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Low Temperature Microwave Regeneration of Catalytic Diesel Particulate Filter

Eugenio Meloni*, Vincenzo Palma

University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA) - Italy
emeloni@unisa.it

Diesel particulate filter (DPF), consisting in alternately plugged parallel square channels with porous walls that trap the soot particles, must be periodically regenerated. In this work, a new procedure for the preparation of microwave susceptible catalytic DPFs based on a preliminary controlled chemical erosion of the porous structure was optimized, so obtaining catalytic filters with higher catalyst load (30 %wt $CuFe_2O_4$). The filters showed pressure drop values very similar to that pertaining to the uncatalysed filters and a higher regeneration activity: consequently their microwave assisted regeneration phase, compared to the traditional fuel post-injection, allowed an energy saving of about 60 %.

1. Introduction

The current Euro-6 legislation for light-duty vehicles imposes a target of 0.0045 g/Km of particulate matter (PM) and a limit on the number of particles larger than 23 nm (in diameter) below 6.0 x 10^{11} particles/Km (Vlachos et al., 2014). These standards are difficult to meet with combustion optimization techniques; the increases of injection pressure and the number of injections have improved the spray atomization, the air-fuel mixing and the distribution of equivalence ratio, but it is not enough yet. Furthermore, the innovative Low Temperature Combustion processes require complex control strategies and lead to an increase in CO and HC emissions (Choi et al., 2007). In such a scenario it is clear that the after-treatment is mandatory. The diesel particulate filter (DPF) is currently the usual aftertreatment system in Diesel engines for soot particle abatement in passenger, heavy-duty and non-road vehicles (Meloni and Palma, 2017). Among different filter solutions, wall-flow monoliths are the DPF type showing the best balance between filtration efficiency and pressure drop performance (Zhang et al., 2017). The DPF consists in alternately plugged parallel square channels, so that the exhaust gases are forced to flow through the porous inner walls: in this way the particles are collected on the surface and in the porosity of the channel walls, progressively blocking the pores (Meloni et al., 2017). Since the pressure loss increases by the formation of a thick soot cake as the PM is accumulated, the DPF needs to be periodically regenerated by burning off the accumulated soot. Regeneration of diesel particulate filters (DPFs) can be obtained in a continuous way (passive regeneration), in which the regeneration temperature is reduced mixing the catalyst in fuel (Shuzhan et al., 2017) or depositing it on filter substrate (Di Sarli et al., 2016), or in a periodic way (active regeneration), in which the exhaust temperature is raised supplying external energy from electricity, fuel or microwave (Meloni et al., 2017). In particular for active regeneration system of DPF, the soot oxidation occurs only if the exhaust mass is heated up to 600 °C. A common configuration consists in a Hydrocarbon Injection (HCI) system and a Diesel Oxidation Catalyst (DOC) placed before the DPF: in this way an amount of extra fuel, by means of an internal (post injection) or external fuel injection, is injected into the exhaust pipe and oxidized in the DOC, so increasing the exhaust temperature to more than 600 °C, and consequently oxidizing the PM trapped in the filter and thus regenerating it (Shuzhan et al., 2017). However, the engine could be damaged by fuel post-injections used for active regeneration, since in this case oil dilution can occur. Furthermore fuel post-injections are responsible also of extra fuel consumption, so alternative regeneration technologies are under investigation (Palma et al., 2013a). An innovative DPF configuration could be the sum of passive and active system: the former could be obtained by depositing an oxidant catalyst on the support, while the latter could be obtained by means of microwaves to heat a SiC filter up to the soot oxidation temperature (Palma et al., 2013b). The catalyst deposition is a critical issue, since the main problem of catalyst-

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coated DPFs (CDPFs) is the increase in pressure drop as compared to the bare filter, since the thinner porous wall of the filter oppose a higher resistance to the gas flow. In this way, it is very important to preserve the pore size distribution of the original bare filter as much as possible, so the high dispersion of the catalyst inside the filter porosity is mandatory. The use of microwaves allows to obtain two important results, (i) the DPF regeneration could be performed not only at high engine rotation speed under a high load as in the actual fuel post-injection strategy, but also at low engine rpms, and (ii) the effective oxidation of diesel soot is obtained, since the good dielectric properties of silicon carbide (SiC), allows to microwaves to heat directly the filter (Palma et al., 2013a). In addition the soot oxidation catalyst can be formulated to absorb microwaves, so combining microwave heating with catalytic combustion for the oxidation of diesel soot at lower temperature and higher reaction rate with respect to a bare DPF (Palma et al., 2013a). Our research was focused on copper ferrite ($CuFe_2O_4$) as catalyst, since some soot oxidation catalysts based on mixed valence oxides such as Fe_3O_4, CuO, Co_2O_3, and NiO can easily absorb microwaves (Ma et al., 1997). As known, the increasing in the catalyst load on the DPF results in the decreasing of the soot oxidation temperature, since a higher catalytic activity is achieved. But the addition of a catalyst to the SiC monoliths currently used in wall flow geometrical configuration, results in decreasing the initial 15-17 μm average pore diameter, and in a consequently increasing the pressure drop. In this regard, many efforts were dedicated to bibliographic studies and laboratory tests in order to optimize a procedure able to change the porosity and the average pore diameter in the bare samples (Meloni and Palma, 2017). So this work focuses on the direct deposition (any washcoat was added) of a microwave susceptible oxidation catalyst on a specifically pretreated wall flow DPF, and on its regeneration by means of microwaves; in particular the acid pretreatment was able to increase the average pore diameter of the bare SiC filter, and therefore increasing the potential active species load on the DPF. In particular in this work we investigated the possibility to modify the catalyst composition by adding K, in order to further reduce the soot oxidation temperature and keep the pressure drop low, so resulting in a lower filter regeneration frequency, by exploiting the NOx normally present in the exhaust gases to increase the catalytic activity, as observed in literature for similar catalytic systems (Liu et al., 2003). Furthermore, the energy balance of the entire process was performed in order to compare the microwave assisted regeneration technology with the regeneration techniques employed currently, and so verify its feasibility.

2. Materials and methods

2.1 Experimental tools

In this work different DPFs catalysed with different loads of K-doped copper ferrite ($Cu_{0.95}K_{0.05}Fe_2O_4$) were prepared and characterized by means of Scanning Electron Microscopy (SEM mod. LEO 420 V2.04, ASSING), Energy dispersive spectroscopy (EDX mod. INCA Energy 350, Oxford Instruments), Hg porosimetry tests, N_2 adsorption at -196 °C, applying BET method for the calculation of sample's surface area, and catalytic activity tests. In addition, the adherence of the catalyst to the filter was evaluated measuring the weight loss caused by exposing the monoliths to ultrasound, according to an optimized experimental procedure (Palma et al., 2015a). The activity tests of soot deposition and on-line microwave (MW) assisted regeneration of catalytic DPFs were performed by means of our diesel emission control laboratory plant (Palma et al., 2015a).

2.2 Catalyst preparation

The bare monoliths used for the preparation of the catalytic filters were commercial Wall Flow monoliths in Silicon Carbide (SiC). The bare monoliths, characterized by 150 cpsi and provided by Pirelli Ecotechnology, were preliminary properly adapted in rectangular shape and calcined at 1,000 °C for 48 hours, so forming a coating of SiO_2 streaks on SiC particles, with the aim to increase the adherence of the active species to the filter even without a washcoat (Meloni et al., 2017). The catalyst ($Cu_{0.95}K_{0.05}Fe_2O_4$) to be deposited on the SiC monoliths were preliminary prepared starting from the nitrate precursors salts mixed with distilled water and continuously stirred at 60 °C. In particular iron, copper and potassium nitrates were mixed in a Cu/K/Fe molar ratio of 0.95:0.05:2. The desired loads of catalyst on the bare monoliths were obtained by repeating the consecutive phases of impregnation in the precursors solution, drying at 60 °C and calcination at 1,000 °C after each impregnation (Meloni and Palma., 2017). In particular a load of active species up to 20 %wt of K-doped copper ferrite was obtained.The bare SiC monoliths were previously dipped in a 1:1 mixture of HF:HNO_3 at a temperature of about 45 °C for 30 min, following an optimized procedure to increase their mean pore diameter (Meloni and Palma, 2017). All the prepared catalytic DPFs, before to be enclosed in the stainless steel wave guide of the experimental plant, were wrapped in a heat expanding intumescent ceramic-mat (Interam® Mat Mount 550 by 3M).

3. Results and discussion

3.1 Bare SiC monoliths

The optimized acid treatment of the bare SiC monoliths had a very positive effect since, after 30 min of dipping, selected as the optimal dipping time (Meloni and Palma, 2017a), the initial mean pore diameter and the specific surface area increased from 17 to 24 μm and from 0.35 m^2/g to 2.20 m^2/g, respectively.

3.2 Catalytic samples

The different catalytic filters typologies were firstly investigated by means of SEM and SEM-EDAX analysis (Figure 1), evidencing that also after the preliminary acid treatment of the bare monoliths, a homogeneous distribution of the active species on the support was obtained. Furthermore these analysis resulted in the detection on the SiC catalytic samples of its structural chemical elements (Si, C and O) and of the catalytic elements (Fe, K and Cu). In particular, the very low signals of C and Si confirmed the good coating of the SiC granules with the catalyst.

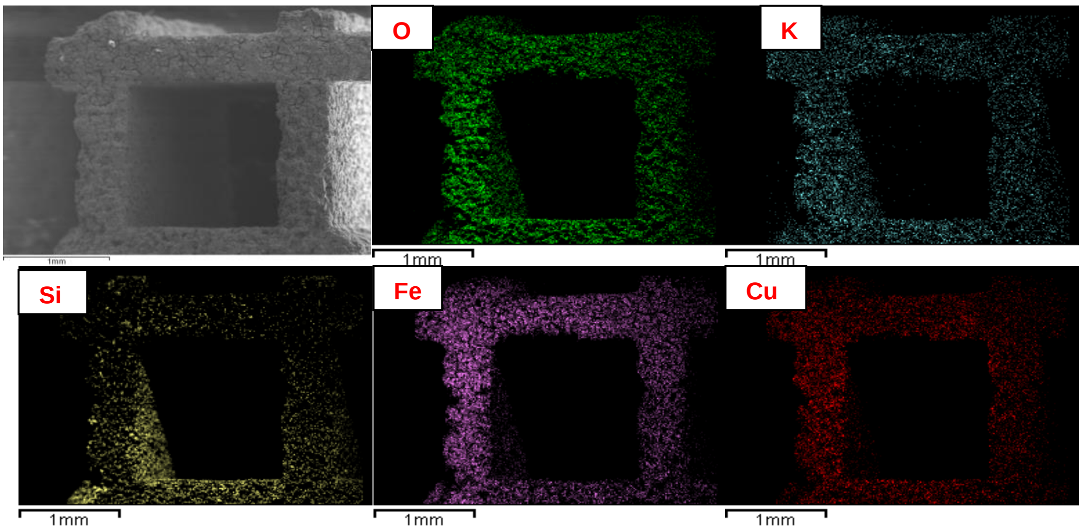

Figure 1: SEM image and distribution of elements, obtained by EDX element mapping, for a 20 %wt $Cu_{0.95}K_{0.05}Fe_2O_4$ *catalysed monolith*

The prepared samples were also characterized in terms of textural properties. The first tests were performed to evaluate the adherence of the active species to the SiC granules by means of ultrasonic treatments. The samples were immersed in a beaker containing petroleum ether (Carlo Erba), and the whole was placed in an ultrasonic bath CP104 (EIA SpA) filled with distilled water, at a temperature of 25 °C for 30 min. Before the test, compressed air was blown through the monoliths in order to remove any possible residue. The weight changes were recorded during the test at regular intervals of 5 min after monoliths drying at 120 °C and cooling up to room temperature. In particular the changes in weight of the samples after each cycle of ultrasonic treatment were evaluated according to the following formula:

$$\text{Weight loss} = (\text{initial weight-final weight}) / (\text{initial weight}) \times 100 \qquad (1)$$

The results evidenced that the weight loss was lower than 0.1 % for all the samples. These important results confirm the good adhesion of the active species also on the monoliths with modified porosity, even without any wash-coating procedure, perfectly according to what reported in our previous works (Meloni and Palma, 2017). In addition it is important to evidence that commonly used washcoated supports are characterized by weight losses higher than that reported for our samples (Palma et al., 2015a). The prepared samples were then characterized in terms of specific surface area and porosimetry. The data relevant to Specific Surface Area of the pretreated catalytic samples with a catalyst load of 20 %wt evidenced a specific surface area of 0.4 m^2/g. As evident, the specific surface area of the catalytic samples are lower than that of the bare monolith after 30 min of dipping time (section 3.1); this decrease in the specific surface area is probably due to catalyst deposition on the roughness caused by the dipping in the acid solution, but this isn't a negative result. In fact it is important to evidence that the catalytic DPFs, being developed to trap the soot emitted by diesel engines, are specifically applied to heterogeneous solid-solid-gas systems (soot-catalyst-oxygen), in which a tight catalyst-soot (solid components) contact condition is mandatory for an effective soot combustion (Piumetti et al., 2016). So the very good catalytic activity towards soot oxidation reported in our previous works for this catalyst configuration could be explained by a very strong interaction between soot and catalyst obtained on the catalytic samples, as also showed by SEM images and ultrasonic tests (Palma et al., 2015a). Table 1 reports the comparison of the average pore diameter for the catalytic samples with the same catalyst load (20 %wt) but with different duration of the acid treatment.

Table 1: Effect of the acid treatment duration

Catalyst	Dipping time [min]	Average pore diameter [μm]
$Cu_{0.95}K_{0.05}Fe_2O_4$	0	11
$Cu_{0.95}K_{0.05}Fe_2O_4$	30	15

The analysis of the results reported in Table 1, allows to state that the increase in the average pore diameter of the bare monoliths structures, determined by their preliminary acid treatment, was preserved even after the catalyst deposition step, so suggesting that by modifying the porous distribution of the bare monoliths it is possible to prepare a catalytic filter characterized by a significantly greater average pore diameter but with the same load of active species.

3.3 Catalytic activity tests

The on-line soot deposition and microwaves assisted regeneration steps were performed according to the previously optimized procedure (Palma et al., 2015a). In detail during the deposition tests the engine operating conditions were set in order to fix the flow rate into the filter at 110 normal liters/min (Nl/min) and the exhaust gas temperature at about 200 °C, while the subsequent microwaves assisted regeneration tests were performed by decreasing the exhaust gas flow rate into the filter to about 30 Nl/min, and the filter heating was obtained by setting the microwave generator at 950 W (50 % of its nominal power). During all the tests the composition of the exhaust gas was continuously monitored. The results of the catalytic activity tests performed using the prepared filters are reported in Figure 2 in terms of pressure drop (DP) and temperature as function of test time. The positive effect of modified porosity, evidenced in our previous work on copper ferrite loaded filters (Meloni and Palma, 2017), is confirmed also in the case of modified monoliths loaded with K-doped copper ferrite.

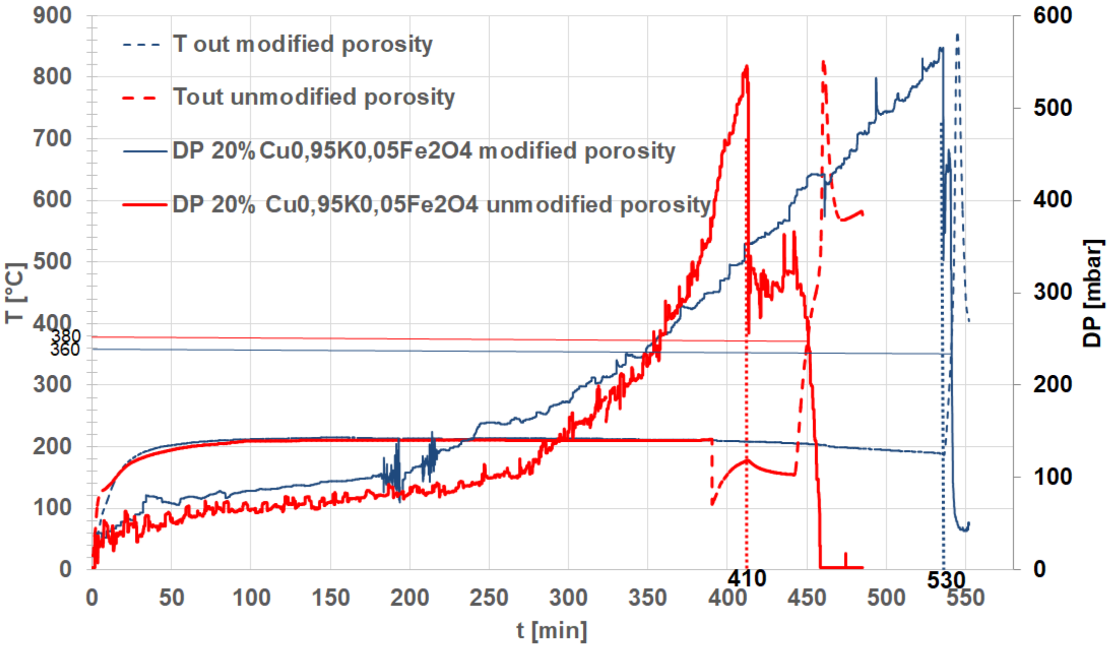

Figure 2: Effect of porosity on DP (continuous lines) and temperature (dotted lines) as function of soot deposition and regeneration time for 20 %wt $Cu_{0.95}K_{0.05}Fe_2O_4$ loaded filters with modified and unmodified porosity.

Form Figure 2 in the case of the catalytic filter with modified porosity (i) the increase of the deposition time from 410 (20 %wt catalyzed filter with unmodified porosity) to 530 min (20 %wt catalyzed filter with modified porosity), (ii) a lower soot oxidation temperature (about 360 °C instead of 380 °C) and (iii) a lower regeneration duration (about 8 min instead of 18 min) can be observed. Another observation arising from Figure 2 is that in the case of the filter with modified porosity, the final DP value is higher than that in the case of the filter with unmodified porosity; this is probably due to the presence of unburned ashes on the filter surface.

3.4 Energy required for the DPF regeneration

The lower threshold temperature and the lower regeneration duration evidenced in the previous paragraphs for the modified porosity catalytic filters, consequently results in a lower energy required to regenerate the filter. The microwave energy supplied for a filter volume of about 0.35 L during the regeneration phase of all the different filters studied in this work is showed in Figure 3, compared to the traditional fuel post-injection and to a traditional DPF. In detail, the traditional fuel post-injection consists in a retarded injection of an extra fuel amount, in order to make burning it in the DOC, held until the soot oxidation is complete. In this way, the exhaust gas is heated up to soot combustion temperature. Typically, about 430 g of extra fuel are required in a 1.9 L four cylinder CIDI diesel engine (Palma et al., 2015a). In the case of microwave assisted regeneration, the energy supplied is calculated by integrating the microwave power curve during the regeneration phase.

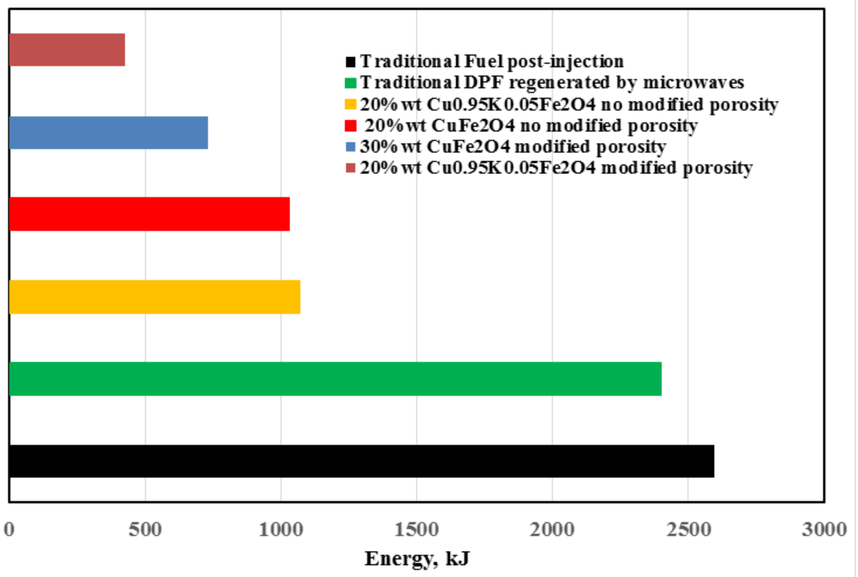

Figure 3: Comparison of the energy required for the regeneration phase of the investigated catalytic filters with the traditional fuel post-injection

From Figure 3, it is evident that the combination of microwave technology and of a microwave susceptible catalyst allowed to reach an energy saving during the regeneration phase of a DPF, if compared to the traditional fuel post-injection and to microwaves assisted regeneration of a traditional uncatalytic DPF. In particular an energy saving of about 60 % (the black curve versus the yellow and green ones) is possible just adding the catalyst; Furthermore, by modifying also the porosity, a further energy saving is achieved, more evident with K addition to copper ferrite (blue and brown curves).

4. Conclusions

This work focuses on the direct deposition (any washcoat was added) of a microwave susceptible oxidation catalyst on a specifically pretreated wall flow DPF, and on its regeneration by means of microwaves. In particular the performance of different SiC Wall Flow Diesel Particulate Filters loaded with K-doped copper ferrite ($Cu_{0.95}K_{0.05}Fe_2O_4$) were studied at different catalyst loading. A preliminary procedure consisting in dipping the monoliths in a 1:1 mixture of $HF:HNO_3$ was optimized, in order to increase the initial average pores diameter of the bare SiC monoliths from 17 to 24 μm. The prepared catalytic samples were characterized in terms of textural properties. The SEM analysis highlighted the very homogeneous distribution of the active species on the filters surface, with the active species depositing on the inner walls of the pores, with the result to decrease their diameter but not plugging them. The elements distribution as obtained by EDX element mapping showed very low signals of C and Si and strong signals of the catalyst active species (Cu, K and Fe), so confirming the good coating of the SiC granules with the active species. The adherence of the catalyst to the SiC granules was verified by means of ultrasonic treatment, and the results showed for the prepared samples much lower weight losses than that reported in literature for washcoated supports, so confirming the good adherence of the active species on the SiC granules, even without any wash-coating procedure. The Hg porosimetry tests showed that the preliminary acid treatment of the bare SiC monoliths resulted in an increased average pore diameter of the catalytic samples, if compared with the analogues without acid treatment. The on-line soot deposition tests showed that, due to porosity modifying procedure, in the case of filters with the 20 %wt active species loading the time needed to reach the DP limit value corresponding to a soot load of about 5 g/l of filter increases from about 410 to about 530 min, consequently decreasing the regeneration step frequency. In addition, during the deposition tests all the filters showed an average filtration efficiency of about 99 %. The on-line microwave assisted regeneration tests showed that all the investigated filters were completely regenerated by microwaves application. In particular the addition of K to the catalyst formulation, even if having no effect on the threshold temperature (about 360 °C) if compared with the analogues copper ferrite loaded filters, resulted in further decreasing the regeneration phase duration to about 8 min. In conclusion, the combination of microwave technology and of a microwave susceptible catalyst allowed to reach an energy saving during the regeneration phase of a DPF, if compared to the traditional fuel post-injection and to microwaves assisted regeneration of a traditional uncatalytic DPF. In particular an energy saving of about 60 % is possible just adding the catalyst; Furthermore, by modifying also the porosity, a further energy saving is achieved, more evident with K addition to copper ferrite.

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