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Microwave Susceptible Catalytic Diesel Particulate Filter

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The diesel internal combustion engine is one of the most environmentally-friendly vehicle devices, because it emits less carbon dioxide and is more fuel efficient than the universal gasoline stoichiometric engine. However, considerable challenges still exist regarding the emission control of particulate matter (PM), commonly known as soot, emitted by the diesel combustion process. These ultrafine particles, which have aerodynamic diameters of less than 2.5 μm ($PM_{2.5}$), are problematic as they can cause serious respiratory diseases, including lung cancer and chronic obstructive pulmonary disease. Various filters are commonly used for soot abatement in diesel exhaust, while catalytic oxidation is preferable to intensify burning of soot trapped in filters. The diesel particulate filters (DPFs) are the most important technologies to maintain soot emissions under EU regulations, consisting 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. 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. The results of our previous deposition and on-line regeneration tests on uncatalysed and Copper-Ferrite catalysed DPF, showed that the simultaneous use of a catalyst properly formulated and microwaves during the regeneration step at lower gas flow rate, allows to reduce the energy supplied and the regeneration time than that required for the uncatalysed filter. Starting by these very promising results, the objectives of this work are to increase the active species load simultaneously modifying the porosimetric characteristics of the support, in order to simultaneously further reduce the PM oxidation temperature and keep low the pressure drop.

1. Introduction

The diesel internal combustion engine is one of the most environmentally-friendly vehicle devices, because it emits less carbon dioxide (diesel, 13.4 kg/km; gasoline, 16.6 kg/km) and is more fuel efficient (diesel, 183.1 MJ/100 km; gasoline, 223.5 MJ/100 km) than the universal gasoline stoichiometric engine (Lee et al., 2015). However, considerable challenges still exist regarding the emission control of particulate matter (PM), commonly known as soot, expelled by the diesel combustion process. These ultrafine particles, which have aerodynamic diameters of less than 2.5μm ($PM_{2.5}$), are problematic as they can cause serious respiratory diseases, including lung cancer and chronic obstructive pulmonary disease (COPD) (Lee et al., 2015). Various filters are commonly used for soot abatement in diesel exhaust, while catalytic oxidation is preferable to intensify burning of soot trapped in filters (Vernikovskaya et al., 2015). The diesel particulate filters (DPFs) are the most important technologies to maintain soot emissions under EU regulations (Palma et al., 2012), consisting of 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 (Palma et al., 2012). 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. As the exhaust gas temperature of diesel is typically about 150 °C, this temperature is far too low compared with the minimum combustion temperature of 600 °C needed to burn PM. As a result, some type of system is necessary in order to forcibly regenerate the filter (Palma et al., 2013). The oxidation step is promoted by the so-called ‘passive’ (at temperatures upstream the DPF of ca. 200 – 400 °C)

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and ‘active’ regeneration (temperatures upstream the DPF of ca. 550 – 600 °C) (Liati et al., 2012). The regeneration of loaded DPF using microwaves (MW) belongs to the active systems of regeneration, because, depending on the filter load, the soot is heated up to the temperature for regeneration. The microwave regeneration differs from conventional systems in the point of heat introduction. In conventional systems the heat is transferred to the filter indirectly by heating the exhaust gas (Imenokhoyev et al., 2011). In the microwave regeneration system the heat is coupled directly into the soot: the good dielectric properties of SiC, catalyst and soot, in combination with MW heating and catalytic combustion may result in the effective oxidation of diesel soot at lower temperature and higher reaction rate (Palma et al., 2015a). The results of our previous deposition and on-line regeneration tests on uncatalysed and Copper-Ferrite catalysed DPF, showed that the K addition to our catalyst formulation and the simultaneous use of microwaves during the regeneration step at lower gas flow rate, allows to reduce the energy supplied and the regeneration time than that required for the uncatalysed filter (Palma et al., 2015b): in particular we observed the positive effect that NOx had on catalytic activity. Starting by these very promising results, the objectives of this work are to increase the active species load simultaneously modifying the porosimetric characteristics of the support, in order to simultaneously further reduce the PM oxidation temperature and keep low the pressure drop.

2. Materials and methods

In this work $CuFe_2O_4$catalysed DPFs with 20 %wt of active species are prepared; the prepared powder of $CuFe_2O_4$was characterized by X-Ray Diffraction (XRD), while the catalysed DPFs were characterized by Scanning Electron Microscopy (SEM), Energy dispersive spectroscopy (EDAX), Hg porosimetry tests, H_2-Temperature Programmed Reduction (TPR) measurements, 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). Furthermore, activity tests of soot deposition and on line MW assisted regeneration of catalytic DPFs were performed by means of our diesel emission control laboratory plant (Palma et al., 2015a).

2.1 Catalyst preparation

Silicon Carbide (SiC) monoliths (Pirelli Ecotechnology, 150 cpsi), were selected as supports for the preparation of the structured catalysts. In order to be adapted to our reactor, the monoliths were suitably shaped to achieve the desired geometrical characteristics. The Copper Ferrite ($CuFe_2O_4$) was prepared starting from iron nitrate and copper nitrate mixed in a 2:1 molar ratio and distilled water, continuously stirred at 60 °C. The catalytic monoliths were prepared according to the previously optimized preparation procedure (Palma et al., 2013), by repeated impregnation phases in the prepared solution, drying at 60 °C and calcination at 1,000 °C after each impregnation, in order to obtain a load of active species up to 20 %wt.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 average pore diameter in the bare samples. As shown 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 immersion in a 1:1 mixture of HF: HNO_3 at a temperature of about 45 °C. Due to the simplicity of implementation in the laboratory, with the same 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. The SiC samples were immersed in the acid solution for a time ranging from 5 to 30 min; at the end of each impregnation their porosimetric characteristics were evaluated.

3. Results and discussion

3.1 Bare SiC monoliths

The median pore diameter of SiC sample as function of the impregnation time in the acid solution is reported in Table 1.

As evident from the results reported in Table 1, by this method a speed of erosion of 0.5 μm/min for the first 10 min of treatment, and of 0.1 μm/min for higher times, is obtained. To verify the absence of cracks and breaks caused from the acid attack, SEM analysis were performed, and the results are shown in Figure 1.

The SEM images showed in Figure 1, evidenced the progressive erosion of the grains and confirmed the increase of the average pores diameter with increasing immersion time, in line with the findings from the porosimetric investigations. From SEM images is, however, possible to observe that, although there are no internal cracks and breakage due to immersion of the monoliths SiC in the acid solution, it is evident the formation of small chips on the grains for immersion time higher than 30 min, indicating their gradual weakening, as confirmed by the compression breaking tests (not reported here). Another important parameter that was evaluated is the change in the specific surface area, calculated with the BET method, varying the duration of the acid treatment. The results are shown in Table 2.

Table 1: Porosimetric characteristics of SiC samples as function of the impregnation time in the acid solution

Impregnation time [min]	Median pore diameter[μm]
0	17.0
2	18.0
4	19.0
6	20.0
8	21.0
10	22.0
20	23.0
30	240
35	24.5

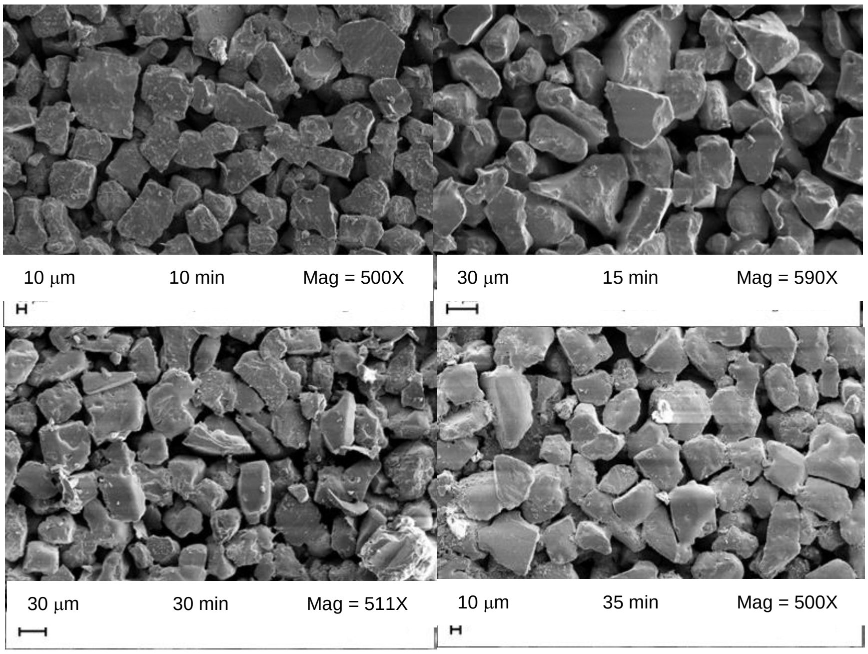

Figure 1: SEM images for SiC bare monoliths at various acid attack times: 10, 15, 30 and 35 min

Table 2: Specific Surface Area of SiC sample as function of the impregnation time in the acid solution

Impregnation time [min]	BET Specific Surface Area[m^2/g]
0	0.35
5	1.87
30	2.16

The data showed in Table 2 highlighted the increase of the specific surface area of the monoliths with the duration of the acid treatment. This is not an unexpected result, since the erosion caused by the acid solution generates roughness on the surface of the grains and within the porosity, thereby increasing the specific surface area. These results led to choose 30 min as the optimal impregnation time of SiC bare monoliths in the acid solution.

3.2 Catalytic samples

After the impregnation of SiC bare monoliths in the acid solution for 30 min, and subsequent calcination in air at 1,000 °C, the active species deposition procedure allowed to obtain an uniform and homogeneous distribution of the active species on the monolith walls and inside the porosity, avoiding the occurrence of the filter fractures shown in literature for the thermal shock of SiC monoliths (Blissett et al., 1997). Furthermore, XRD analysis showed the presence in our prepared Copper Ferrite of the typical peaks of $CuFe_2O_4$ in its tetragonal and cubic form (Palma et al., 2012), and the absence of mixed oxides peaks. The BET specific surface area value of the catalytic samples is of 0.43 m^2/g: by comparing this result with the one of the bare monolith (Table 1), is evident a decrease in the specific surface area after the active species deposition, 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, applied to limit the soot emissions, are heterogeneous solid-solid-gas systems, in which the key parameter is the soot-catalyst-oxygen contact. The median pore diameter of the catalytic sample is reported in Table 3, in comparison with other catalytic samples.

Table 3: Median pore diameter of catalytic samples with 20 %wt of active species as function of the impregnation time in the acid solution

Impregnation time [min]	Median pore diameter[□m]
0	13.30
30	17.25

From the results showed in Table 3 is evident that the preliminary acid treatment of the bare SiC monoliths, resulting in an increased median pore diameter of the ceramic matrix (Table 1), allows, as expected, the increase of the median pore diameter of the catalytic sample if compared with the analogue without acid treatment (from 13,30 to 17,25 μm).This important result has the consequence to decrease the pressure drop of the catalytic filter under equal load of active species (in this case 20 %wt), with consequent decrease in the frequency of regeneration step and without affecting the filtration efficiency.

Also catalytic samples were investigated by Scanning Electron Microscopy (SEM), using a Scanning Electron Microscope (SEM mod. LEO 420 V2.04, ASSING), and Energy Dispersive X-ray Spectroscopy (EDX), performed in an Energy Dispersive X-Ray analyser (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK). From SEM images 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. In particular, in Figure 2 is reported the SEM image and the elements distribution as obtained by EDX element mapping, 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. These results confirm that with our catalytic filter preparation procedure, we can obtain the deposition of the active species on the support without any washcoat.

The results of the catalyst adherence tests are reported in Figure 3, in terms of weight loss (%) vs number of cycles.

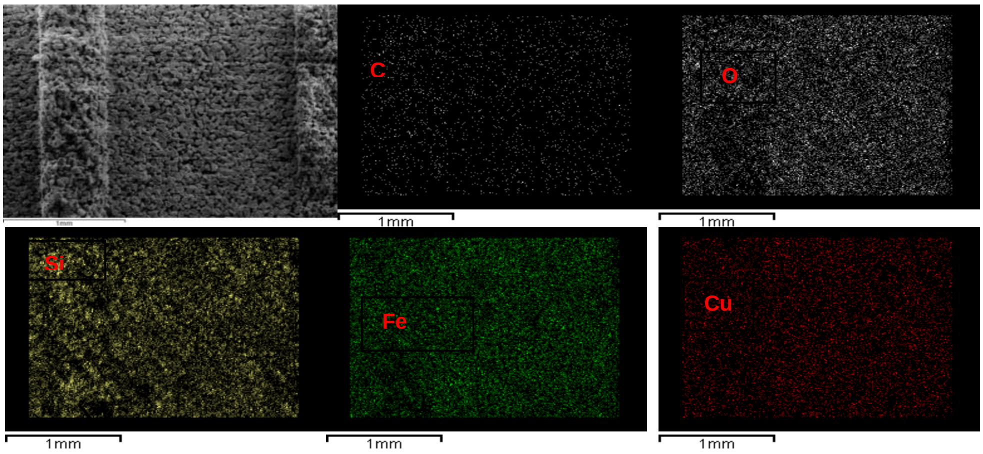

Figure 2: SEM image and distribution of elements, as obtained by EDX element mapping, for the 20 %wt $CuFe_2O_4$catalysed filter

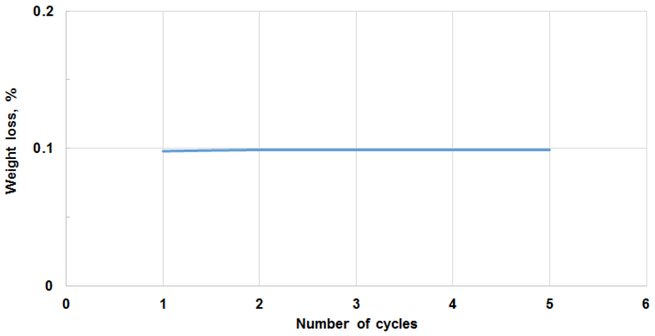

Figure 3: Ultrasonic tests performed on 20 %wt $CuFe_2O_4$catalysed filter

The above reported results, characterized by weight losses lower than that reported in literature for wash coated supports (Giani et al., 2006), demonstrate the good adhesion of the active species on the SiC granules even in absence of a wash coat. This is due to the preliminary thermal treatment of the bare supports (calcination at 1,000 °C for 48 h) that results in a growing coating of the SiC particles with SiO_2 streaks, that can greatly help the adherence of the active species to the filter, even in the absence of a wash coat (Palma et al., 2013).

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/m^3.The deposition and MW assisted regeneration phases were performed following the previously optimized procedure (Palma et al., 2015a).The behaviour of the pressure drop through the filter (DP) during the soot deposition phase as function of the deposition time for a 20 %wt catalytic filter with and without modified porosity is reported in Figure 4.

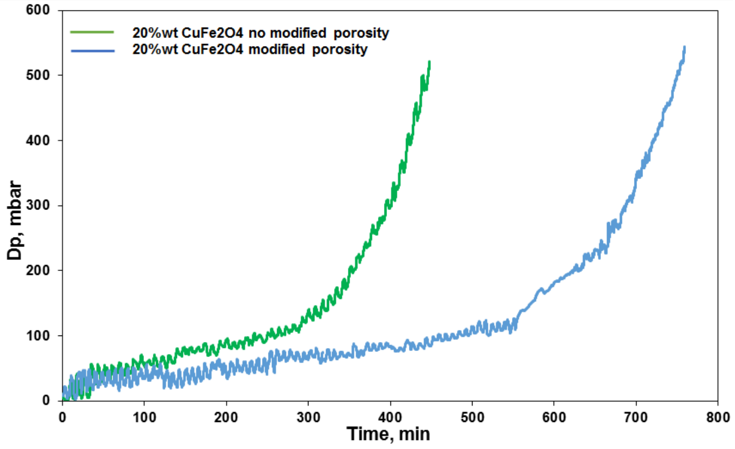

Figure 4: DP as function of soot deposition time for a 20 %wt catalytic filter with and without modified porosity

From Figure 4 is evident that the porosity modifying procedure results in better filter performances, since with the same active species load the time needed to reach the limit value of DP (about 550 mbar) increase from about 450 to about 750 min: this important result allows to consequently decrease the frequency of regeneration step. It is important to underline that during the tests the opacity of the exhaust stream at the filter inlet and outlet have the mean values of 22 % and 0.2 % , with an average filtration efficiency of about 99.0 % for both filters. The behaviour of the pressure drop through the filter (DP) and the temperature profile during the last 15 min of the deposition phase and the complete MW assisted regeneration phase of a 20 %wt $CuFe_2O_4$ loaded monolith is reported in Figure 5. As evident from Figure 5, the MW application results in the contemporary increase of the outlet gas temperature and of the slope of DP-time curve; in particular it is possible to emphasize that when the temperature reaches the value of about 330 °C (the catalyst threshold temperature), the DP curve shows a plateau indicating that the catalytic soot combustion rate is comparable to the soot deposition rate. Furthermore, we can observe that when the temperature increases, the DP curve decreases, so indicating that the complete filter regeneration occurs in about 25 min.

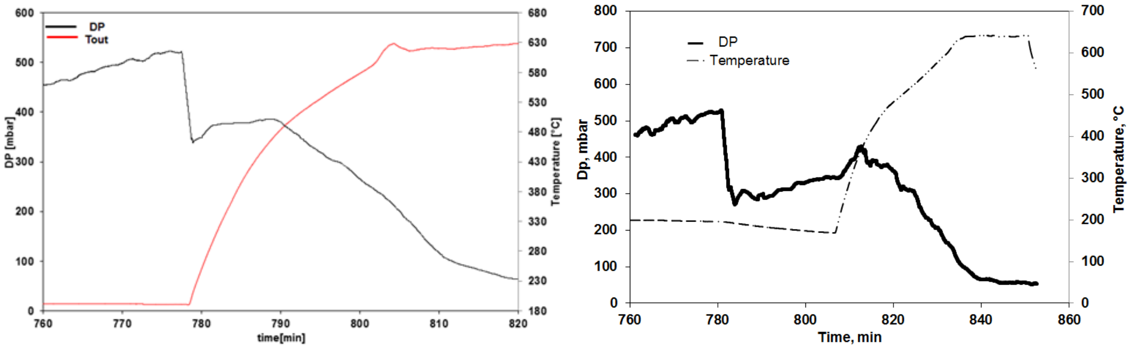

Figure 5: DP and T_{out} as function of regeneration time for a 20 %wt catalytic filter with modified porosity

4. Conclusions

In this work the performances of a 20 % wt copper ferrite ($CuFe_2O_4$) catalysedSiC Wall Flow Filter was verified in terms of diesel soot oxidation, by modifying the initial porosimetric characteristics of bare SiC monoliths. The analysis performed on the modified monoliths showed that the optimal time of impregnation in the HF:HNO_3 solution is of 30 min, and that is possible to increase the initial median pore diameter from 17 to 24 μm. In this way, under equal load of active species, we are able to increase the median pore diameter of the catalytic samples from 13,30 to 17,25 μm. The SEM-EDX analysis evidenced the presence on the catalytic filter not only of C, O and Si (the structural elements of the filter),but also of Cuand Fe, the catalyst active species, homogeneously distributed on the support and in its porosities. The catalytic activity tests performed using the catalytic monolith with 20%wt catalyst load showed that the porosity modifying procedure results in better filter performances, since with the same active species load the time needed to reach the limit value of DP (about 550 mbar) increase from about 450 to about 750 min. This important result allows to consequently decrease the frequency of regeneration step. Furthermore, also after the impregnation in the acid solution the filter has a filtration efficiency of about 99 %, and is able to completely regenerate by microwaves in about 25 min, with a threshold temperature of about 330 °C. In the future we will evaluate the effect of the active species load on these modified filters, with the aim to optimize the catalyst load in terms of pressure drop and frequency of regeneration step.

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