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Optimising the Catalyst Load for Microwave Susceptible Catalysed DPF

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The Wall-Flow Diesel Particulate Filters (DPFs) represent the best technology available to reduce Particulate Matter (PM or soot) emissions under EU standards: but they need a periodic regeneration. In the last years there has been a growing interest in using MW energy for DPF regeneration because of its instantaneous and selective heating process, which depends on the material dielectric properties. In a previous work presented at the PRES11 Conference, we showed that the simultaneous use of a Microwave applicator and a specifically catalysed DPF with 15 %wt of active species, allows to significatively reduce the energy and the time required for the filter regeneration. Starting by these very promising results, we continued to study in order to further improve the performances of the catalyzed DPF in terms of catalytic activity, in order to try to further lower the regeneration temperature, reducing so the energy required to ignite the combustion of the accumulated soot. In our work we want also verify the activity of the catalyzed DPF towards the NOx present in the diesel exhausts and verify the feasibility of this technology by assessing the energy balance of the entire process, in order to compare it to the regeneration technologies actually employed.

1. Introduction

During the last few decades, concerns have grown on the negative effects that Diesel Particulate Matter (PM or soot) has on health. As a consequence, soot emissions were subjected to restrictions and various emission-reduction technologies were developed and applied. Actually, Diesel particulate filter (DPF) is regarded as the most useful technology to reduce particulate matter from exhaust gas of a diesel engine, with filtration efficiencies in excess of 90 % (Figure 1). Exhaust gas entering the channel is forced to flow through the ceramic porous walls into the adjoining cells and thus leaving the particulates behind (Schejbal et al., 2009). During the filtration, the porosity is progressively blocked by the trapped soot particles, causing a growing pressure drop. So the collected particulate matter inside the trap has to be periodically oxidized to regenerate the DPF.

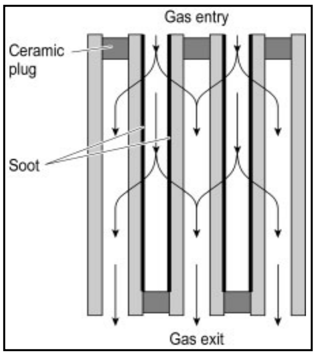

Figure 1: Wall Flow Filter (DPF)

The soot ignition temperature (about 600 °C), is generally higher than the exhaust gas temperatures, and can be slightly lowered by adding active catalytic species (Fe, Cu, or Ce), present in the inner filter coating (Continuous Regenerating Trap or CRT® and Catalysed DPF) or in form of fuel additives (Fuel-

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Borne Catalyst) (V. Dvorak, 2010). For the mentioned cases, no external heat source are applied heating-up the gas, and the so called “passive regeneration“ process takes place. In most cases, although in the presence of catalysts, the difference between the temperature of exhaust gas and the soot ignition temperature is so large that an additional heating device, such as a fuel burner, electric heater or MW heater is necessary to start the regeneration step (Dvorak, 2010). Recently, there has been many interest in using MW energy for DPF regeneration due to the instantaneous penetration of microwaves into the filter body, without heating the exhaust gases; so a filter material with high both dielectric constant and loss factor can easily absorb the MW energy and convert it into heat (Ma et al., 1997). Among the others, due to its dielectric properties, SiC seems to be the most suitable filter material and also the soot is a good MW absorber (Meredith, 1998). Furthermore, if the oxidation catalyst is formulated to absorb MW, one may combine MW heating with catalytic combustion for the effective oxidation of diesel soot at lower temperature and higher reaction rate, lowering the time and the energy required for the filter regeneration step (Palma et al., 2004; Palma et al., 2007; Palma et al., 2011). The DPFs used in this work are 200 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, presented at the PRES11 Conference, showed that our laboratory system is able to achieve the complete filter regeneration and 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 technique of the catalytic DPF and the load of the active species on the filter, to verify the activity towards the other pollutants present in the diesel exhausts (such as NOx), 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 $CuFe_2O_4$ catalysed DPFs with different %wt of active species are prepared; the prepared powder of $CuFe_2O_4$ is characterized by X-Ray Diffraction (XRD) and TG-DTA analysis, while the catalysed WFFs are characterized by Scanning Electron Microscopy (SEM), Energy dispersive spectroscopy (EDAX), TG-DTA analysis and Hg porosimetry tests.

2.1 Catalyst preparation

The Copper Ferrite ($CuFe_2O_4$) is prepared starting from iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), copper nitrate ($Cu(NO_3)_2{\bullet}3H_2O$), and distilled water. Iron nitrate and copper nitrate were mixed in a 2:1 molar ratio and were added over the distilled water. These precursors were mixed and continuous stirred at 60 °C for a better homogeneity. The catalytic DPFs has 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 rate of the drying step by lowering the temperature value (60 °C instead of 120 °C). In this way, we realized a more uniform and homogeneous distribution of the active species precursors on the DPF walls and inside the porosity, reducing the occlusion of the inner walls pores, allowing the possibility to increase the catalyst load on the DPF.

2.1.1 $CuFe_2O_4$ X-Ray Diffraction analysis

In order to verify the formation of the desired $CuFe_2O_4$, we analyzed the powder obtained from the precursors solution after drying at 60 °C and calcination at 1000 °C by X-ray Diffraction (XRD), performed with a microdiffractometer Rigaku D-max-RAPID, using Cu-Kα radiation. The results are reported in Figure 2, where the diffraction pattern of the sample obtained as previously described is compared with different samples of Cubic (database 77-0010) and Tetragonal (database 34-0425) Copper Ferrite and with a commercial Copper Ferrite (Sigma-Aldrich). XRD analysis show the presence in the prepared Copper Ferrite of the typical peaks of $CuFe_2O_4$ in its tetragonal and cubic form; in Figure 2 we also observe the presence of two peaks correspondent to CuO and to Fe_2O_3. In the future work we propose to eliminate these unwanted impurities.

2.2 SEM-EDAX results

Our samples have been also 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), perfomed in an Energy Dispersive X-Ray analyzer (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK).

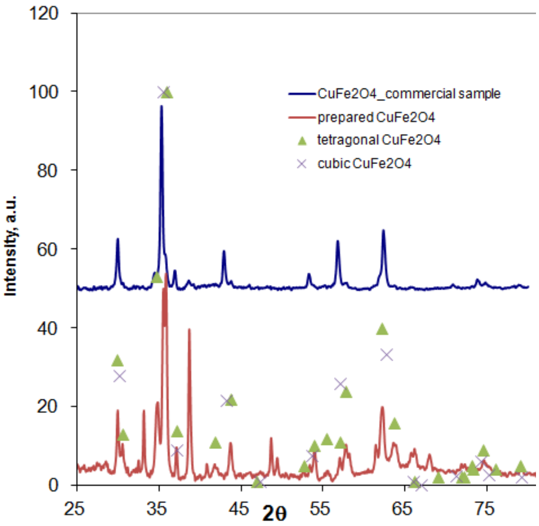

Figure 2: XRD spectra of $CuFe_2O_4$ and prepared $CuFe_2O_4$

In Figure 3 and Figure 4 are shown the results relative to the uncatalysed and catalysed filters.

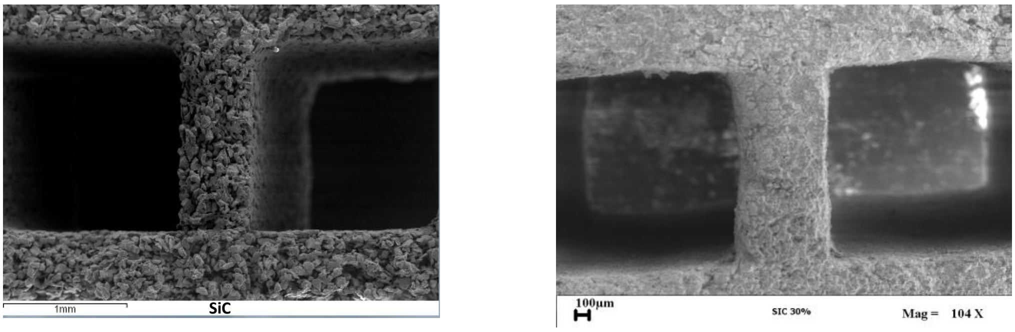

Figure 3: SEM images of the frontal channels of an uncatalysed SiC DPF (on the left) and a catalysed DPF with 30 %wt of $CuFe_2O_4$ (on the right)

2.3 Hg porosimetry tests

In order to evaluate the real decrease in the medium pore diameter showed in the figures 3 and 4, the porosimetric characteristics of the uncatalytic and of the catalytic 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.

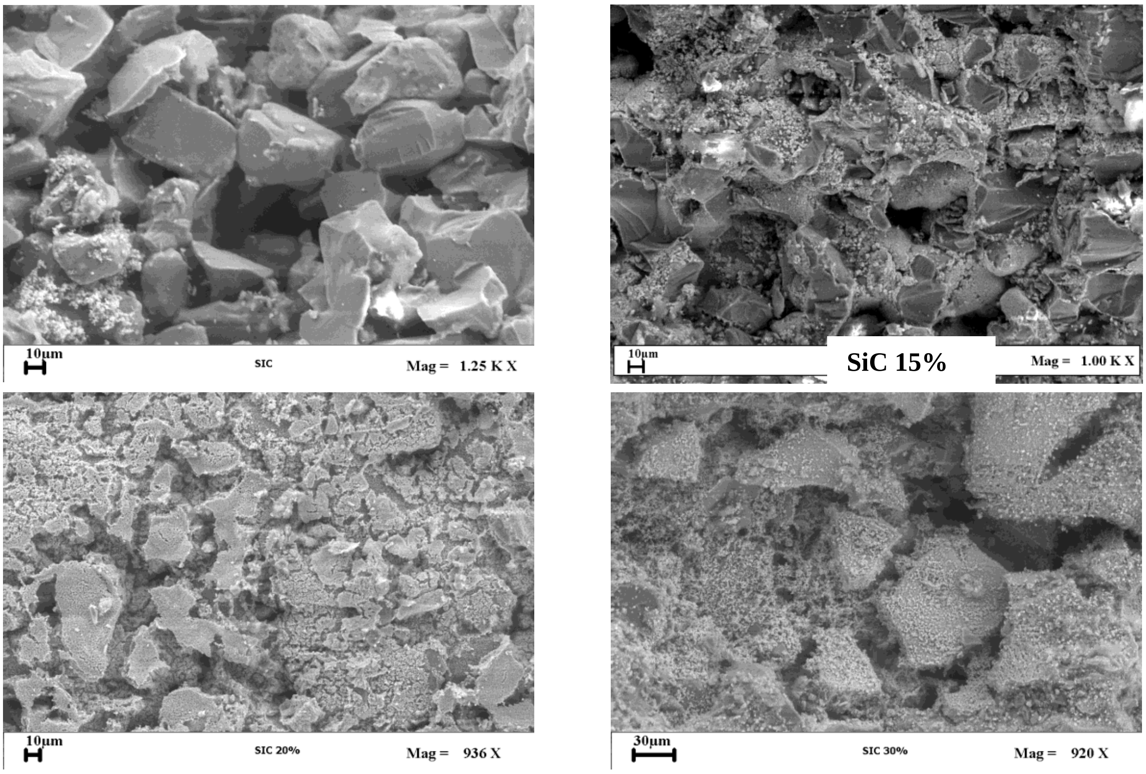

Figure 4: SEM images of the uncatalysed DPF and of the catalysed DPF with 15%, 20% and 30%wt of $CuFe_2O_4$

Table 1: Porosimetric characteristics of the catalysed and uncatalysed filters

	Medium pore diameter (µm)	Total pore volume (mm^3)
Uncatalytic SiC WFF	17,0	329,8
Catalytic WFF with 15 %wt of $CuFe_2O_4$	14,7	263,6
Catalytic WFF with 20 %wt of $CuFe_2O_4$	13,3	246,7
Catalytic WFF with 25 %wt of $CuFe_2O_4$	12,2	143,1
Catalytic WFF with 30 %wt of $CuFe_2O_4$	12,1	134,2

From these data, it is evident that by increasing the load of active species, the medium pores diameter decrease as well as the total pore volume. In particular, the change in the pores diameter is mainly observed up to about 20% of active species, while the further increase from 20 to 30 % gives only a little lost of total porosity, and an almost unappreciable decrease of pores diameter. 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.
Anyway, 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 still acceptable pressure drop value, in order to avoid too high pressure drops across the DPF and a consequently abnormal engine’s operation.

2.4 TG-DTA analysis

The catalytic activity of powder catalysts 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 catalysed DPF samples at different catalyst load(15, 20, 25 and 30%wt of Copper Ferrite). Samples were heated in air (flow rate = 100 Ncm^3 min^{-1}) from 293 to 973 K with a heating rate of 10 K min^{-1}. The results are reported in Figure 5, 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 very low reactivity of this material, that is ignited only at temperatures of about 550 °C, with a maximum of 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, demonstrating its very good activity toward the soot oxidation. By comparing the results relevant to the soot mixed with $CuFe_2O_4$ catalyzed DPF at different catalyst load, one can see that increasing the load of active species on the filter the ignition temperature and the temperature of maximum combustion rate (Tm) are both lowered and, more important, the rate of the catalytic combustion reaction increase.

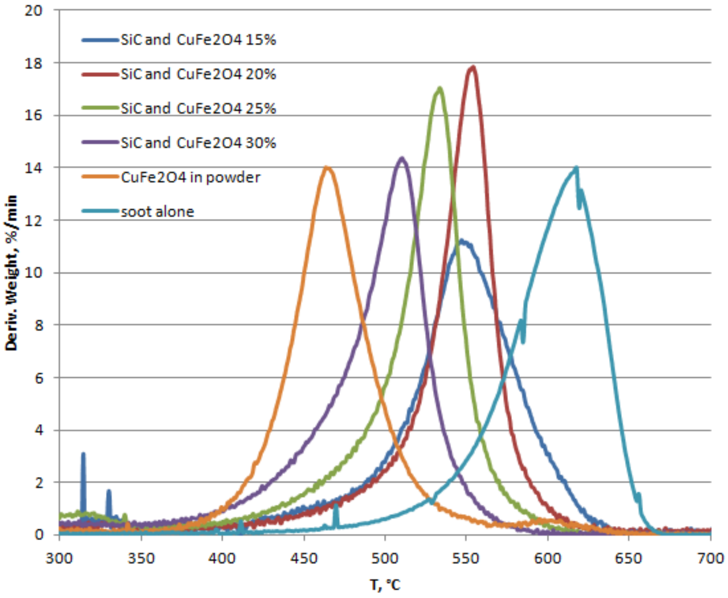

Figure 5: TG test performed on soot alone, soot and CuFe2O4, soot and SiC WFF with 15 %wt, 20 %wt, 25 %wt and 30 %wt of CuFe2O4

3. Conclusions

Starting from our successfully previous deposition and on line microwave assisted regeneration tests performed using a catalytic DPF with 15 %wt of $CuFe_2O_4$ (Palma et al., 2011), we continued to study in order to further improve the performances of our DPF in terms of catalytic activity, in order to try to further lower the regeneration temperature, reducing so the energy required to ignite the combustion of the accumulated soot. In particular, the objectives of our work are to optimize the preparation technique of the catalytic DPF and the load of the active species on the filter, to verify the activity towards the other pollutants present in the diesel exhausts (such as NOx), and to verify the feasibility of this technology by assessing the energy balance of the entire process, in order to compare it to the actually employed regeneration technologies. So we analyzed the prepared $CuFe_2O_4$ and the catalytic DPFs obtained by repeated phases of impregnation in the aqueous catalytic solution, drying at 60 °C and calcinations at 1000 °C. Differently from the previous preparation procedure (Palma et al., 2011), we changed the rate of the drying step by lowering the temperature value (60°C instead of 120°C). In this way, we realized a more uniform and homogeneous distribution of the active species precursors on the DPF walls and inside the porosity, reducing the occlusion of the inner walls pores, allowing the possibility to increase the catalyst load on the DPF. The results of XRD analysis of the prepared $CuFe_2O4$ confirmed the presence of the characteristic peaks of the Copper Ferrite in its tetragonal and cubic form, so indicating that with our preparation technique we can obtain the desired catalyst; the XRD spectrum also shows the presence of the peaks of CuO and Fe_2O_3: in the future work we propose to eliminate these impurities. The TG-DTA analysis performed mixing the soot with our Copper Ferrite powder demonstrate the good activity of this catalyst toward the soot oxidation, with a lower ignition temperature (about 380 °C) and maximum combustion rate temperature (about 450 °C). The analysis performed on the DPF with 15 %wt, 20 %wt, 25 %wt and 30 %wt of $CuFe_2O_4$ shows that the increase in the load of active species results in:

- lower soot oxidation temperature and increased reaction rate (as evident from the TG-DTA tests);
- decrease of the medium pore diameter and total pore volume (as evident from Hg porosimetry tests and SEM-EDAX images).

In particular, the change in the pores diameter is mainly observed up to about 20% of active species, while the further increase from 20 to 30 % gives only a little lost of total porosity, and an almost unappreciable decrease of pores diameter. 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.

Anyway, 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 still acceptable pressure drop value, in order to avoid too high pressure drops across the DPF and a consequently abnormal engine’s operation: further researches are still in progress to evaluate the effect of the load of active species on the pressure drops across the filter when it is applied at the diesel engine exhaust in our laboratory plant. Subsequently, we will prepare a catalytic DPF with the optimal load of $CuFe_2O_4$, in terms of pressure drops and soot oxidation temperature, in order to verify the activity of our catalyst also with regard to the other pollutants present in the diesel exhausts (such as NOx), so completing the activity screening of our catalyzed DPF, and to verify the feasibility of the microwave assisted regeneration technology by assessing the energy balance of the entire process, in order to compare it to the actually employed regeneration technologies.

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