

EFFECT OF THE SOOT CAKE THICKNESS ON THE REGENERATION PERFORMANCE OF A CATALYTIC DIESEL PARTICULATE FILTER

V. Di Sarli*, G. Landi*, L. Lisi*, A. Di Benedetto**

valeria.disarli@irc.cnr.it

*Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche,
P.le V. Tecchio, 80 – 80125 Napoli (Italy)

**Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,
Università degli Studi di Napoli Federico II, P.le V. Tecchio, 80 – 80125 Napoli (Italy)

Abstract

In this work, the effect of the soot-catalyst contact on the regeneration performance of a diesel particulate filter (DPF) wash-coated with nanometric ceria particles was investigated. The catalyst was highly dispersed inside the filter walls. Furthermore, its load was suitably chosen to avoid major changes in pore size distribution of the bare filter. Different amounts of soot were loaded into the filter, thus varying the conditions of soot-catalyst contact.

At the lowest soot load explored, the deep penetration of soot particles into the macro-pores of the filter walls and the consequent good contact with the catalyst particles result in a large fraction of soot burned via catalytic path at low temperatures. At the highest soot load explored, in addition to the soot particles trapped inside the macro-pores, a rather thick soot cake layer accumulates on top of the catalytic walls of the filter. The soot cake is oxidized via thermal path at high temperatures, being substantially segregated from the catalyst.

Introduction

Catalytic regeneration of diesel particulate filters (DPFs) has been proposed as an alternative or complementary approach to bypass or mitigate the drawbacks associated with thermal regeneration (additional energy costs, complex means of control, local temperature excursions sufficiently high to damage the DPF, etc.) [1-3]. In principle, the catalyst may be used to achieve soot oxidation at lower temperatures (250-550°C) than those required for thermal regeneration (> 600°C), and/or to shorten the regeneration time period, thus allowing for energy saving.

The ability of a catalytic DPF to oxidize soot at low temperatures is strictly dependent not only on the intrinsic catalyst activity, but also on the efficiency of the contact between the soot particles and the active sites of the catalyst particles [4,5]. Ceria is among the most active catalysts for soot oxidation due to its redox properties (Ce^{4+}/Ce^{3+}) and oxygen storage capacity [6,7]. The oxygen transfer, which occurs by superficial diffusion between ceria and soot, makes the solid-solid contact a key issue for an efficient soot combustion [7].

In catalytic DPFs, two zones may be conceptually distinguished: an internal zone

and an external zone. The internal zone is the catalytic porous wall of the filter. The external zone is the soot cake layer accumulated on top of the catalytic wall. In the internal zone, good soot-catalyst contact may be established. Conversely, for the external zone, the contact with the catalyst remains rather poor.

In this work, the role played by both external (non-catalytic) and internal (catalytic) zones in affecting the filter regeneration performance was investigated. To this end, lab-scale catalytic filters were prepared starting from a commercial silicon carbide (SiC) DPF. They were wash-coated with nanometric ceria particles and, then, loaded with different amounts of soot, thus varying the conditions of soot-catalyst contact.

Materials and Methods

A commercial SiC filter (IBIDEN - 180 cpsi; 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. In order to harden the plugs, the filters were left at room temperature for about 24 h and, then, calcined at 950°C for 5 h.

The so prepared filters were coated with ceria. To this end, a dip coating procedure was employed starting from a colloidal suspension (NYACOL, CeO₂ (AC)) consisting of nano-sized ceria particles dispersed in a solution of acetic acid (particle size: 10-20 nm). After dipping, the filter was vigorously shaken to eliminate the excess material, dried at 120°C for 40 min and, then, calcined at 450°C for 2 h. The whole operation was repeated three times to achieve the desired target (~ 1 g), which corresponds to about 17 wt % with respect to the final weight of the filter. The catalyst weight per unit volume of the filter is about 250 g/l.

After the catalyst-coating, the filters were loaded with soot. In particular, each filter was dipped in a suspension of soot (1 g - Degussa Printex U) in heptane (100 ml - Sigma Aldrich). The duration time of the dipping phase and the number of repetitions of the whole procedure were varied to vary the soot load and, thus, the catalyst/soot ratio. After dipping, the filter was vigorously shaken and, then, dried for 1 h at room temperature (to allow the heptane evaporation).

The pore size distribution of filter samples in the region of macro-pores was evaluated using a Micromeritics Autopore IV by the Hg intrusion porosimetry technique. Specific surface area measurements (BET method) and micro- and meso-pore analysis (BJH method) were performed with a Quantachrome Autosorb 1-C by N₂ adsorption at 77 K. 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.

Temperature programmed soot combustion tests were performed in a lab-scale rig. The filter was placed in a tubular quartz reactor located in a tubular electric oven (LENTON LTD mod. PTF 12/38/500). The filter was pre-heated at 250°C in N₂

stream (0.5 l(STP)/h) and, then, heated up to 700°C (heating rate of 5°C/min) in O₂-N₂ stream (47 l(STP)/h, O₂ concentration equal to 15 vol. %). Reaction products (CO, CO₂ and O₂) were analyzed by a Fisher-Rosemount NGA2000 analyzer.

The filter was weighted before and after each regeneration test to verify the carbon balance through the comparison between the amount of consumed soot and the amount of produced CO and CO₂. The carbon balance was verified with an error of ±10 %.

Results and Discussion

The original filter exhibits a quite narrow pore distribution peaked at 11000-12000 nm, resulting from SiC inter-particle spaces. After the catalyst-coating, the pore distribution slightly changes (the peak is found at about 10000 nm). Indeed, the deposition of ceria nanoparticles inside the filter walls results in a limited occlusion of macro-pores. Thus, the filtering properties are substantially preserved. SEM analysis showed the absence of a catalytic layer accumulated on top of the filter walls, thus confirming the penetration of the catalyst into the macro-pores.

The pore size distribution is modified by the soot loading: the fraction of larger pores is reduced, while smaller pores (< 5000 nm) appear.

The specific surface area and the volume of micro- and meso-pores, negligible for the original filter, significantly increase upon ceria coating and soot loading (Table 1). The catalyst coating results in a large increase of pores in the range 10-40 Å, along with a more pronounced micro-porosity peaked at around 7 Å. The soot-loaded filter exhibits pores in the same range as the catalyst-coated filter, even if more centered at higher size. The co-presence of ceria and soot results in a less than additive increase of surface area and pore volume, independently of the ceria/soot ratio (Table 1). However, the pore size distribution is significantly affected by the ceria/soot ratio. At high ceria/soot ratio (95 w/w), the average pore size is centered at lower values, whilst at low ceria/soot ratio (28 w/w), there is a larger contribution of pores with size higher than 20 Å.

Table 1. BET surface area and volume of micro- and meso-pores.

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Original filter	3	0.0033
Soot-loaded filter	10	0.017
Ceria-coated filter	16	0.022
Filter with ceria/soot ratio = 95 w/w	22	0.033
Filter with ceria/soot ratio = 28 w/w	24	0.034

Figure 1 shows the results of the EDX elemental mapping of the cross section of the filter channel for low (28 w/w) and high (95 w/w) ceria/soot ratios.

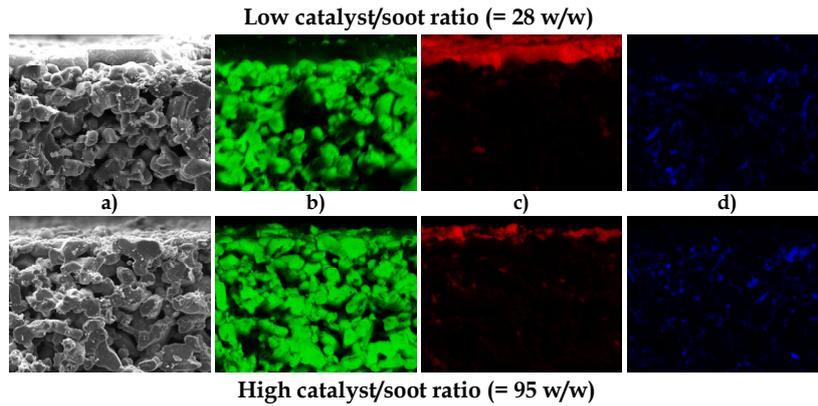


Figure 1. EDX mapping of cross section of filter channel for two samples with low (top) and high (bottom) ceria/soot ratio: (a) SEM images and distribution of (b) Si, (c) C, (d) Ce.

At low catalyst/soot ratio (high soot load), the external zone of the filter (i.e., the soot cake layer) is detected (its thickness is around 15-20 μm), along with a small fraction of soot that deeply penetrates into the macro-pores of the catalytic wall (internal zone of the filter) thus coming in close touch with highly dispersed ceria. On the contrary, at high catalyst/soot ratio (low soot load), the external zone is very thin, while most of the soot is inside the filter wall. Thus, the high ceria/soot ratio assures a better soot-catalyst contact, avoiding a large accumulation of soot on top of the wall in the form of cake, which is substantially segregated from the catalyst. Figure 2 shows the results, in terms of normalized CO_x ($= \text{CO}_2 + \text{CO}$) concentration versus filter temperature, of regeneration tests carried out by varying the catalyst/soot ratio from 0 - thermal regeneration - to 98 w/w.

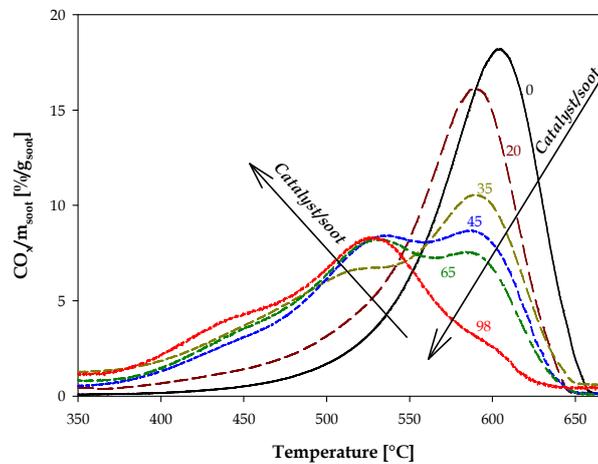


Figure 2. Normalized CO_x concentration as a function of the filter temperature for different catalyst/soot ratios (w/w).

The selectivity to CO_2 is about 40 % for thermal regeneration, whereas it is always ≥ 98 % (CO_x is substantially CO_2) for catalytic regeneration. This means that ceria also activates CO oxidation.

Starting from catalyst/soot ratio equal to 35 w/w, a double-peaked shape appears. As the catalyst/soot ratio is increased, the catalytic contribution (low temperature peak) increases and becomes almost the unique one for catalyst/soot ratio equal to 98 w/w. This is in agreement with the results of Figure 2 showing that, at high ceria/soot ratio (95 w/w), a good soot-catalyst contact is established in the internal zone of the filter (i.e., the catalytic wall), whereas the external zone (i.e., the cake) almost disappears.

In Figure 3, the fraction of catalytically converted soot (with respect to the overall amount of combusted soot) is plotted as a function of the catalyst/soot ratio. This fraction was obtained by deconvolution of the CO_x concentration curves of Figure 2 into the two (catalytic and thermal) contributions.

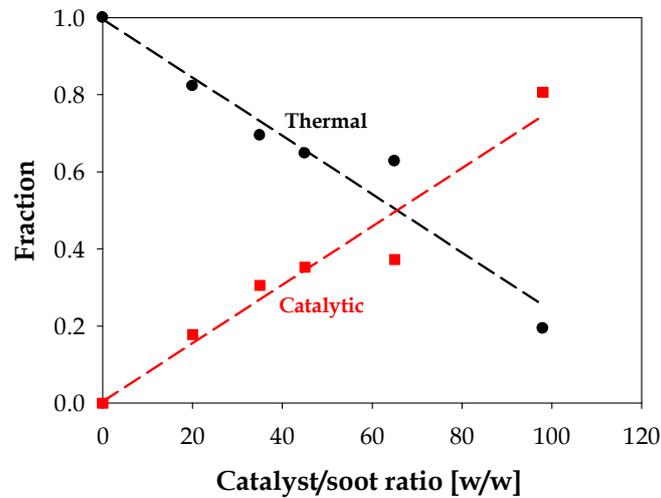


Figure 3. Fraction of catalytically converted soot (along with the complementary fraction of thermally converted soot) as a function of the catalyst/soot ratio.

The catalytic fraction increases roughly linearly with increasing catalyst/soot ratio. In the case of catalyst/soot ratio = 98 w/w, it is equal to around 0.8.

Figure 4 shows the plots of $T_{10\%}$ (temperature at which 10 % of the initial soot is converted, i.e., onset temperature) and $T_{50\%}$ (temperature at which 50 % of the initial soot is converted, i.e., half-conversion temperature) versus the catalyst/soot ratio as extracted from the concentration curves of Figure 2. Both temperatures decrease with the catalyst/soot ratio. However, $T_{10\%}$ is more sensitive than $T_{50\%}$ to variations in the catalyst/soot ratio and, thus, to variations in the soot-catalyst contact conditions. In particular, when increasing the catalyst/soot ratio from 0 to 98 w/w, $T_{10\%}$ decreases from $\sim 525^\circ\text{C}$ to $\sim 350^\circ\text{C}$.

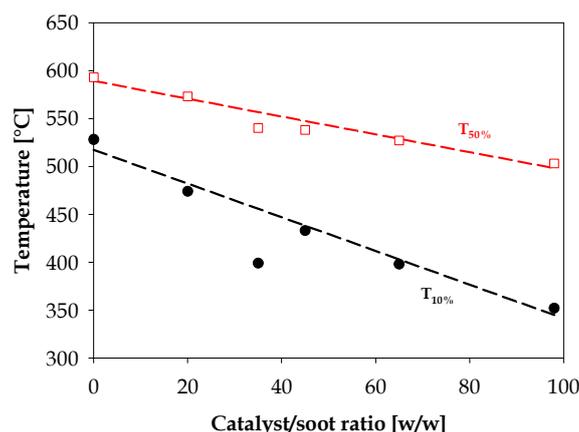


Figure 4. $T_{10\%}$ and $T_{50\%}$ versus the catalyst/soot ratio.

Conclusions

The results obtained in this work highlight the importance of strategies that avoid or minimize the segregation between the soot cake layer and the catalytic wall of the filter to operate catalytic DPFs in an effective manner.

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