

Catalyst Load Optimization for Microwave Susceptible Catalysed DPF

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Diesel Particulate Filter (DPF) is the most applied device to control the Particulate Matter (PM) from diesel engine exhaust: it consists of alternately plugged parallel square channels (wall-flow monolith) so that the exhaust gases flow through the porous inner walls and the particles are collected on the surface and in the porosity of the channel walls, progressively blocking the pores, causing a growing pressure drop. The accumulated PM is removed by periodic combustion, triggered by an increase in the exhaust temperature, i.e. by injection of fuel into the exhaust gases. The exothermic PM combustion leads in some cases to excessive temperature rise, resulting in filter damage. The development of a cost effective, fast and safe regeneration procedure is the major remaining technological challenge in the use of this device. In our previous works we showed that the simultaneous use of a Microwave (MW) applicator and a specifically catalysed DPF, with 15%wt of CuFe_2O_4 , allows to reduce the temperature, the energy and the time required for the DPF regeneration. Starting by these very promising results, we continued to study in order to further improve the performances of the catalysed DPF in terms of catalytic activity, to reduce the temperature and the MW energy required for the regeneration. The objectives of this work are to optimize both the preparation procedure of the catalytic DPF and the load of active species, and to verify the feasibility of the MW technology by assessing the energy balance of the regeneration phase, comparing it to the actually employed regeneration technologies. In the future we want to evaluate the activity towards the other pollutants present in the diesel exhausts (such as NO_x).

1. Introduction

The continuous evolution of the automotive industry is now accelerating in order to meet the increasingly stringent regulations, and diesel cars must integrate sophisticated after-treatment techniques to fulfill the limits in NO_x and Particulate Matter (PM) emissions (Lapuerta et al., 2012). With regard to the PM issue, most light-duty diesel vehicles are equipped with filters (DPFs) in the exhaust line (Figure 1). These filters, with a filtration efficiency higher than 95% (Palma et al., 2010), have alternately plugged parallel square channels and the exhaust gas flows through the porous walls: in this way PM in exhaust gas is trapped on the wall surface and in the wall inner pores (Tsuneyoshi et al., 2012).

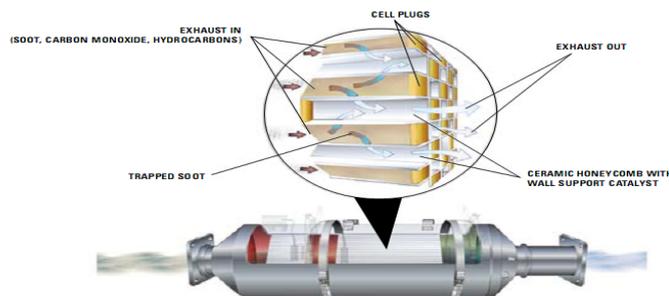


Figure 1: Wall Flow Diesel Particulate Filter.

With time the soot collected in the trap leads to a growing exhaust back-pressure, so a regeneration process (active or passive) must be induced in order to obtain the combustion of the accumulated soot realized by increasing the exhaust temperature up to the soot oxidation temperature (Dilip et al., 2011). In the last years, a growing interest occurred in the use of MW energy for DPF regeneration due to the instantaneous penetration of microwaves into the filter, without heating the exhaust gases; so a filter material, such as SiC, with high dielectric properties, can easily absorb the MW energy and convert it into heat (Ma et al., 1997). Furthermore, since also the soot is a good MW absorber (Meredith, 1998), formulating the oxidation catalyst to absorb MW, the combination of MW heating with catalytic combustion may result in the effective oxidation of diesel soot at lower temperature and higher reaction rate (Palma et al., 2004; Palma et al., 2007; Palma et al., 2011). The DPFs used in this work are 150 cpsi Pirelli Ecotechnology SiC wall-flow monoliths; the selected catalyst is based on the CuFe_2O_4 , due to its very well known dielectric properties and good oxidation activity (Palma et al., 2011). The results of our previous deposition and on-line regeneration tests on uncatalysed and catalysed DPF, showed that the simultaneous use of the MW and the catalysed filter 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., 2011). Based on these very promising results, the objectives of our work are to optimize the preparation procedure of the catalytic DPF and the load of the active species on the filter, and to verify the feasibility of this technology by assessing the energy balance of the entire process, in order to compare it to the above described actually employed regeneration technologies.

2. Results and discussion

In the present work CuFe_2O_4 catalyzed DPFs with different %wt of active species are prepared; the prepared powder of CuFe_2O_4 is characterized by X-Ray Diffraction (XRD) and Thermo gravimetric-Differential Thermal Analysis (TG-DTA), while the catalysed DPFs are characterized by Scanning Electron Microscopy (SEM), Energy dispersive spectroscopy (EDAX), Hg porosimetry tests and TG-DTA analysis.

2.1 Catalyst preparation

The Copper Ferrite (CuFe_2O_4) is prepared starting from iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), mixed in a 2:1 molar ratio, and distilled water, continuously stirred at 60°C . The catalytic DPFs have been prepared by repeated impregnation phases in the prepared solution, drying at 60°C and calcination at 1000°C , in order to obtain a 15%wt, 20%wt, 25%wt and 30%wt load of active species. Differently from the previous preparation procedure (Palma et al., 2011), we changed the drying step (by lowering the temperature value to 60°C , instead of 120°C , and increasing the duration time to about 30 hours, instead of 6 hours) and the calcination step (abrupt heating to 1000°C , slow cooling to 500°C and then quenching to room temperature), since that in the conditions previously developed and optimized for the lower catalyst load, we observed that at higher catalyst load the pores occlusion occurs, together with the occurrence of filter fractures (Figure 2) which compromised its use, as also shown in literature (Blissett et al., 1997). With this new procedure, we realized a more uniform and homogeneous distribution of the active species on the DPF walls and inside the porosity (and not only on the channels external surface), reducing the occlusion of the inner walls pores, allowing to increase the catalyst load up to 30%wt.



Figure 2: fractures in SiC catalysed samples.

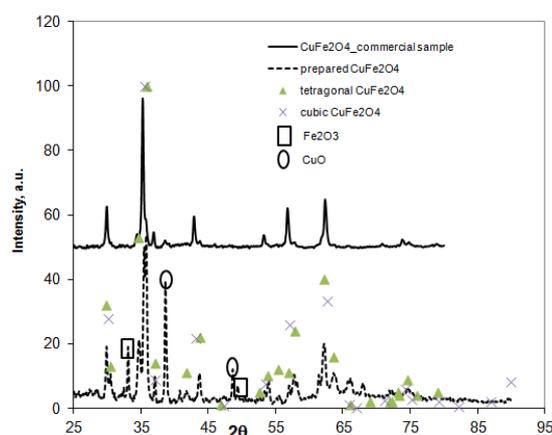


Figure 3: comparison of CuFe_2O_4 XRD spectra.

2.2 CuFe₂O₄ X-Ray Diffraction analysis

In order to verify the formation of the desired CuFe₂O₄, we analyzed the powder obtained from the precursors solution, after drying at 60°C and calcination at 1000°C, by XRD performed with a microdiffractometer Rigaku D-max-RAPID, using Cu-K α radiation. The results are reported in Figure 3, where the diffraction pattern of the sample obtained as previously described is compared with different samples of Cubic (database 77-0010), Tetragonal (database 34-0425) and commercial (Sigma-Aldrich) Copper Ferrite. XRD analysis show the presence in the prepared Copper Ferrite of the typical peaks of CuFe₂O₄ in its tetragonal and cubic form; in Figure 3 we also observe the presence of two minor peaks correspondent to low amounts of CuO and Fe₂O₃.

2.3 SEM-EDAX results

Catalyzed and uncatalysed samples have been investigated by SEM analysis, using a Scanning Electron Microscope (LEO 420 V2.04, ASSING), and Energy Dispersive X-ray Spectroscopy (EDX), performed in an Energy Dispersive X-Ray analyzer (INCA Energy 350, Oxford Instruments, Witney, UK). The comparison between a frontal channel of an uncatalysed and a 30%wt of CuFe₂O₄ catalyzed DPF (Figure 4), shows the very homogeneous distribution of the active species on the filter surface. In Figure 5 the comparison among the channel walls of the uncatalysed filter and the catalyzed filter with 15%, 20%, 25% and 30%wt of CuFe₂O₄ is shown: besides the homogenous distribution of the active species, is clear that their increasing load results in the decrease of the pore diameter, but not in their occlusion, so allowing its use as catalytic filter.

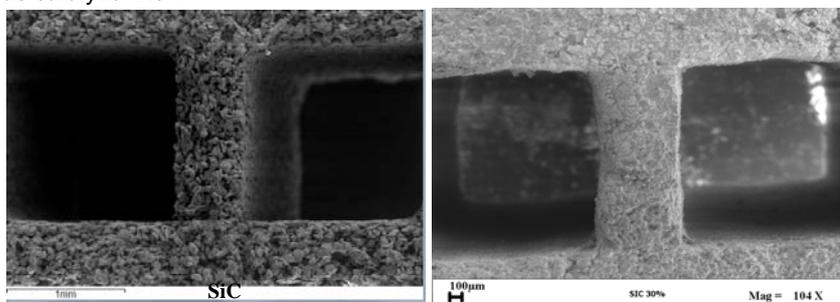


Figure 4: SEM images of an uncatalysed and a 30%wt of CuFe₂O₄ catalysed DPF frontal channel.

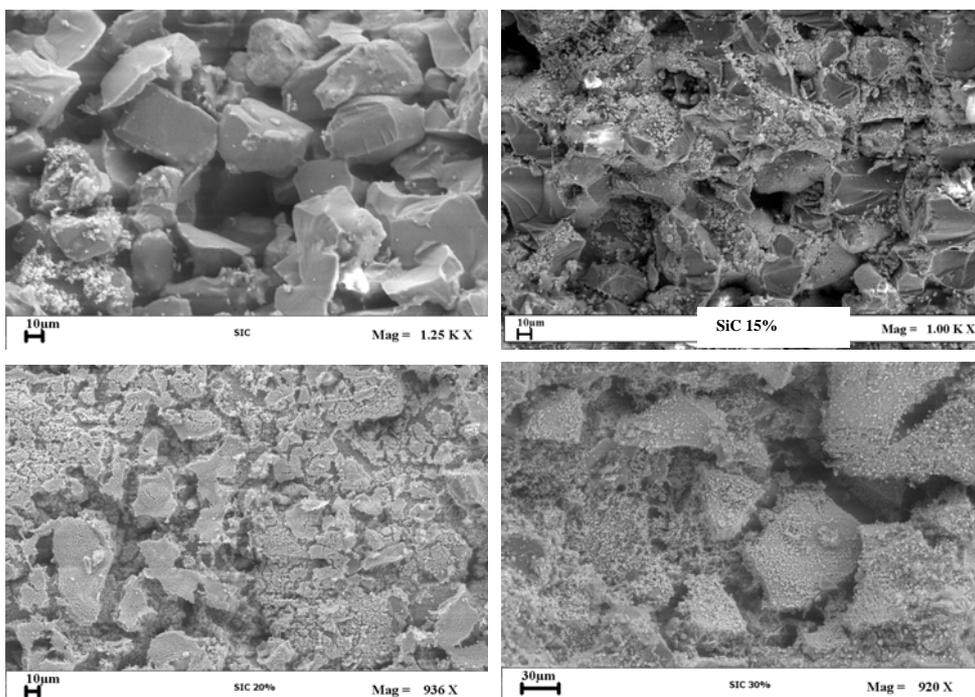


Figure 5: SEM images of the uncatalysed and the catalysed DPF with 15%, 20% and 30%wt of CuFe₂O₄.

2.4 Hg porosimetry tests

In order to evaluate the decrease in the medium pore diameter showed in Figure 5, the porosimetric characteristics of the filters have been measured by the Hg penetration technique using the "PASCAL 140" and "PASCAL 240" Thermo Finnigan instruments: the results are reported in table 1.

Table 1: porosimetric characteristics of the catalysed and uncatalysed filters

	Medium pore diameter (μm)	Total pore volume (mm^3/g)
Uncatalytic SiC DPF	17,0	329
Catalytic DPF with 15%wt of CuFe_2O_4	14,7	264
Catalytic DPF with 20%wt of CuFe_2O_4	13,3	247
Catalytic DPF with 25%wt of CuFe_2O_4	12,3	143
Catalytic DPF with 30%wt of CuFe_2O_4	12,0	134

From these data, it is evident that the increase of CuFe_2O_4 load results in the medium pores diameter and total pore volume reduction. In particular, the main changes of these values are observed up to 20%wt of active species, while the further increase from 20% to 30%wt gives only little decreases. These results can be likely due to the behavior deposition of the catalyst that occurs inside the pores and on the walls of the DPF at the lower load, while only on the external surface at the higher catalyst load.

2.5 TG-DTA analysis

The catalytic activity of powder catalyst and catalyzed DPF, was evaluated by simultaneous TG-DTA analysis (SDT Q600 TA Instruments) of soot alone and of soot mixed in a mortar with milled catalyzed DPF samples at different catalyst load (15, 20, 25 and 30%wt of Copper Ferrite) and with the powder catalyst. Samples were heated in air (flow rate = $100 \text{ Ncm}^3 \text{ min}^{-1}$) from 25 to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$. The results are reported in Figure 6, as Derivative Weight (in %/min), referred to the total amount of soot in the sample, in function of Temperature. The TG curve of soot alone shows the typical behavior of this material (ignition temperature of about 550°C and maximum reaction rate at about 620°C). The results relevant to the TG of soot mixed with the CuFe_2O_4 powder show that the ignition temperature is lowered to 380°C and the maximum combustion rate temperature is lowered to about 450°C , confirming its very good activity toward the soot oxidation. The comparison of the results relevant to the soot mixed with different CuFe_2O_4 loads catalyzed DPF, shows that increasing the load of active species, the ignition temperature and the maximum combustion rate temperature are both lowered and, more important, the rate of the catalytic combustion reaction increases.

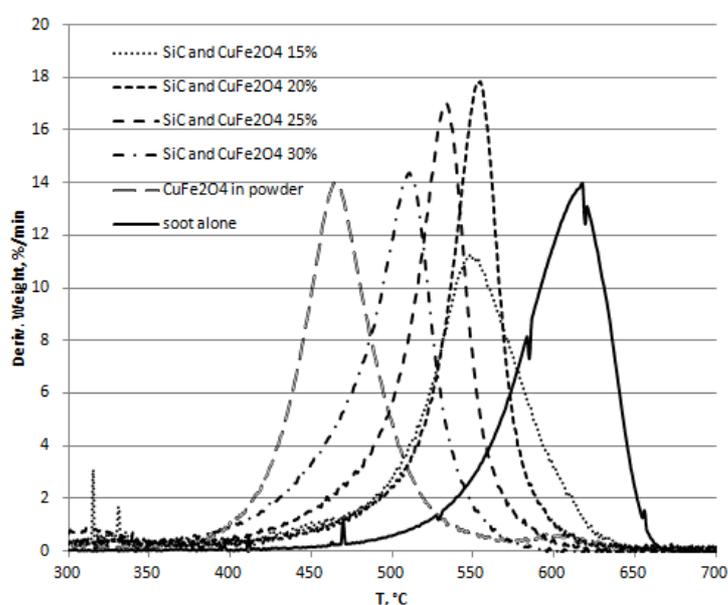


Figure 6: TG test performed on soot alone, soot and CuFe_2O_4 , soot and SiC WFF with 15%wt, 20%wt, 25%wt and 30%wt of CuFe_2O_4 .

2.6 Bending strenght tests

In table 2 the results of the bending strength tests performed in the Pirelli Ecotechnology laboratory on the catalysed and uncatalysed SiC samples are shown.

Table 2: bending strength of catalysed and uncatalysed SiC samples

	Wall thickness (mm)	Channel (mm)	Bending strength (MPa)
Uncatalytic SiC DPF	0,58	1,56	30
15 %wt of CuFe_2O_4 Catalytic DPF	0,58	1,53	50
30 %wt of CuFe_2O_4 Catalytic DPF	0,55	1,56	52

As evident from these data, the increase in the catalyst load results in a higher DPF bending strength, even if the main gain is observed up to 15%wt of CuFe_2O_4 , while the further increase to 30% gives an almost unappreciable rise. These results confirm our assumptions on the catalyst deposition behavior.

2.7 Catalytic activity tests

Some deposition and MW assisted regeneration tests have been performed on catalytic DPFs with different CuFe_2O_4 load, directly at the exhaust of our Diesel engine (Palma et al., 2011). The typical Pressure Drop (ΔP) profile of a DPF during the deposition phase at the operating engine conditions of 1500 rpm and Poil = 30 bar, with a fixed flow rate into the filter of about 100 l/min, is reported in Figure 7. The data show the stages involved in the soot loading in the DPF: depth filtration, in which soot disperse deep inside the filter-wall pores and form pore bridges thus causing a significant decrease in filter wall porosity and a further increase in the pressure drop values, and cake filtration, in which the soot layer reaches an appreciable thickness on the DPF surface, and starts to act itself as a filter. When the valued soot load is about 5 g/l, we started the MW assisted regeneration phase. In Figure 8 are reported the ΔP and the outlet gas temperature as function of time during the regeneration phase of two catalytic DPFs, with 15% and 20% wt load of active species. In all the tests, as showed in our previous works (Palma et al., 2010; Palma et al., 2011), we heat the DPF with a lower gas flow rate (30 l/min), with the MW generator set at 50% of its maximum power. In all the tests the DPF average filtration efficiency is about 99.5%. As evident from the Figure 8, simultaneously to the MW application, both the outlet gas temperature and the slope of ΔP -time curve increase; by looking more deeply, it is possible to emphasize that the increase in the catalyst load results in higher initial pressure drops across the filter (30 mbar vs 50 mbar), in a lower maximum combustion temperature (350°C vs 400°C) and in a faster regeneration phase. The comparison of the MW energy supplied during the regeneration of the two different DPFs (about 2000 kJ and 1185 kJ for the 15% and 20%wt of active species catalysed filters, respectively), indicates that the increase of the active species load results in a higher catalytic activity and a further lower energy consumption.

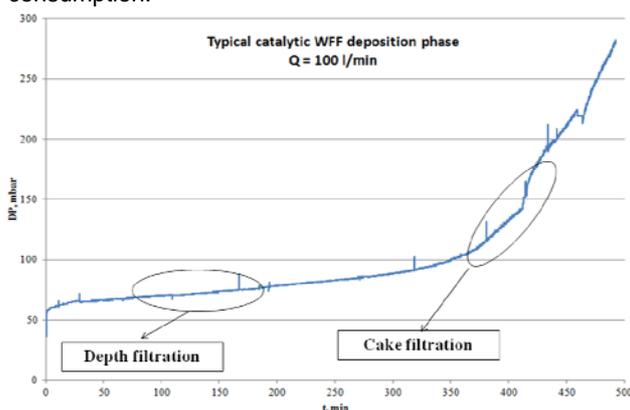


Figure 7: ΔP profile during a soot deposition test on a DPF.

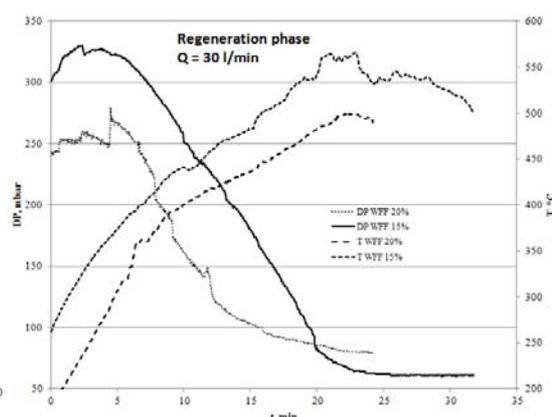


Figure 8: ΔP and temperature profiles during the regeneration phase.

3. Conclusions

The new preparation procedure (drying step at a lower temperature, 60°C instead of 120°C, and for a longer time, and different calcination step) assures a more homogeneous distribution of the active species on the DPF so avoiding the occlusion of the inner walls pores and the filter fractures. The XRD analysis of the prepared CuFe_2O_4 confirmed the presence of the characteristic peaks of the Copper Ferrite in its tetragonal and cubic form, so indicating that with our preparation procedure we can obtain the desired catalyst. The analysis performed on the DPFs show that the increase in the load of active species up to 30%wt results in lower soot oxidation temperature and increased reaction rate, decrease of the medium pore diameter and total pore volume, higher bending strength. The deposition and on-line regeneration tests performed using a catalytic DPF with 15% and 20%wt catalyst load show that the increase in the active species load results in higher initial pressure drops across the filter, in a lower maximum combustion temperature and in a faster regeneration phase, so confirming the TG-DTA results, and, more important, in a further lower energy consumption. In the future work we will verify the effect of a 30% wt catalyst load on the pressure drops across the filter and on the catalytic activity of the DPF, since it is important to note that the optimal catalyst load is represented by the maximum load at which the activity is the highest, with a simultaneous acceptable ΔP value, in order to avoid too high pressure drops across the DPF and a consequently abnormal engine's operation.

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