

Ceria-Coated Diesel Particulate Filters for Continuous Regeneration

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Abstract

The potential of diesel particulate filters wash-coated with highly dispersed nano-metric ceria particles for continuous regeneration has been investigated. To this end, catalytic filters were prepared, soot-loaded (avoiding the formation of the cake layer), and regenerated—under isothermal conditions—at temperature ranging from 200–600 °C. Results have shown that catalytic oxidation of soot starts from 300 °C and, at all temperatures, the selectivity to CO₂ is higher than 99%. 475 °C is the minimum temperature at which the filter is regenerated via catalytic path. At this temperature, the catalytic filter maintains substantially the same performance over repeated cycles of soot loading and regeneration, indicating that the thermal stability of ceria is preserved. This has been further confirmed by comparison between the outcomes obtained from characterization (X-ray powder diffraction, N₂ adsorption at 77 K, Hg intrusion porosimetry, and scanning electron microscope/energy dispersive X-ray analysis) of fresh filter and filter subjected to repeated regeneration tests.

Keywords: diesel soot, catalyst-coated diesel particulate filters, continuous regeneration, catalyst thermal stability, ceria.

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Introduction

Diesel particulate filters (DPFs) are the most efficient option for removing particulate matter (PM), which is mostly made of soot, from diesel engine exhaust [1]. They are obtained from “flow-through” monoliths by alternatively plugging adjacent channels at each end. The resulting “wall-flow” configuration forces the exhaust gas to pass through the porous walls of the substrate which, thus, retain the soot particles. In order to prevent excessive buildup of pressure drop, the DPF is regenerated periodically to remove the accumulated soot by combustion.

During thermal regeneration of DPFs, the exhaust gas temperature (200-500°C) is increased up to the point that soot oxidation can be self-sustained at fast enough rates ($> 600^{\circ}\text{C}$) [2,3]. Such an approach, also referred to as “active regeneration”, incurs additional energy costs and requires complex means of control. Furthermore, in some cases, local temperature excursions may arise that are sufficiently high to melt the DPF. At least in principle, catalytic regeneration may allow to overcome these drawbacks [4].

The ability of a catalyst to diminish the temperature required for soot combustion is surely dependent on its intrinsic activity. However, due to the solid-solid reaction occurring in catalytic soot oxidation, also the efficiency of the soot-catalyst contact plays a crucial role [5,6]. Ceria-based materials are among the most active catalysts for soot oxidation [7,8]. This is due to the redox properties of the Ce^{4+} - Ce^{3+} couple as well as to the capability of ceria to exchange oxygen with the gas phase. In particular, the oxygen transfer, which occurs by superficial diffusion between ceria particles and soot particles, makes the solid-solid contact a key issue for an efficient soot combustion [8].

In order to increase the number of soot-catalyst contact points, thus improving the efficiency of the solid-solid contact, ceria-based catalysts with morphology tuned at a nanoscale level have been proposed and tested in powdered soot-catalyst mixtures [9-13]. Such test conditions are

substantially far from the conditions of solid-solid contact actually established during a process of catalytic filter regeneration. In particular, within the filter, the accessibility of soot to ceria nanoparticles may be very limited, thus making the increased surface area of ceria related to the special morphology in most cases ineffective.

Catalytic soot oxidation has also been investigated in both “flow-through” monoliths [14] and filters [15-17] coated with ceria-based materials. In particular, the issue of the soot-catalyst contact has been explored under realistic conditions of filter regeneration in Refs. [15,16]. In both works, temperature programmed regeneration tests were performed.

In Ref. [15], filters were coated with the same amount of an optimized ceria-praseodymia active phase and loaded with different amounts of soot. Results have allowed the identification of a critical catalyst/soot ratio below which the solid-solid contact becomes so weak as to hinder catalytic regeneration.

Our previous work has been focused on the study of the effect of the catalyst/soot ratio on the regeneration regime for filters wash-coated with nano-metric ceria particles [16]. The procedure adopted for the deposition of ceria along with its limited load allowed to obtain a high dispersion with a deep penetration of the catalyst into the macro-pores of the filter walls. Indeed, in order to preserve the filtration properties, the accumulation of a wash-coat layer on top of the channel walls was prevented, thus ensuring the accessibility of soot to the porosity of the filter. Results have shown that, a transition occurs, with decreasing catalyst/soot ratio (i.e., increasing soot load), from a regime of almost purely catalytic regeneration to a regime of catalyst-assisted thermal regeneration. In the former regime, most of the soot is trapped inside the macro-pores of the filter walls, thus coming in close contact with highly dispersed catalyst. As a consequence, regeneration occurs via catalytic path at low temperatures. In the latter regime, most of the soot is accumulated in the form of a rather thick cake layer on top of the filter walls.

The soot cake is substantially segregated from the catalyst and, as such, it burns via thermal path at high temperatures.

From these results, it has been concluded that, once assured a good catalyst dispersion inside the macro-pores of the filter walls, in order to optimize the soot-catalyst contact, it is essential to minimize the thickness of the cake layer. Indeed, the segregation between the soot cake and the catalytic wall is the main obstacle to making catalytic regeneration a real alternative approach to thermal regeneration. This is further confirmed by the fact that, in the presence of cake, the formation of hot zones remains a critical issue also for regeneration of catalytic DPFs [18-22]. In addition, it is worth highlighting that active regeneration of catalytic DPFs may lead to nano-metric PM emissions as well as to modified production of other gaseous pollutants [23]. The amount of soot trapped inside the filter walls is much lower than the amount of soot accumulated as cake on top of them (typically, 20 % versus % 80 of the total). As a consequence, when minimizing the cake thickness, the frequency of switching between the two steps of filtration and regeneration would be too high and likely not feasible.

In order to prevent the formation of the soot cake, while still ensuring a feasible process, catalytic regeneration should proceed simultaneously with filtration. In an ideal continuous process, the soot particles enter an empty filter and, thus, easily come into contact with the catalyst. Under such conditions, soot is burned off without remaining deposited within the filter. The absence of soot storage and, in particular, of cake also prevents the formation of hot zones, thus allowing to regenerate the filter under isothermal conditions.

In this work, the potential of ceria-coated DPFs for continuous regeneration has been investigated. To this end, isothermal regeneration tests were carried out on catalytic filters loaded with a very low amount of soot suitably chosen to minimize the formation of the cake layer. Different temperatures were explored, thus identifying the minimum temperature that allows filter regeneration via catalytic path. At that minimum temperature, the thermal stability

of the ceria coating was verified by repeating the steps of soot loading and regeneration more times on the same filter. X-ray powder diffraction (XRD), N₂ adsorption at 77 K, Hg intrusion porosimetry, and scanning electron microscope (SEM)/energy dispersive X-ray (EDX) analysis were used to characterize the filter subjected to repeated regeneration tests. Outcomes were compared with those obtained from characterization of samples of fresh ceria-coated filter.

Materials and Methods

The method of filter preparation method and the set-up for filter regeneration tests were detailed in our previous paper [16]. In this section, they are only briefly recalled.

Filter Preparation

A commercial silicon carbide (SiC) filter (IBIDEN - 180 cps; porosity = 0.42) was cut to obtain lab-scale filters with the desired shape and size (cylinder with diameter = 1.3 cm and length = 3 cm). During the cutting operation, the original plugs of the filter were lost. They were recovered (thus recovering the original filter configuration) by plugging the opposite ends of adjacent channels of the monolith with a ceramic paste (Rescor Castable Ceramics, 770, COTRONICS CORP.).

For catalyst coating, a dip-coating technique was employed. A colloidal suspension (NYACOL, CeO₂ (AC)) of ceria nano-particles (10-20 nm) was the catalyst source. After dipping, the filter was dried and, then, calcined at 450°C. About 1 g of ceria was loaded corresponding to ~ 17 % of the final weight of the filter, and to a catalyst weight per unit volume of the filter equal to ~ 250 g/l. The procedure adopted for the deposition of ceria along with its limited load allowed us to obtain a high dispersion of the catalyst inside the filter macro-pores, avoiding major changes in pore size distribution compared to the original bare filter [16].

Soot was loaded by dipping the washcoated filter in a suspension of Degussa Printex U (1 g) in heptane (100 ml - Sigma Aldrich) [24]. This surrogate soot is less reactive than diesel soot [25]. The soot load was around 0.01 g, thus obtaining a catalyst/soot ratio equal to ~ 100 w/w in correspondence to which the formation of the cake layer was minimized [16]. This is an essential issue when assessing the performance of catalytic filters for continuous regeneration through batch-mode tests. On the other hand, under such conditions, most of the loaded soot was trapped inside the filter macro-pores, thus coming in close contact with ceria [16].

Isothermal Regeneration Tests

Tests of filter regeneration were performed in a lab-scale rig under O₂/N₂ atmosphere. In the absence of NO, ceria-catalyzed soot combustion takes place only according to the “active oxygen” mechanism, whereas the “NO₂-assisted” mechanism is ruled out [8].

The soot-loaded catalytic filter was placed in a tubular quartz reactor located in a tubular electric furnace (LENTON LTD mod. PTF 12/38/500). A typical test consisted of three phases: 1) pre-heating phase; 2) isothermal phase; 3) heating-ramp phase. During Phase 1), the filter was preheated in N₂ stream (47 l(STP)/h) by increasing the furnace temperature (10°C/min) up to the temperature of Phase 2). During Phase 2), the filter was kept at constant temperature for around 2 h, while feeding 15 vol. % O₂/N₂ (47 l(STP)/h). During Phase 3), the furnace temperature was increased up to 700°C (heating rate of 10°C/min), while still feeding O₂/N₂ to oxidize residual soot not burned during Phase 2).

Different temperatures of the isothermal phase were explored (from 200 to 600°C), thus identifying the minimum temperature for filter regeneration via catalytic path. At that minimum temperature, the thermal stability of the ceria coating was verified by repeating three cycles of soot loading and regeneration on the same filter. These regeneration tests consisted only of Phase 1) and Phase 2), whereas Phase 3) (heating ramp up to 700°C) was skipped to avoid high temperatures and, thus, thermal sintering with consequent irreversible deactivation of ceria.

The filter temperature was measured by the insertion of thermocouples at the entrance and exit of the central channel. In all tests, both temperatures were substantially the same.

The gas mixture exiting the reactor entered an analysis system including a Fisher-Rosemount NGA2000 analyzer for simultaneous analysis of CO and CO₂ by IR detectors, and O₂ by a paramagnetic detector. The filter was weighted before and after each regeneration test to verify the carbon balance, which was closed within an error of ± 10 %.

Filter characterization

The catalytic filter that underwent repeated regeneration tests was deeply characterized. X-ray powder diffraction (XRD) patterns were recorded with a Bruker D2 Phaser diffractometer (operated at diffraction angles ranging between 10 and $80^\circ 2\theta$, with a scan velocity equal to $0.02^\circ 2\theta \text{ s}^{-1}$). XRD analysis was also extended to fresh ceria-coated and original (bare) filters. The BET surface area was estimated using a Quantachrome Autosorb 1-C by N_2 adsorption at 77 K after degassing the samples for 2 h at 150°C . The pore size distribution (PSD) in the region of macro-pores was evaluated using a Micromeritics Autopore IV by the Hg intrusion porosimetry technique. The internal morphology of filter channels was observed using a FEI Inspect Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray (EDX) probe for the elemental mapping.

The BET surface area, the PSD in the region of macro-pores and the internal channel morphology were compared to the outcomes previously obtained from characterization of samples of fresh ceria-coated filter [16].

Results and Discussion

In this section, results of isothermal regeneration tests performed on ceria-coated filters at different temperatures are described and discussed. Three cases representative of two extreme conditions (i.e., low temperature and high temperature) and an intermediate condition (i.e., intermediate temperature) are first presented, starting from this latter case. Then, the transition from low to high temperature is illustrated, thus identifying the minimum temperature required to get regeneration of the filter via catalytic path. At that temperature, the thermal stability of the ceria catalyst was assessed by repeating the steps of soot loading and regeneration three times on the same filter. The final part of this section is focused on those results as well as on the characterization of the filter that underwent all three regeneration tests.

It is worth reminding that, for all tests, the catalyst/soot ratio (~ 100 w/w) was suitably chosen to minimize the formation of the cake layer and, thus, to promote catalytic filter regeneration, as expected from the results reported in our previous work showing that, with this ratio, 50 % of the soot initially loaded into the filter is burned via catalytic path within around 500°C in a temperature programmed test [16].

Intermediate, Low and High Temperature

Figure 1 shows the time histories of CO_2 concentration and filter temperature as registered during the catalytic regeneration test carried out by setting the furnace temperature for the isothermal phase to 475°C . CO concentration (not shown) is negligible over the whole temperature range ($25\text{-}700^{\circ}\text{C}$), resulting in an almost complete selectivity to CO_2 ($> 99\%$). This confirms our previous results obtained from catalytic regeneration tests under temperature programmed conditions, showing selectivity to $\text{CO}_2 > 99\%$ provided that the catalyst/soot ratio is ≥ 35 w/w [16].

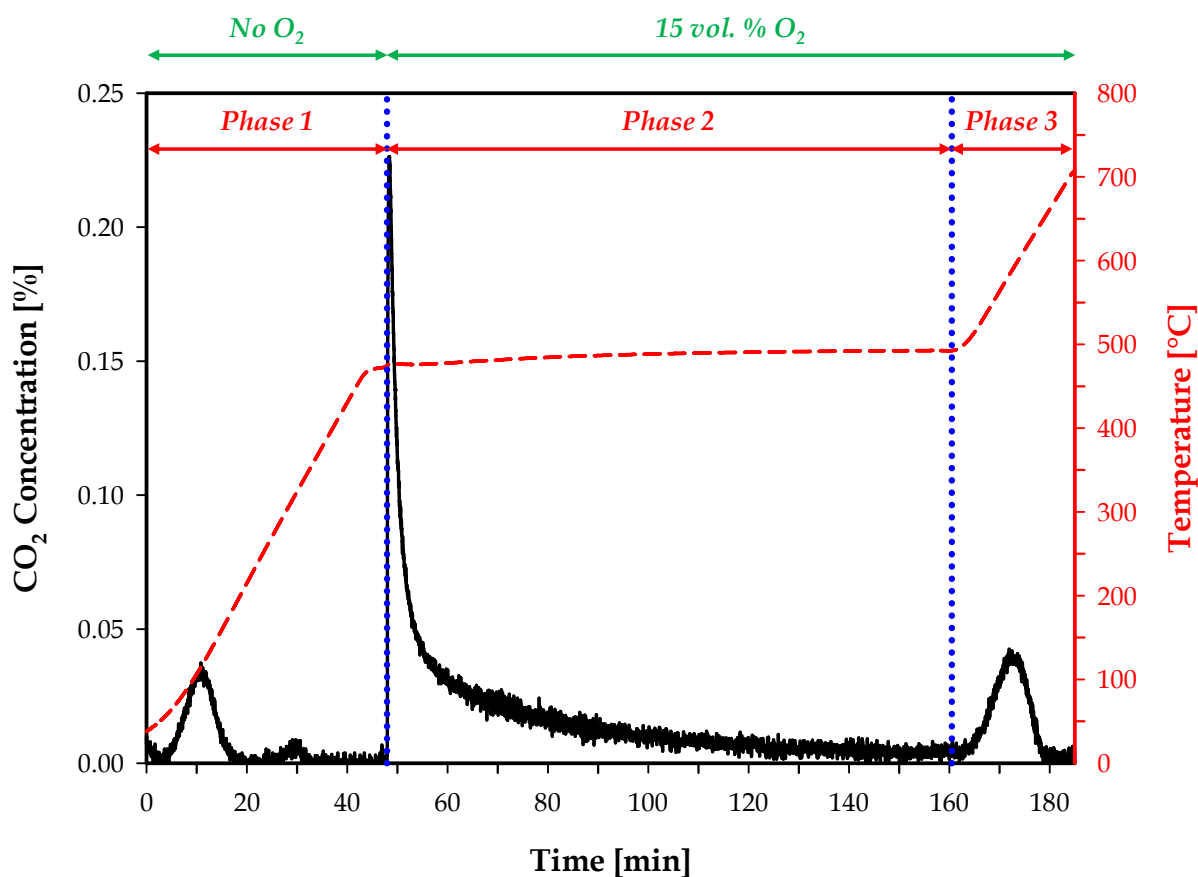


Figure 1. Time histories of CO₂ concentration and filter temperature: Catalytic regeneration test carried out by setting the furnace temperature for the isothermal phase (Phase 2) to 475°C.

During Phase 1, despite the absence of O₂ in the feed, a CO₂ peak centered at around 115°C is detected. This temperature is too low to address the peak to soot combustion. Indeed, it corresponds to desorption of CO₂ physically pre-adsorbed over ceria (at room temperature). This has been confirmed by tests performed on ceria-coated filters, not loaded with soot, heated in N₂ atmosphere from 25°C to 250°C. It has been found that the amount of CO₂ desorbed is directly linked to the amount of ceria covering the filter. On the other hand, good capacity of CO₂ adsorption for ceria has also been found in our previous work [26]. In that work, desorption of CO₂ pre-adsorbed over ceria has been observed in the same temperature range as Phase 1 in this work.

No other significant CO₂ emission is detected under inert flow conditions up to 475°C.

During Phase 2, a second CO₂ peak is found as soon as O₂ is introduced into the feed. This peak corresponds to the oxidation of around 85 % of the soot initially loaded into the filter, meaning that the filter is almost completely regenerated during Phase 2. The remaining soot is oxidized during Phase 3, when the furnace temperature is increased up to 700°C, producing a third small CO₂ peak centered at about 580°C.

In Figure 2, the results of the catalytic regeneration test of Figure 1 are shown along with the results (CO and CO₂ profiles) of a thermal regeneration test carried out under the same conditions (but in the absence of catalytic washcoat). For Phase 1 and Phase 3, both involving a heating ramp, the data are plotted versus the filter temperature. For Phase 2, the data are plotted versus time (starting from the instant when O₂ is fed).

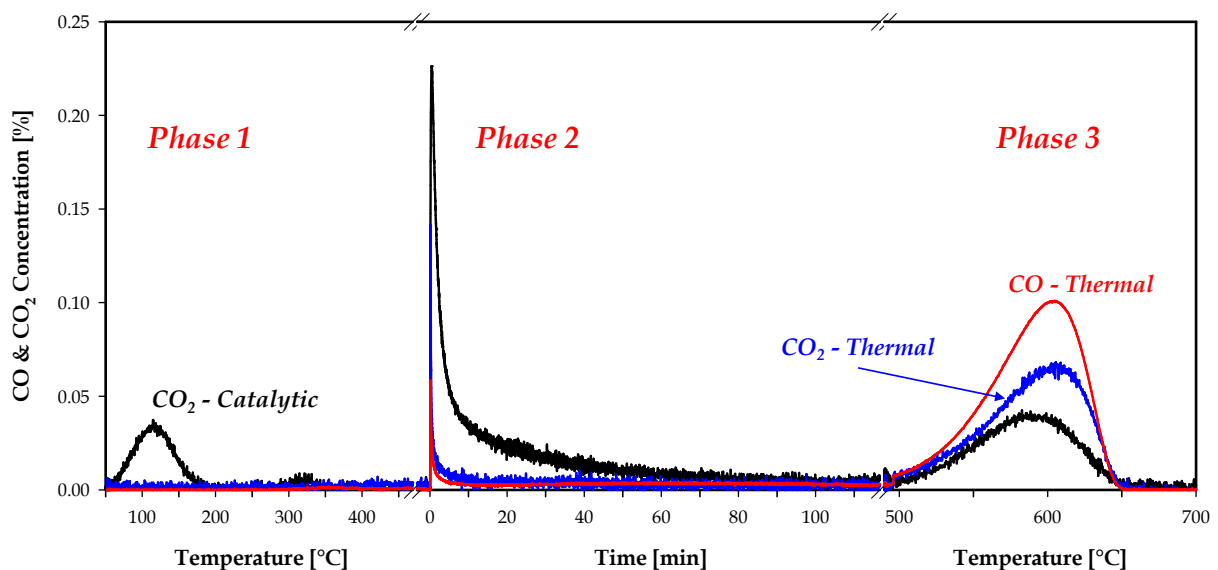


Figure 2. Results of catalytic and thermal regeneration tests carried out by setting the furnace temperature for the isothermal phase (Phase 2) to 475°C. For thermal regeneration, CO and CO₂ profiles are shown. For catalytic regeneration, only CO₂ profile is shown, being selectivity to CO₂ > 99 %.

In the case of the thermal regeneration test, the low temperature CO₂ emission of Phase 1 is not observed, as expected due to the absence of the ceria coverage. Furthermore, the introduction of O₂ into the feed at 475°C does not provide a significant oxidation of soot. Only 15 % of the

soot initially loaded into the filter is burned during Phase 2. Indeed, most of the soot (85 %) is oxidized at higher temperatures during Phase 3. A limited soot combustion over the range 400-500°C has also been observed in a temperature programmed test of thermal regeneration reported in our previous work [16].

Global assessment of Figure 2, thus, demonstrates that the nature of the second CO₂ peak is essentially catalytic. The abrupt appearance of this peak in concomitance with the introduction of O₂ into the feed highlights the key role played by the gas-phase O₂ in activating ceria-catalyzed soot combustion. On the other hand, as already found in our previous work [16], in going from catalytic to thermal regeneration, the selectivity to CO₂ drops from ~ 99 % to ~ 40 %, meaning that ceria also activates CO oxidation.

Figure 3 shows the time histories of CO₂ concentration and filter temperature as registered during the catalytic regeneration test carried out by setting the furnace temperature of the isothermal phase to 200°C.

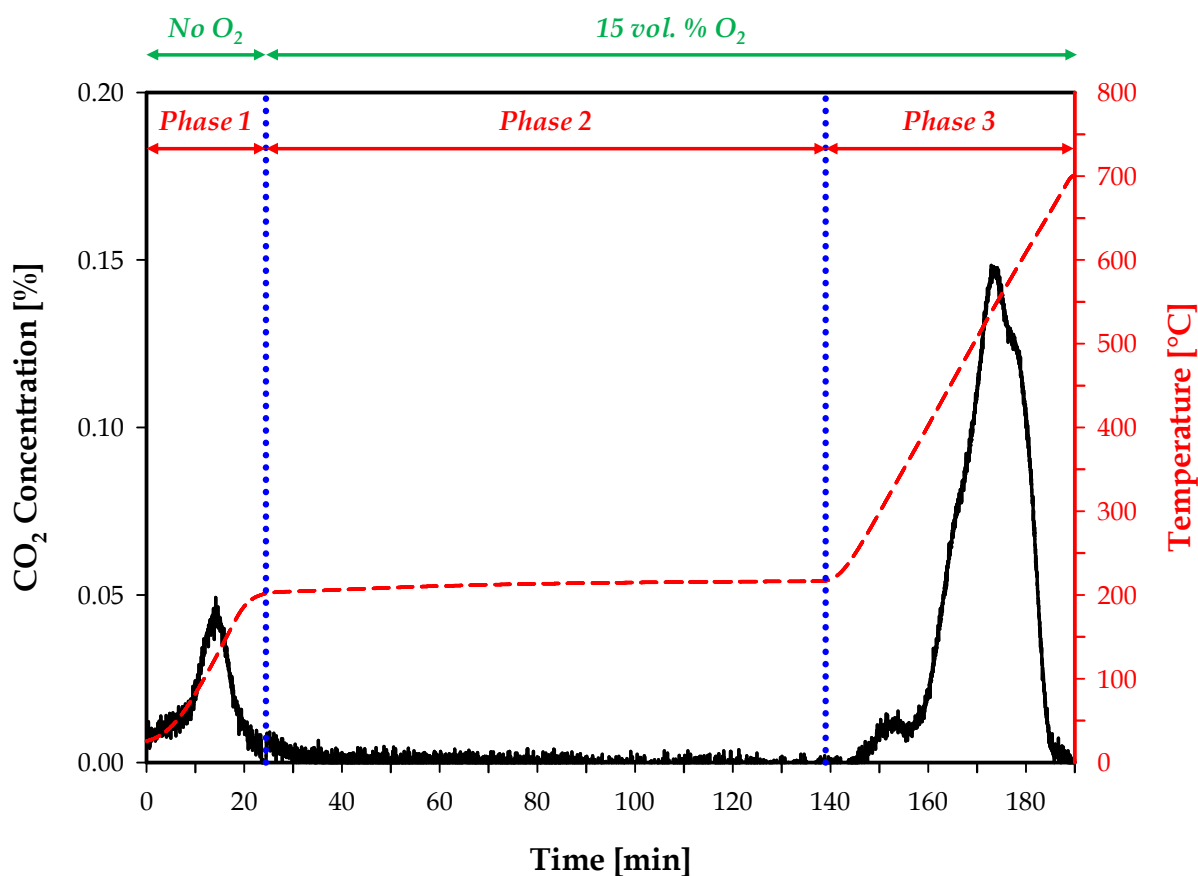


Figure 3. Time histories of CO₂ concentration and filter temperature: Catalytic regeneration test carried out by setting the furnace temperature for the isothermal phase (Phase 2) to 200°C.

As expected, the first peak of Phase 1 is still present and unchanged, being related to CO₂ pre-adsorbed over ceria. However, as far as Phase 2 and Phase 3 are concerned, significant qualitative and quantitative differences can be observed when moving from 475°C to 200°C. In particular, differently from the isothermal phase at 475°C, no peak is detected during Phase 2 carried out at 200°C, whereas all soot is burned during Phase 3. In this case, the filter temperature is too low to promote catalytic oxidation of soot during the isothermal phase. All soot is burned during the phase of heating ramp at temperatures higher than 200°C and, thus, via both catalytic and thermal oxidation. This results in a CO₂ peak centered at around 540°C, as already observed in a previous catalytic regeneration test performed under temperature

programmed conditions [16]. The small shoulder appearing at about 300°C is likely of purely catalytic nature.

Finally, in Figure 4, the time histories of CO₂ concentration and filter temperature are shown as registered during the catalytic regeneration test carried out by setting the furnace temperature of the isothermal phase equal to 550°C.

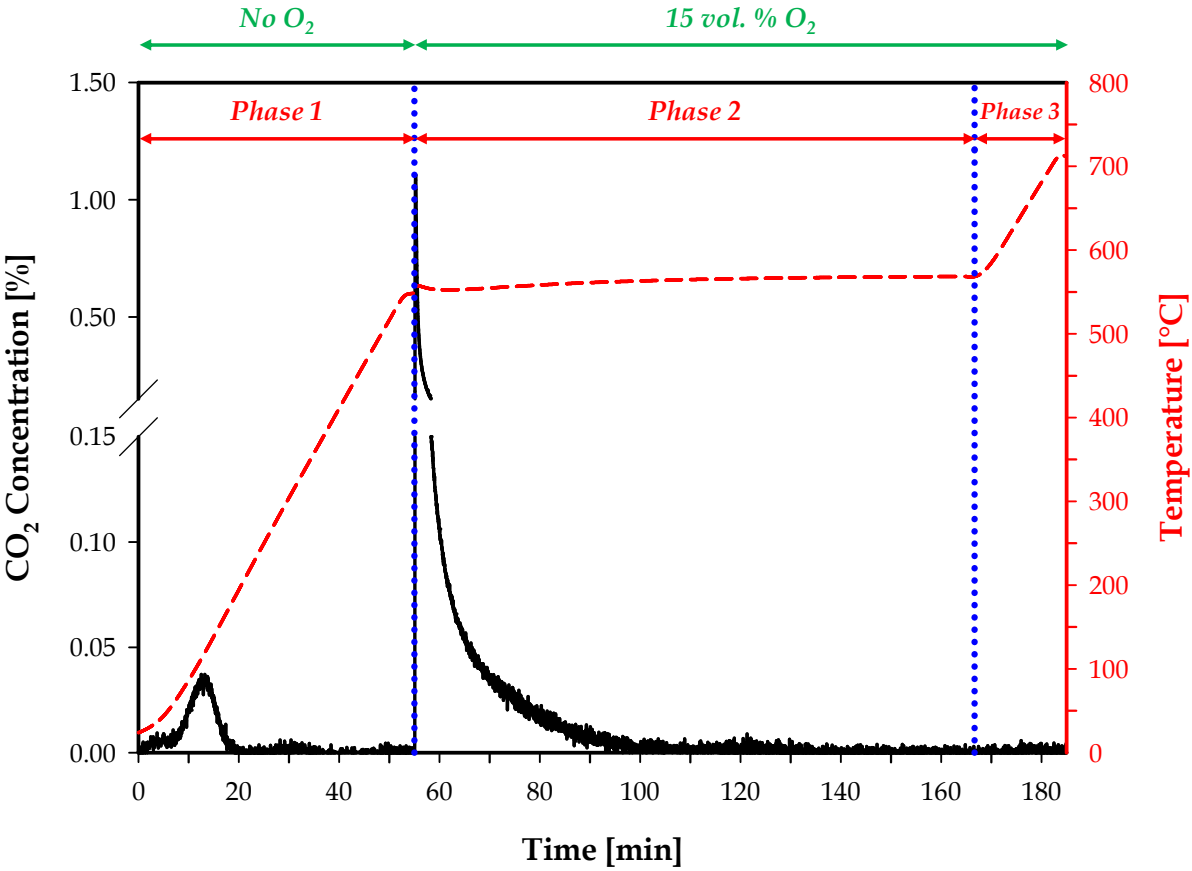


Figure 4. Time histories of CO₂ concentration and filter temperature: Catalytic regeneration test carried out by setting the furnace temperature for the isothermal phase (Phase 2) to 550°C.

Leaving out the description of Phase 1, which is substantially the same as in Figures 1 and 3, Phase 2 and Phase 3 strongly differ. In this case, the filter temperature is sufficiently high to promote the complete oxidation of soot during the isothermal phase. Indeed, no CO₂ peak is found during Phase 3.

Minimum Temperature for Catalytic Regeneration

Figure 5 provides a general overview, in terms of CO₂ concentration normalized with respect to the mass of soot initially loaded into the filter, of catalytic regeneration tests carried out by varying the furnace temperature for the isothermal phase (Phase 2) from 200°C to 600°C.

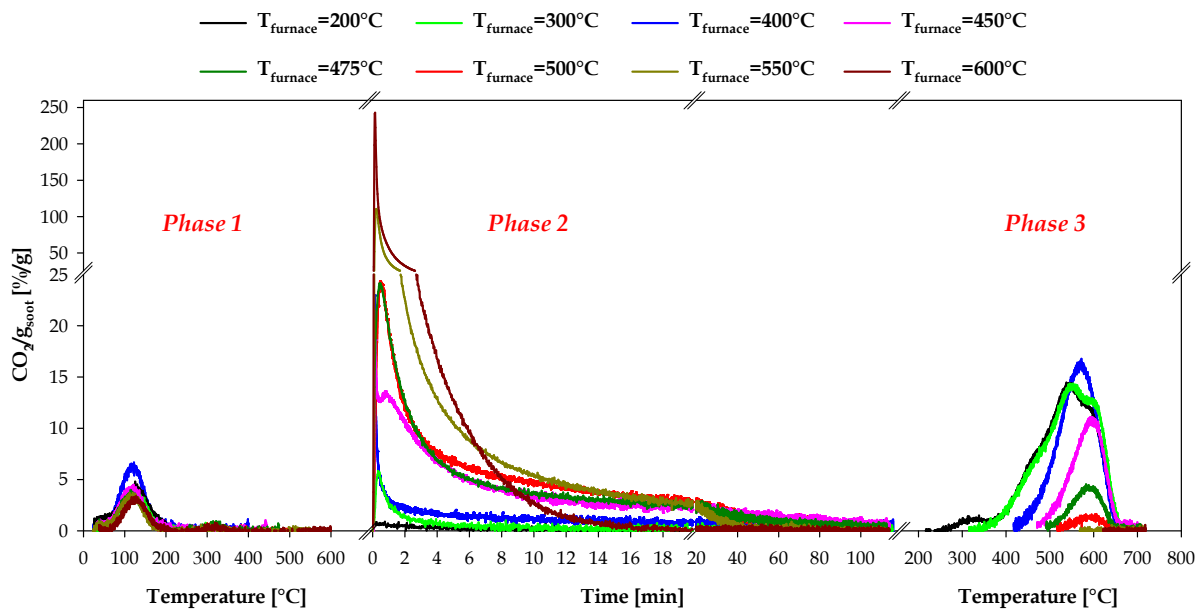


Figure 5. CO₂ concentration (normalized with respect to the mass of soot initially loaded into the filter) obtained from catalytic regeneration tests carried out by varying the furnace temperature for the isothermal phase (Phase 2) from 200°C to 600°C. For Phase 1 and Phase 3 (phases of heating ramp), the data are plotted versus the filter temperature. For Phase 2, the data are plotted versus time (starting from the instant when O₂ is fed).

Let us focus on Phases 2 and 3. As the furnace temperature for the isothermal phase is increased, a transition occurs from a profile of CO₂ characterized by only one peak during Phase 3 (at low temperature: 200°C) to profiles characterized by only one peak during Phase 2 (high temperature: 550°C and 600°C). Soot (catalytic) oxidation starts from around 300°C. In going from low to high temperature, the area underlying the peak of Phase 2 increases, whereas the area underlying the peak of Phase 3 decreases. This means that the role played by Phase 2 increases, whereas the role played by Phase 3 decreases.

The role of Phase 2 is quantified in Figure 6 where the soot conversion for this phase (red curve) is plotted as a function of the furnace temperature. Triangles represent the results of repeated tests (at 475°C, 500°C and 600°C), showing good repeatability. These data are compared with those extracted from a previous catalytic regeneration test performed under temperature programmed conditions (black plot) [16].

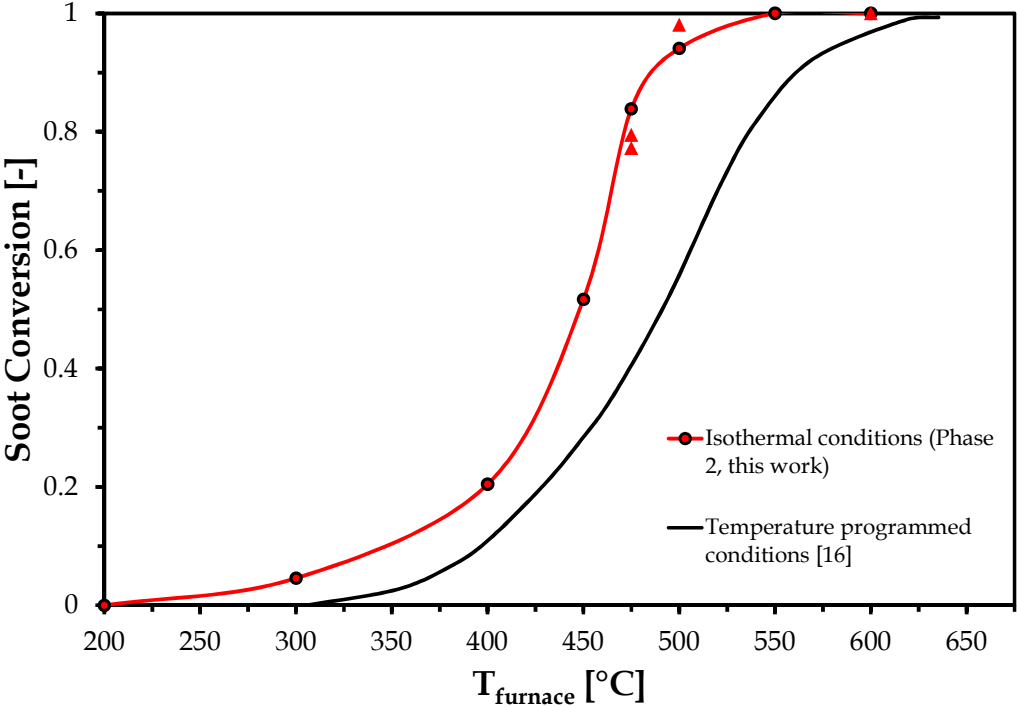


Figure 6. Soot conversion versus furnace temperature of Phase 2 (isothermal phase). Triangles represent results of repeated tests. The black plot corresponds to results extracted from a previous catalytic regeneration test performed under temperature programmed conditions [16].

In the range 450-475°C the slope of the curve strongly rises. Indeed, in going from 450°C to 475°C, the soot conversion under isothermal conditions increases from about 0.5 to about 0.85. 475°C is, thus, a turning temperature. In particular, this temperature is assumed as the minimum temperature for a substantially complete filter regeneration via catalytic path.

Under temperature programmed conditions, the soot conversion is underestimated, being lower than that found under isothermal conditions at each temperature. This suggests that tests under

temperature programmed conditions can be useful for a fast screening of catalytic filters (and, more generally, catalysts), however isothermal tests are more adequate for a quantitative assessment of their performance.

Thermal Stability of the Ceria Coating

The thermal stability of the ceria coating, which is a basic prerequisite for the continuous operation of the catalytic filter, was verified at the minimum temperature for filter regeneration via catalytic path (i.e., 475°C). To this end, the steps of soot loading and regeneration were repeated three times on the same filter. In these regeneration tests, Phase 3) (heating ramp up to 700°C) was skipped to avoid high temperatures and, thus, thermal sintering with consequent irreversible deactivation of ceria. Figure 7 shows the results of these repeated regeneration tests.

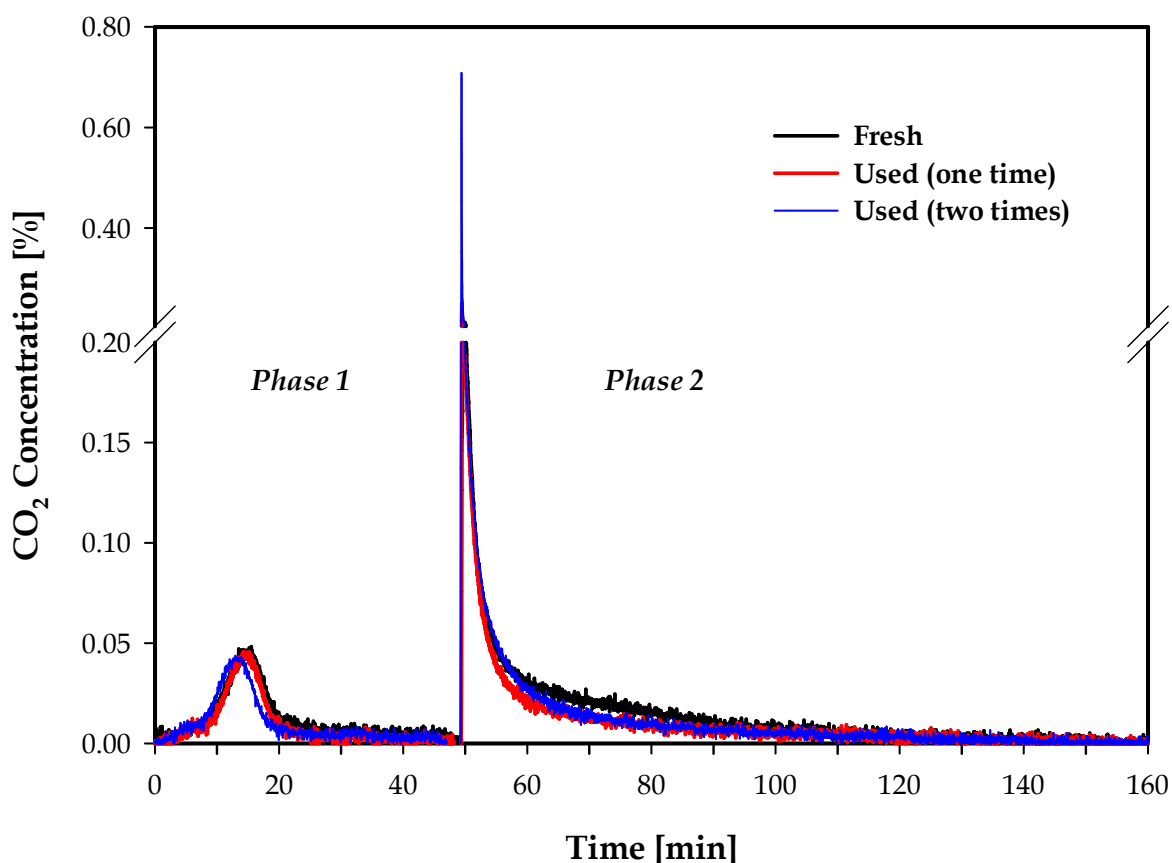


Figure 7. CO₂ concentration versus time: Catalytic regeneration tests repeated on the same filter (furnace temperature for the isothermal phase - Phase 2 - set to 475°C).

The regeneration performance is substantially the same in all tests, thus suggesting that, at 475°C, the thermal stability of the ceria coating is preserved.

Filter characterization

In order to confirm the thermal stability of the ceria coating, supposed on the basis of the repeatability of the regeneration performance, the filter that underwent the three regeneration tests of Figure 7, hereafter referred to as the “regenerated filter”, was deeply characterized.

The SEM images of Figure 8 show the channel cross section of the regenerated filter (a) and that of the fresh ceria-coated filter (b). This latter image is from our previous work [16].

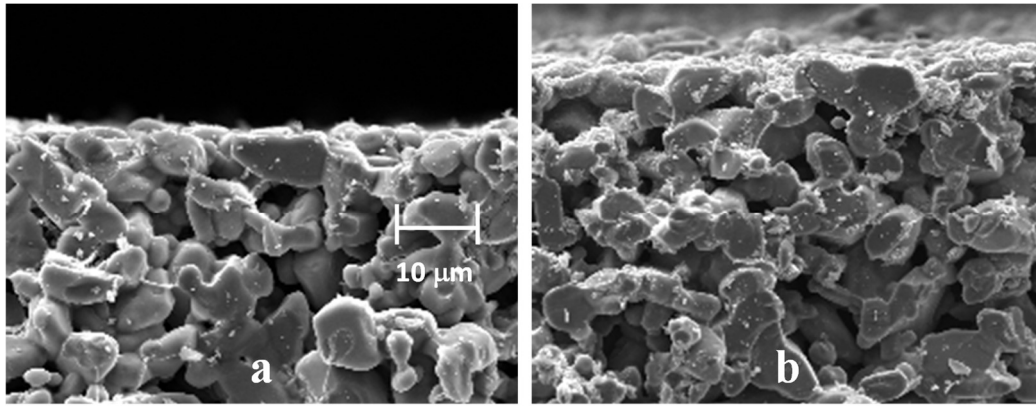


Figure 8. SEM images of the cross section of a filter channel: (a) regenerated filter; (b) fresh ceria-coated filter (from Ref. [16]).

The original morphology of the fresh ceria-coated filter is still preserved in the regenerated filter. Indeed, the repeated cycles of regeneration do not lead to relevant modification in the sample morphology at least at a macroscopic level.

Figure 9 shows the XRD patterns of the regenerated and fresh ceria-coated filters. The pattern of the original (bare) filter, which allows the identification of the signals assigned to SiC, is also shown.

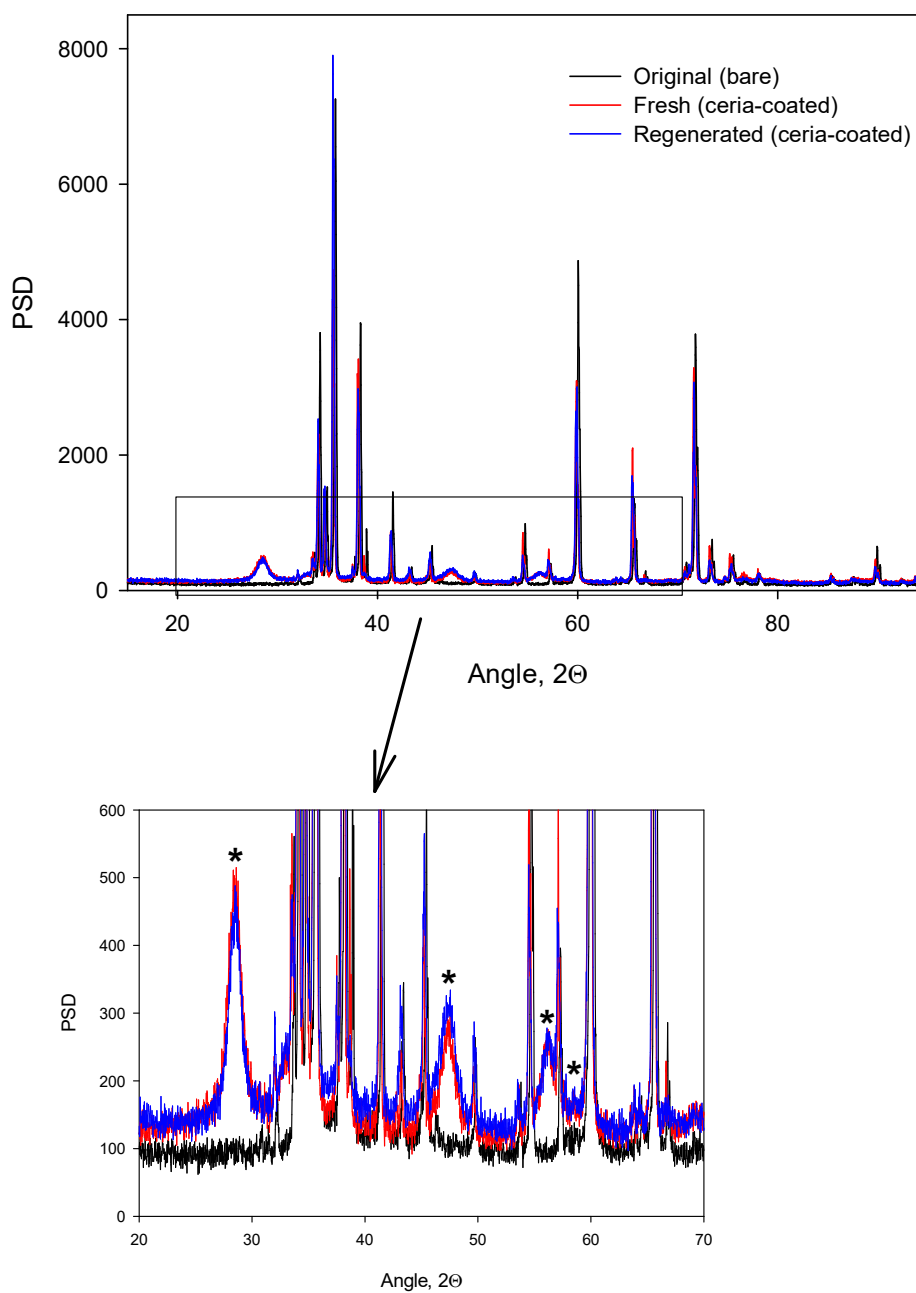


Figure 9. XRD patterns of original, fresh ceria-coated and regenerated filters. Stars correspond to fluorite ceria signals.

As clearly detectable in the magnification of the main figure, both the regenerated and fresh filters exhibit signals of the ceria fluorite structure (JCPDS 34-394) that are essentially superimposable. On the other hand, the BET surface area of the regenerated filter is substantially the same as that of the fresh filter ($16 \text{ m}^2/\text{g}$) [16]. Thus, it can be concluded that

no relevant aggregation and sintering of ceria occur over repeated regeneration cycles, ensuring the same performance as a result of basically unchanged soot-catalyst contact. This is further confirmed in Figures 10 and 11.

Figure 10 shows the PSD in the region of macro-pores for the regenerated filter (green plot). In the same figure, the results obtained in our previous work on samples of original (bare) filter (black plot) and fresh ceria-coated filters without soot (blue plot) and with soot (ceria/soot ratio equal to 95 w/w) are also shown for comparison [16].

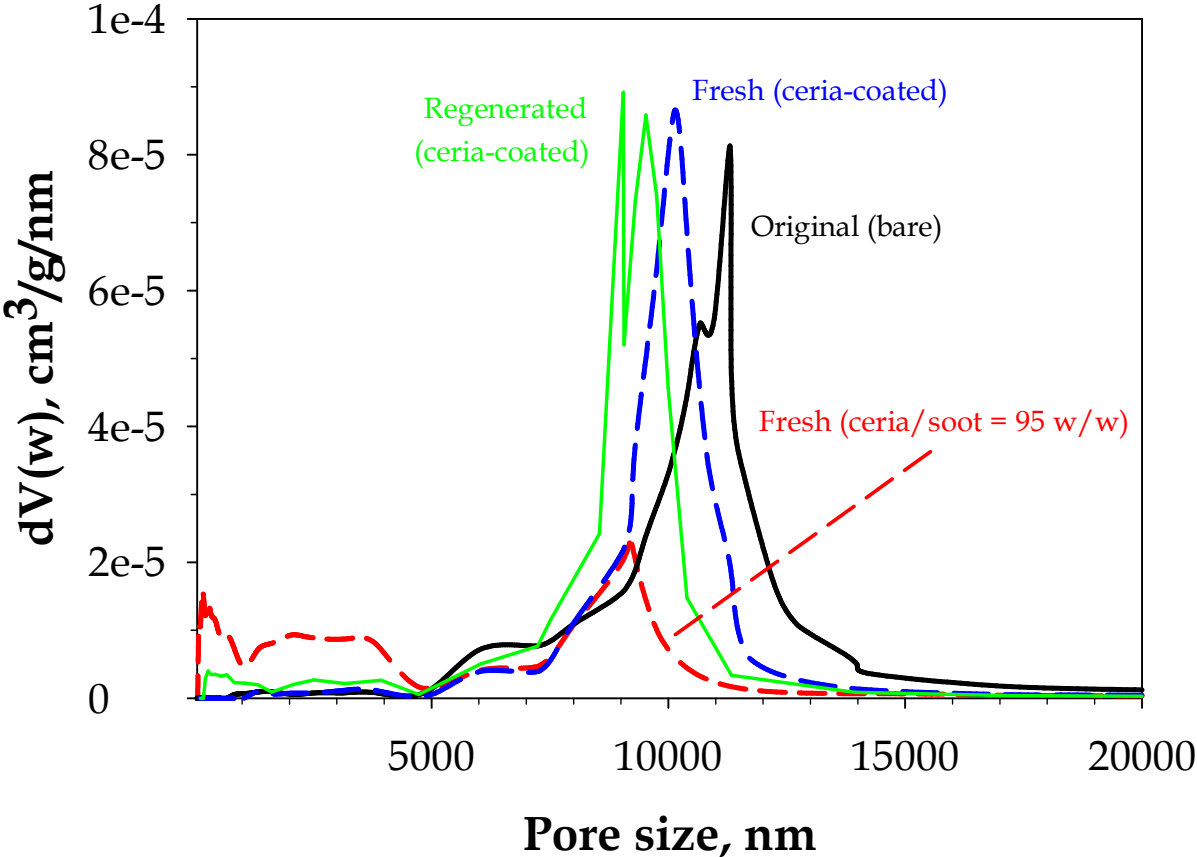


Figure 10. Pore size distribution (PSD) in the region of macro-pores for a sample of regenerated filter (green plot). Results obtained in our previous work on samples of original (bare) filter (black plot) and fresh ceria-coated filters without soot (blue plot) and with soot (ceria/soot ratio equal to 95 w/w) are also shown for comparison [16].

The fresh ceria-coated filter without soot shows a mono-modal distribution of macro-pores centered at about 10000 nm, indicating a very slight pore shrinkage with respect to the original filter. On the contrary, the addition of soot dramatically reduces the volume of macro-pores leading, at the same time, to the appearance of smaller pores (< 5000 nm). Three cycles of regeneration do not severely modify the PSD. Indeed, although the green and blue plots do not overlap, they are very close to each other, meaning that the regeneration process at 475°C has substantially “cleaned” the filter macro-pores with a very good recovery of their volume and the simultaneous disappearance of the soot contribution to the region of smaller pores.

Figure 11 shows the results of the EDX mapping for the regenerated filter. In the top sequence, the tilt angle of radiation is 90° (i.e., the sample is perpendicular to the radiation); in the bottom sequence, the tilt angle of radiation is higher than 90° (i.e., the sample is rotated) to better show the surface of the channel wall.

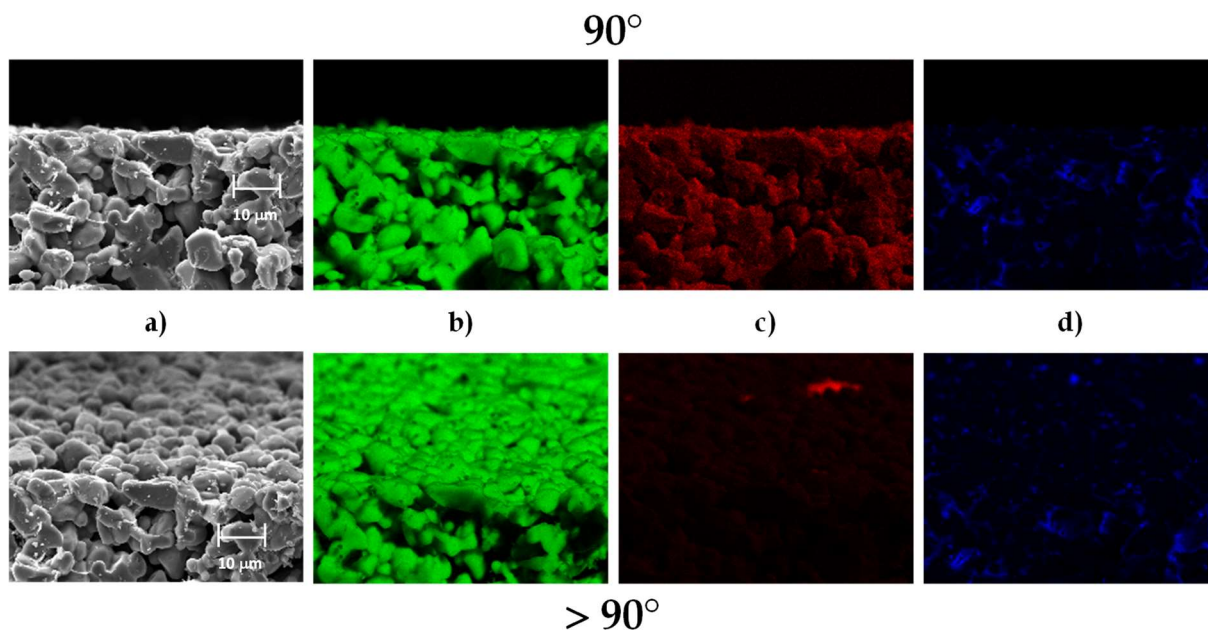


Figure 11. EDX mapping of the cross section of a channel of the regenerated filter: (a) SEM images and distribution of (b) Si, (c) C, (d) Ce. In the top sequence, the tilt angle of radiation is 90 degrees (i.e., the sample is perpendicular to the radiation); in the bottom sequence, the tilt angle of radiation is higher than 90 degrees (i.e., the sample is rotated).

While from Figure 10 it can be deduced that the macro-pores of the filter channels are substantially regenerated via catalytic path, Figure 11 shows residual (unburned) soot accumulated on top of the channel wall as isolated small aggregates that do not participate into the catalytic process of filter regeneration, being somewhat segregated from the catalyst. It is worth noting that, in our experiments, regeneration occurs after dipping the filter in a suspension of soot in heptane and, as such, does not proceed simultaneously with filtration. Thus, this residual soot, which can burn only via thermal path at temperatures higher than 475°C (i.e., during Phase 3 of Figure 1), is soot loaded in slight excess over that required to definitely avoid any form of local stratification on top of the filter walls.

Overall, the results in Figures 10 and 11 further support the validity of assuming that 475°C is the minimum temperature for a substantially complete filter regeneration via catalytic path.

Conclusions

In this work, the potential of diesel particulate filters wash-coated with highly dispersed ceria for continuous regeneration has been investigated. To this end, catalytic regeneration tests were performed, under isothermal conditions, on filters loaded with a very low amount of soot suitably chosen to minimize the formation of the cake layer. Under such conditions, most of the soot was trapped inside the macro-pores of the filter walls, thus coming in close contact with the ceria catalyst. The test temperature was varied from 200 to 600°C.

It has been found that soot catalytic oxidation starts from 300°C and, at all the investigated temperatures, the selectivity to CO₂ is higher than 99 %. The minimum temperature at which the filter is regenerated via catalytic path is equal to around 475°C. At that minimum temperature, the catalytic filter maintains substantially the same performance over repeated cycles of soot loading and regeneration, indicating that the thermal stability of the ceria coating is preserved. Conversely, the outcomes of filter characterization have shown that no relevant aggregation and sintering of the catalyst occur after repeated regeneration tests, whereas both morphology and porous structure of the fresh ceria-coated filter (not loaded with soot) are basically recovered.

These results have been obtained using a simple oxide, in other words, the catalyst formulation has not been optimized. The intrinsic activity of ceria can be further improved through doping with a proper active metal, thus further decreasing the temperature required for filter regeneration to values included in the operative range of diesel exhausts. This will pave the way for a process of continuous passive regeneration of ceria-coated filters. Future work will be focused on this issue.

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References

- [1] J. Adler, Ceramic diesel particulate filters, *Int. J. Appl. Ceram. Technol.* 2 (2005) 429-439.
- [2] P. Eastwood, *Critical Topics in Exhaust Gas After Treatment*, Research Studies Press Ltd, Baldock, 2000 (pp. 400).
- [3] S. Bensaïd, C.J. Caroca, N. Russo, D. Fino, Detailed investigation of non-catalytic DPF regeneration, *Can. J. Chem. Eng.* 89 (2011) 401-407.
- [4] D. Fino, S. Bensaïd, M. Piumetti, N. Russo, A review on the catalytic combustion of soot in diesel particulate filters for automotive applications: from powder catalysts to structured reactors, *Appl. Catal. A-Gen.* 509 (2016) 75-96.
- [5] B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, Realistic contact for soot with an oxidation catalyst for laboratory studies, *Appl. Catal. B-Environ.* 28 (2000) 253-257.
- [6] K. Hinot, H. Burtscher, A.P. Weber, G. Kasper, The effect of the contact between platinum and soot particles on the catalytic oxidation of soot deposits on a diesel particle filter, *Appl. Catal. B-Environ.* 71 (2007) 271-278.
- [7] E. Aneggi, C. de Leitenburg, A. Trovarelli, Ceria-based formulations for catalysts for diesel soot combustion, in: A. Trovarelli, P. Fornasiero (Eds.), *Catalysis by Ceria and Related Materials* (second ed.), Imperial College Press, London, 2013, pp. 565-621.
- [8] A. Bueno-López, Diesel soot combustion ceria catalysts, *Appl. Catal. B-Environ.* 146 (2014) 1-11.
- [9] Z. Yang, K. Zhou, X. Liu, Q. Tian, D. Lu, S. Yang, Single-crystalline ceria nanocubes: size-controlled synthesis, characterization and redox property, *Nanotechnology* 18 (2007) 185606 (4 pp).
- [10] E. Aneggi, D. Wiater, C. de Leitenburg, J. Llorca, A. Trovarelli, Shape-dependent activity of ceria in soot combustion, *ACS Catal.* 4 (2014) 172-181.

- [11] M. Piumetti, S. Bensaid, N. Russo, D. Fino, Nanostructured ceria-based catalysts for soot combustion: investigations on the surface sensitivity, *Appl. Catal. B-Environ.* 165 (2015) 742-751.
- [12] T. Andana, M. Piumetti, S. Bensaid, N. Russo, D. Fino, R. Pirone, Nanostructured ceria-praseodymia catalysts for diesel soot combustion, *Appl. Catal. B-Environ.* 197 (2016) 125-137.
- [13] M. Piumetti, T. Andana, S. Bensaid, D. Fino, N. Russo, R. Pirone, Ceria-based nanomaterials as catalysts for CO oxidation and soot combustion: effect of Zr-Pr doping and structural properties on the catalytic activity, *AIChE J.* (DOI: 10.1002/aic.15548).
- [14] L.F. Nascimento, J.F. Lima, P.C. de Sousa Filho, O.A. Serra, Control of diesel particulate emission based on Ag/CeO_x/FeO_y catalysts supported on cordierite, *Appl. Catal. B-Environ.* 197 (2016) 125-137.
- [15] V. Rico Pérez, A. Bueno-López, Catalytic regeneration of diesel particulate filters: comparison of Pt and CePr active phases, *Chem. Eng. J.* 279 (2015) 79-85.
- [16] V. Di Sarli, G. Landi, L. Lisi, A. Saliva, A. Di Benedetto, Catalytic diesel particulate filters with highly dispersed ceria: effect of the soot-catalyst contact on the regeneration performance, *Appl. Catal. B-Environ.* 197 (2016) 116-124.
- [17] K. Yamazaki, Y. Sakakibara, S. Daido, S. Okawara, Particulate matter oxidation over ash-deposited catalyzed diesel particulate filters, *Top. Catal.* 59 (2016) 1076-1082.
- [18] K.S. Martirosyan, K. Chen, D. Luss, Behavior features of soot combustion in diesel particulate filter, *Chem. Eng. Sci.* 65 (2010) 42-46.
- [19] K. Chen, K.S. Martirosyan, D. Luss, Transient temperature rise during regeneration of diesel particulate filters, *Chem. Eng. J.* 176-177 (2011) 144-150.
- [20] K. Chen, K.S. Martirosyan, D. Luss, Counter-intuitive temperature excursions during regeneration of a diesel particulate filter, *AIChE J.* 57 (2011) 2229-2236.

- [21] V. Di Sarli, A. Di Benedetto, Modeling and simulation of soot combustion dynamics in a catalytic diesel particulate filter, *Chem. Eng. Sci.* 137 (2015) 69-78.
- [22] V. Di Sarli, A. Di Benedetto, Operating map for regeneration of a catalytic diesel particulate filter, *Ind. Eng. Chem. Res.* 55 (2016) 11052-11061.
- [23] J. Ko, W. Si, D. Jin, C.L. Myung, S. Park, Effect of active regeneration on time-resolved characteristics of gaseous emissions and size-resolved particle emissions from light-duty diesel engine, *J. Aerosol. Sci.* 91 (2016) 62-77.
- [24] B.A.A.L. van Setten, P. Russo, S.J. Jelles, M. Makkee, P. Ciambelli, J.A. Moulijn, Influence of NO_x on soot combustion with supported molten salt catalysts, *React. Kinet. Catal. L.* 67 (1999) 3-7.
- [25] I. Atribak, A. Bueno-López, A. García-García, Uncatalysed and catalysed soot combustion under $\text{NO}_x + \text{O}_2$: real diesel versus model soots, *Combust. Flame* 157 (2010) 2086-2094.
- [26] A. Di Benedetto, G. Landi, L. Lisi, G. Russo, Role of CO_2 on CO preferential oxidation over CuO/CeO_2 catalyst, *Appl. Catal. B-Environ.* 142-143 (2013) 169-177.