.2. Wet Spray Deposition. With the aim of improving the dispersion of the active phase as well as the catalytic and mechanical stability, a wet spray method was developed. This method represents a modification of that reported by Tuler et al.[18] in which a dry spray was used, yielding a poor mechanical stability of the deposited particles. An ultrasonic nebulizer (Aspen NU410) was employed, and several catalytic papers were prepared by varying the Co−Ce atomic ratio in the precursor solution. To the impregnation stage, it is necessary to use a vacuum system. Ceramic papers were cut into discs (Ø = 16 mm) and inserted into a sample holder (see Figure 13).

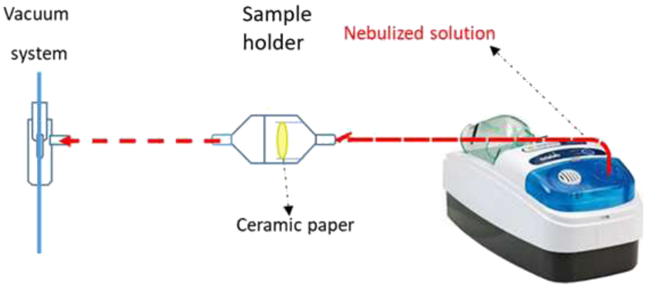

Figure 13. Scheme of the equipment used for the “wet spray” deposition.

The disc was submitted to the fog generated from the corresponding solution for 2 min by each side. After that, the ceramic papers were dried at room temperature for 24 h, and then, they were calcined in air at 600 °C during 2 h. In this way, catalytic ceramic papers were obtained.

The catalytic ceramic papers were named as Co*X*Ce*Y* (*Z* − *S*), where *X* and *Y* are the relative molar percentages of Co and Ce, respectively, *Z* is the molar concentration of the (Ce + Co) solution, and S is the solvent used to dissolve the precursors: water (W), ethanol 40% v/v (E), isopropyl alcohol 60% v/v (I), and poly(vinyl alcohol) 0.5% w/v (P). The concentration of alcohol was selected in order to modify the surface tension in the 20−70 mN m^{-1} range.

4.3. Characterization. The morphology of the synthesized papers was observed by SEM with a Phenom World ProX equipment (10 kV acceleration voltage). The composition and elemental dispersion were studied by EDX analysis with a device coupled to the microscope and 20 kV of acceleration voltage.

A Shimadzu XD-D1 instrument (Cu Kα radiation) was used in order to analyze crystalline phases. A range between 15° and 80° at a scan rate of 2°/min was measured.

A Horiba Jobin Yvon LabRAM HR instrument was employed to obtain laser Raman spectra. The excitation wavelength was 532.13 nm and the laser power was set at 30 mW.

Surface tension values were obtained by the ring method using a Du Noüy tensiometer.

4.4. Catalytic Activity Tests. Soot particles were obtained by burning commercial diesel fuel (YPF, Argentina). Then, the soot was dried in a stove at 120 °C for 24 h. Finally, it was dispersed in *n*-hexane and suspensions of different concentrations of soot were prepared, ranging from 600 to 2400 ppm. A thorough characterization of the prepared soot is reported elsewhere.[24]

First, catalytic ceramic discs were impregnated by dripping with the soot suspension. Then, they were dried overnight at room temperature. To evaluate the catalytic activity and stability, soot-impregnated ceramic paper discs were stacked into a quartz reactor and then they were heated at 5 °C/min, from 25 up to 600 °C. The feeding was composed by O_2 (18%) + NO (X) diluted in high purity He. The used NO concentration was 0 or 0.1%, according to the test. The total flow rate was maintained in 20 mL/min. The exhaust gases were analyzed by a Shimadzu GC-2014 chromatograph with a thermal conductivity detector.

Stability runs were carried out using the same ceramic paper discs and incorporating soot after each TPO run. Both the feeding composition and the amount of soot loaded for each run were varied.

Despite the soot-to-catalyst contact conditions are far from those found in a real engine, they were selected in order to study the soot combustion reaction under controlled experiments. In this way, it is possible to regulate the amounts of soot loaded, which allows the comparison of the catalytic behavior of different structured systems.

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Notes

The authors declare no competing financial interest.

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