

Improved Microwave-Susceptible Catalytic Diesel Particulate Filter

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Emission standards forced the manufacturers to adopt several aftertreatment devices as effective way to comply with the stringent limits for gaseous and particle emissions. The diesel particulate filter (DPF) is currently the usual aftertreatment system in Diesel engines for soot particle abatement. Among different filter solutions, flow-through filters, such as ceramic foams or open honeycomb structures, are characterized by low pressure drop but by a filtration efficiency of only 40 - 70%, while wall-flow monoliths, consisting in alternately plugged parallel square channels, so that the exhaust gases flow through the porous inner walls, showed the best balance between filtration efficiency and pressure drop performance. Since pressure loss increases with soot filtration, the DPF needs to be periodically regenerated by burning off the accumulated soot. In our previous work we showed that the simultaneous use of a microwave applicator and a specifically catalysed DPF with a catalyst load up to 30%wt of CuFe_2O_4 , allows to reduce the temperature, the energy and the time required for the filter regeneration with respect to the uncatalysed filter. These results were more evident in particular by adding K to our catalyst formulation and by lowering gas flow rate during the regeneration step. Starting by these very promising results, a procedure to increase the initial medium pore diameter of the bare monoliths was optimized, so aiming at increasing the active species load: in this way the further reduction of soot oxidation temperature is possible, keeping acceptable the pressure drop, and, more important, allowing a decreased regeneration frequency of the filter. The feasibility of the microwave heating technology was also verified by comparing the energy balance of the entire process to the actually employed regeneration technologies.

1. Introduction

Emission standards in US, Europe and Japan, progressively adopted also elsewhere, forced the manufacturers to use several post-treatment processes with the aim to comply the stringent limits for gaseous pollutants and particle emissions. Currently, some new combustion modes (Jiaqiang et al., 2016) were proposed and studied to remove the particulate from the emissions. However the diesel particulate filter (DPF) is currently the usual post-treatment system in Diesel engines for soot particle abatement in passenger, heavy-duty and non-road vehicles (Bermúdez et al., 2015). Among different filter solutions, wall-flow monoliths are the DPF type that showed the best balance between filtration efficiency and pressure drop performance. While flow-through filters, such as ceramic foams, open honeycomb structures, metallic wire-mesh or metal-wools, are characterized by low pressure drop, due to reduced affinity with soot and, consequently, the filtration efficiency is low (40-70%) (Choi et al., 2007). The wall flow 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 collected on the surface and in the porosity of the channel walls, progressively block the pores (Palma et al., 2012). Since the pressure drop increases with soot accumulation, the DPF needs to be periodically regenerated by burning off the deposited soot. There are three kinds of regeneration techniques (Zhang et al., 2016): i) **passive regeneration** in which the catalyst is mixed in fuel or deposited on filter substrate to reduce the regeneration temperature, ii) **active regeneration** that is a method to raise the exhaust temperature by the supply of external energy from electricity, fuel and microwave (Palma and Meloni, 2016), and iii) **composite regeneration** with combining the above two methods to accelerate the DPF regeneration process (Zhang et al., 2016). The innovative DPF regeneration technology involving the use of

microwaves to heat the filter up to the soot oxidation temperature (An et al., 2005) allowed to obtain two important results, (i) instantaneous penetration of microwaves into the filter and their selective absorption allow the combustion of soot whereas the DPF remains undisturbed, and (ii) the regeneration treatment can be performed independently of the engine operating conditions (Barba et al., 2012). In our previous works we showed that the use of microwaves to regenerate the DPF is a feasible technology, since in this case, the good dielectric properties of SiC, catalyst and soot, may result in the effective oxidation of diesel soot at lower temperature and higher reaction rate (Palma et al., 2013a) (Palma et al., 2016a). In particular we showed that the simultaneous use of a microwaves applicator and a specifically catalysed DPF with a catalyst load up to 30%wt of CuFe_2O_4 , allows to reduce the temperature, the energy and the time required for the filter regeneration (Palma et al., 2015a). Furthermore we evidenced the positive effect of NO_x normally present in the exhaust gases on catalytic activity, so confirming the results observed in literature for similar systems (Palma et al., 2015b). One way to decrease the soot oxidation temperature is to increase the content of the active species on the DPF, in order to have a higher catalytic activity: but despite being characterized by high filtering surfaces, the silicon carbide monoliths currently available on the market in Wall Flow geometrical configuration are characterized by a median pore diameter of about 15-17 μm , which decreases after the deposition of the catalyst, with the additional effect of increasing the pressure drops. In this regard, bibliographic studies and laboratory tests were performed to change the porosity and the median pore diameter in the bare samples. As shown in literature by Alok and Baliga (1995), it is possible to erode SiC samples producing on its surface some trenches with a depth of 0.3-0.8 μm , by dipping in a 1:1 mixture of $\text{HF}:\text{HNO}_3$ at a temperature of about 45°C. Due to the simplicity of this method, with the results in terms of erosion and no deterioration in the quality of the SiC crystals, the method proposed by Alok and Baliga was deemed suitable for laboratory experimentation (Palma and Meloni, 2016b). So the objectives of this work are to increase the active species load on the DPF by increasing the average pore diameter of the bare SiC filter: in this way it is possible to further reduce the PM oxidation temperature and keep low the pressure drop, allowing so a lower filter regeneration frequency. Furthermore, the feasibility of the microwaves heating technology was verified by comparing the energy balance of the entire process to the actually employed regeneration technologies.

2. Materials and methods

2.1 Experimental tools

In this work CuFe_2O_4 catalysed DPFs with different loads of active species were prepared; the catalysed DPFs were characterized by Scanning Electron Microscopy (SEM mod. LEO 420 V2.04, ASSING), Energy dispersive spectroscopy (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK), 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

Silicon Carbide (SiC) monoliths (Pirelli Ecotechnology, 150 cpsi), were selected as supports for the preparation of the structured catalysts. The monoliths were suitably shaped to achieve a rectangular form, in order to be inserted in our reactor. The Copper Ferrite (CuFe_2O_4) was prepared starting from iron nitrate and copper nitrate mixed, in distilled water, in a 2:1 molar ratio, continuously stirred at 60 °C. The catalytic monoliths were prepared according to the previously optimized preparation procedure (Palma et al., 2013b), by repeated impregnation phases in the prepared solution, drying at 60 °C and calcination at 1000 °C after each impregnation, in order to obtain a load of active species up to 30 %wt. The bare SiC monoliths were previously immersed in a 1:1 mixture of $\text{HF}:\text{HNO}_3$ at a temperature of about 45°C for 30 min, following an optimized procedure to increase their median pore diameter (Palma and Meloni, 2016).

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, allowed to increase the initial median pore diameter from 17 to 24 μm , and the specific surface area from 0.35 m^2/g to 2.16 m^2/g .

3.2 Catalytic samples

The active species deposition on the modified porosity SiC monoliths allowed to obtain a uniform and homogeneous distribution of the active species on the monolith walls and inside the porosity. The BET specific surface area value of the catalytic samples is of 0.43 m²/g: by comparing this result with the one of the bare monolith (2.16 m²/g), a decrease in the specific surface area after the active species deposition is evident, probably due to catalyst occupation of the roughness caused by acid treatment. It is important to underline that this isn't a negative result, since these catalytic systems, developed to limit the soot emissions, are specifically applied to a heterogeneous solid-solid-gas systems, in which the key parameter is the soot-catalyst-oxygen contact and the feasibility of soot combustion depends to a great extent on the catalyst-soot contact conditions: so, it is necessary to maximize the interactions between the catalyst surface and soot particles, both of which are solid components. In our catalytic systems a very strong interaction between soot and catalyst is obtained, as reported in our previous works (Palma et al., 2015a), demonstrating the high catalytic activity towards soot oxidation with the oxygen present in the exhaust. The median pore diameter of the catalytic sample is reported in table 1, in comparison with other catalytic samples.

Table 1: median pore diameter of catalytic samples with different loads of active species as function of the dipping time in the acid solution

Dipping time [min]	%wt of CuFe ₂ O ₄	Median pore diameter [μm]
0	20	13.30
30	20	17.25
0	30	9.00
30	30	15.00

The above reported results evidenced the positive effect of the preliminary acid treatment on the bare SiC monoliths, since the increased median pore diameter of the ceramic matrix, allowed, as expected, the increase of the median pore diameter of the catalytic sample if compared with the analogue without acid treatment. From SEM images (figure 1) we observe the very homogeneous distribution of the active species on the filter surface, so confirming the results reported in our previous works (Palma et al., 2012). We can also observe the absence of cracks due to preliminary acid treatment. Furthermore, the SEM image and the elements distribution as obtained by EDX element mapping (not reported here), evidenced that for the same filter the encountered elements are, apart from C, O and Si (the structural elements of the filter), also Cu and Fe, the catalyst active species.

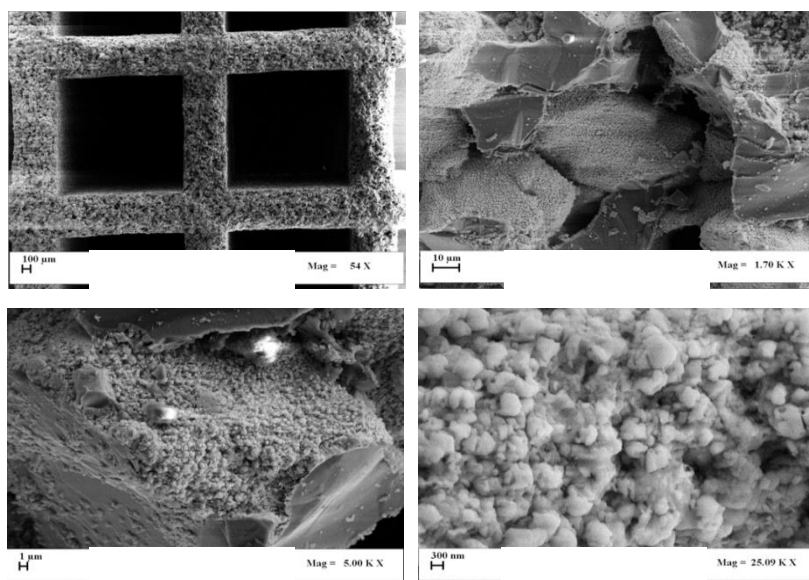


Figure 1: SEM images of 30%wt CuFe₂O₄ loaded monolith at various magnitudes: (a) 54 KX, (b) 1.70 KX, (c) 5.00 KX, (d) 25.09 KX

The results of the catalyst adherence tests are reported in figure 2, in terms of weight loss (%) vs number of cycles. The reported results, characterized by weight losses lower than that reported in literature for washcoated supports (Giani et al., 2006), demonstrated the good adhesion of the active species on the SiC granules even in absence of a washcoat. This is due to the preliminary thermal treatment of the bare supports

(calcination at 1000°C for 48 hours) that resulted in a growing coating of the SiC particles with SiO₂ streaks, so greatly helping the adherence of the active species to the filter, even in the absence of a washcoat (Palma et al., 2013b).

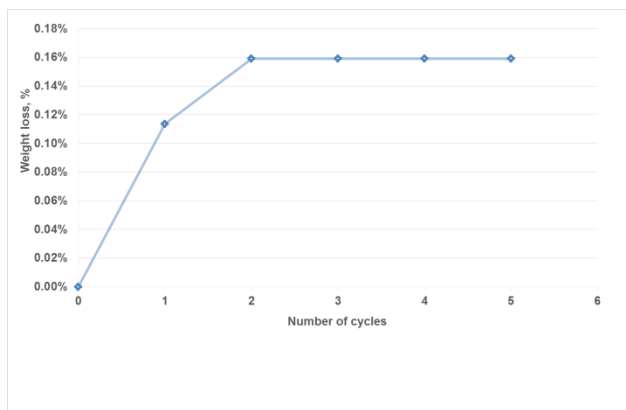


Figure 2: Ultrasonic tests performed on 30 %wt CuFe₂O₄ catalysed monolith

3.3 Catalytic activity tests

All the deposition tests were performed at the operating engine conditions of 920 rpm and Poil = 30 bar, with a fixed flow rate into the filter of about 110 l/min, with the exhaust gas temperature of 200°C, and with a soot concentration in the exhaust gas of about 45 mg/m³. The deposition and on-line MW assisted regeneration steps were performed following the previously optimized procedure (Palma et al., 2015a). The behavior of the pressure drop through the filter (DP) during the soot deposition phase as function of the deposition time for a 20%wt and 30%wt catalytic filter with modified porosity is reported in figure 3, compared with a 20%wt catalytic filter without modified porosity.

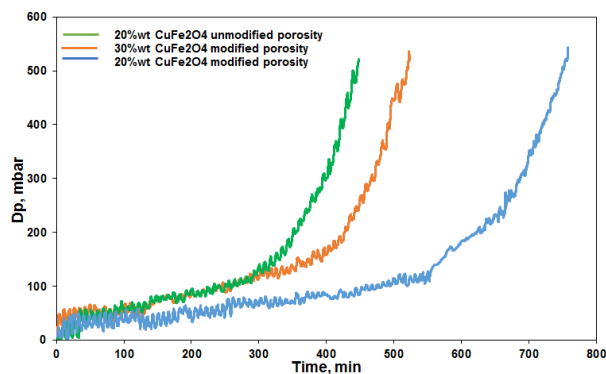


Figure 3: Behavior of pressure drop as function of soot deposition time for different catalytic filters with and without modified porosity

The better filter performances in terms of deposition duration due to porosity modifying procedure are clearly evident: with the same active species loading (green and blue bars) the time needed to reach the limit value of DP (about 550 mbar, corresponding to a soot load of about 5 g/l of filter) increases from about 450 to about 750 min, so allowing a consequently decrease of the regeneration step frequency. Furthermore, the increase of the catalyst load up to 30% wt on a filter with modified porosity (orange bar) results in a deposition time still higher than the one relevant to the unmodified filter even with a lower loading of catalyst (green bar). This very important result allows on one hand to obtain a higher duration of the deposition phase, and, on the other hand to better exploit the increased catalytic activity during the regeneration phase due to the higher catalyst loading. It is important to underline that during all the tests the opacity of the exhaust stream at the filter inlet and outlet has the mean values of 22% and 0.2% respectively, with an average filtration efficiency of about 99% for all the filters. The behavior of the pressure drop through the filter (DP) and the temperature profile during the MW assisted regeneration phase of the two catalytic filters investigated is reported in figure 4: this phase was performed by setting the microwave applicator at 50% of its nominal power (about 950 W) and by reducing the exhaust flow rate to about 30 l/min. It is important to underline that before the MW application,

the exhaust gas temperature was constant at about 200 °C. As evident, the microwaves application resulted in the contemporary increase of the outlet gas temperature and of the slope of DP-time curve, due to microwave heating of the DPF. Figure 4 highlights that the modified porosity and the simultaneous higher catalyst content had a positive effect on the threshold temperature and on the regeneration phase duration, since the first decreased from about 380°C (blue bar) to about 350°C (orange bar), and the second decreased from about 22 min (blue bar) to about 15 min (orange bar). Furthermore we can observe that at the end of the regeneration phase the DP/DP0 bars are constant, so indicating that the on-line MW application is able to completely regenerate the filter, differently from what reported by Pallavkar et al. (2009), whose researches evidenced an efficient off-line regeneration of DPF by microwave energy, but an insufficient on-line regeneration.

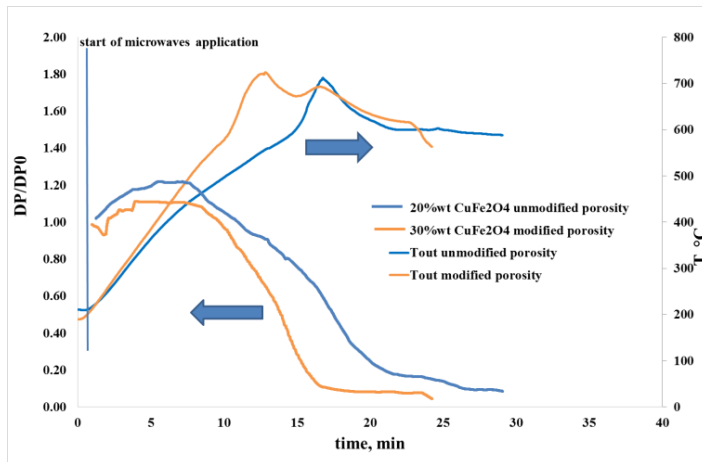


Figure 4: DP and T_{out} as function of regeneration time for 20%wt $CuFe_2O_4$ catalytic filter with unmodified porosity (blue bar) and 30%wt $CuFe_2O_4$ catalytic filter with modified porosity (orange bar)

As showed in figure 5, it is evident that the simultaneous use of microwave technology and a microwave susceptible catalyst is able to reach an energy saving during the regeneration phase of a DPF, with respect to the traditional fuel post-injection. In particular the comparison of the microwave energy supplied, considering the same filter volume (about 0.35 litres), highlighted that the addition of the catalyst allows an energy saving of about 60% (the blue bar versus the yellow one); if the modified porosity is also considered, a further energy saving is achieved, more evident with a higher catalyst load (green bar).

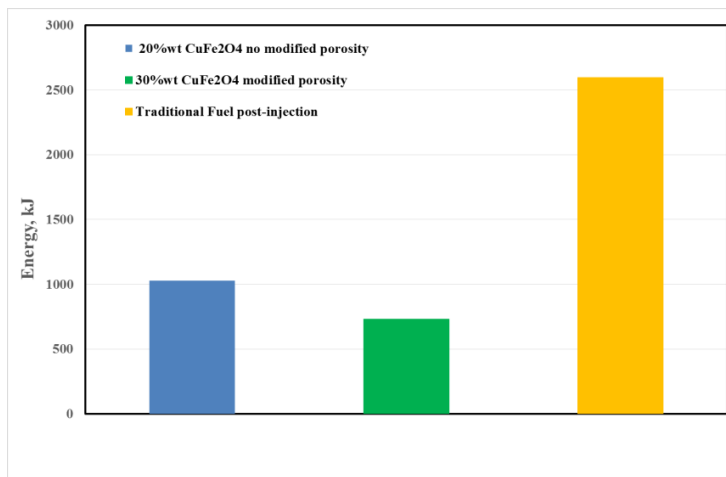


Figure 5: Energy per unit regeneration cycle for the investigated catalytic filters compared with the traditional fuel post-injection

4. Conclusions

In this work the performances of copper ferrite catalysed SiC Wall Flow Filters were investigated in terms of diesel soot oxidation, at different catalyst loading. The SEM analysis performed on the prepared catalytic

samples evidenced the very homogeneous distribution of the active species on the filters surface, the good adherence and the tight contact between the active species and the SiC granules. The active species adherence tests evidenced that the catalytic filter preparation procedure allows a very good and strong active species deposition on the support without any washcoat. The Hg porosimetry tests showed that the preliminary acid treatment of the bare SiC monoliths had a very positive effect, resulting in an increased median pore diameter of the two catalytic samples, if compared with the analogues without acid treatment. The deposition and on-line microwave assisted regeneration tests showed better filter performances in terms of deposition duration due to porosity modifying procedure: with the same active species loading (20%wt), the time needed to reach the limit value of DP (about 550 mbar, corresponding to a soot load of about 5 g/l of filter) increases from about 450 to about 750 min, so allowing a consequently decrease of the frequency of regeneration step. Furthermore, the increase of copper ferrite loading up to 30%wt on a modified porosity filter resulted in a deposition time still higher than the one of the unmodified filter but with a lower loading of catalyst: this very important result allows on one hand to obtain a higher duration of the deposition phase, and on the other hand to exploit the better catalytic activity during the regeneration phase due to the higher catalyst loading. The regeneration tests showed that all the investigated filters were completely regenerated by on-line microwaves application. In particular the results showed that the simultaneous porosity modification and a higher catalyst loading (30%wt) allowed to decrease the threshold catalyst temperature to about 350°C, and the regeneration step duration from about 22 to about 15 min. The very positive effect of the modified porosity procedure on the catalytic performances is consequently reflected on the energy needed to regenerate the filter: the comparison of the microwave energy supplied, considering the same filter volume (about 0.35 liters), during the microwave assisted regeneration phase of all the filter typologies considered in this work, compared to the traditional fuel post-injection, showed that just the addition of the catalyst allows an energy saving of about 60%, that increased up to 75% with a higher catalyst load and modified porosity.

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