

Optimal Loading of a MW Susceptible Catalysed DPF

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Diesel engines have low fuel consumption and enough torque compared with equivalent gasoline engines. Diesel engines emitted less CO₂ which is known well as the greenhouse gas, and a percentage of new diesel passenger car registrations is increasing in EU year by year. However, NO_x and soot (particulate matter, PM) emitted by diesel engines are a source of pollution with impact on the environment and human health. Since the automobile regulations have been stricter, new technologies for diesel emissions abatement have been proposed, including the addition of fuel additives for diesel smoke reduction. A diesel particulate filter (DPF) is one of the most important technologies for the above strict PM 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. In our previous works we showed that the simultaneous use of a microwave (MW) applicator and a specifically CuFe₂O₄ catalysed DPF, allows to reduce the temperature, the energy and the time required for the filter regeneration. Starting by these very promising results, the objectives of this work are to modify the active species formulation in order to simultaneously further reduce the PM oxidation temperature and keep low the pressure drop.

1. Introduction

Diesel engines combine a high fuel economy with high durability and low maintenance costs and are, therefore, used on a large scale for transportation purposes. However, their exhausts environmental pollution has become more and more serious in the last decade, and currently the regulation of diesel emissions becomes tightened especially with respect to NO_x and PM. Since the reduction of both NO_x and PM to the admitted level cannot be accomplished by engine modifications alone, aftertreatment processes for the reduction of diesel emissions should be developed (Liu et al., 2003). The difficulty to reduce NO_x emissions, led to their reduction as much as possible through engine management known as EGR (Exhaust Gas Recirculation), while emissions of PM are generally controlled through the use of a diesel particulate filter (DPF), that consists of a silicon carbide (SiC) structure in the Wall Flow configuration, with alternately plugged parallel square channels (Palma et al., 2012). As a consequence, the exhaust gases are forced to flow through the porous channel walls that act as filters, so achieving a PM trapping efficiency >95 % (Palma et al., 2011). Since the pressure loss increases by the formation of a thick soot cake as the soot 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 PM (Ohno, 2008). The oxidation step is promoted by the so-called 'passive' (at temperatures upstream the DPF of about 200 – 400 °C) and 'active' regeneration (temperatures upstream the DPF of about 550 – 600 °C) (Liati et al., 2012). The regeneration of loaded DPF using microwaves 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, 2011). In the MW 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., 2013). The results of our previous deposition and on-line regeneration tests on uncatalysed and Copper-Ferrite catalysed DPF, showed that the increase of catalyst load up to 30 %wt and the simultaneous use of MW during the regeneration step at lower gas flow rate, allows to reduce the energy supplied and the regeneration time (Palma et al., 2015). Starting by these very promising results, the objectives of this work are to modify the active species formulation, with the aim to verify the effect of K addition to our catalyst formulation, since Liu et al. (2003) observed that in the case of a DPF loaded with a K-doped copper ferrite ($\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$), the NO_x presence in the exhaust stream had a positive effect on the catalytic activity.

2. Materials and methods

In this work $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ catalysed DPFs with different %wt of active species are prepared; the prepared powder of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ were characterized by X-Ray Diffraction (XRD) and TG-DTA analysis, 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.

2.1 Catalyst preparation

The K-doped Copper Ferrite ($\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$) was prepared starting from iron nitrate, copper nitrate mixed in a 2:1 molar ratio, potassium nitrate, 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 1000 °C after each impregnation, in order to obtain a load of active species up to 30 %wt.

3. Results and discussion

3.1 Prepared samples

The preparation 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.

3.2 TG-DTA analysis

The catalytic activity of differently loaded monoliths in powder, mixed with soot in a mortar, was evaluated by simultaneous TG-DTA analysis (SDT Q600 TA Instruments). Samples were heated in air (flow rate = 100 $\text{Ncm}^3 \text{min}^{-1}$,) from 20 to 700 °C with a rate of 10 °C min^{-1} . The results are reported in Figure 1, as Derivative Weight (in % min^{-1}), referred to the total amount of soot in the sample, in function of Temperature. The curve of soot alone shows its typical behavior (ignition temperature of about 530 °C and maximum reaction rate at about 620 °C). The results relevant to soot mixed with the $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ loaded monoliths powder show that the ignition temperature is lowered to about 420 °C; it is important to highlight that the increase of the active species load, even if it doesn't influence the ignition temperature, results in the increase of the catalytic combustion reaction rate.

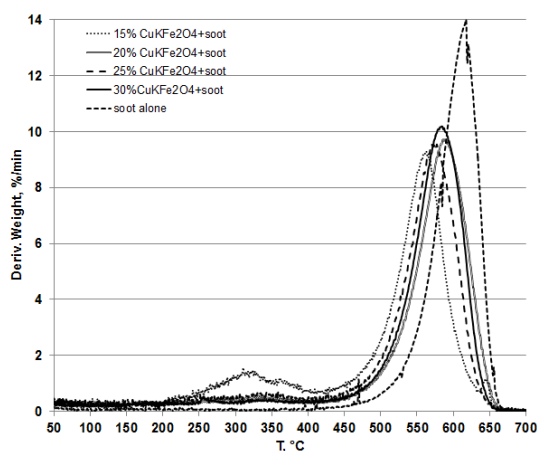


Figure 1: TG tests performed on soot alone, soot mixed with SiC DPF loaded with 15 %wt, 20 %wt, 25 %wt and 30 % wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$

3.3 SEM-EDAX results

Catalysed and uncatalysed samples have been 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 analyzer (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK): the results reported in our previous works (Palma et al., 2012) showed the very homogeneous distribution of the active species on the filter surface, and the comparison among the uncatalysed filter and the catalysed filter with various $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ loads showed that the active species cover all the SiC granules surface and that increasing their load, they don't deposit inside the inner wall pores but only on the external surface, and so on another layer of catalyst: in this way there is only the decrease of the pore diameter, but not their occlusion, so allowing its use as catalytic filter. In Figure 2 is reported the SEM image and the elements distribution as obtained by EDX element mapping, for the 15 %wt catalysed filter: on the catalytic filter the encountered elements are, apart from C, O and Si (the structural elements of the filter), also Cu, K 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.

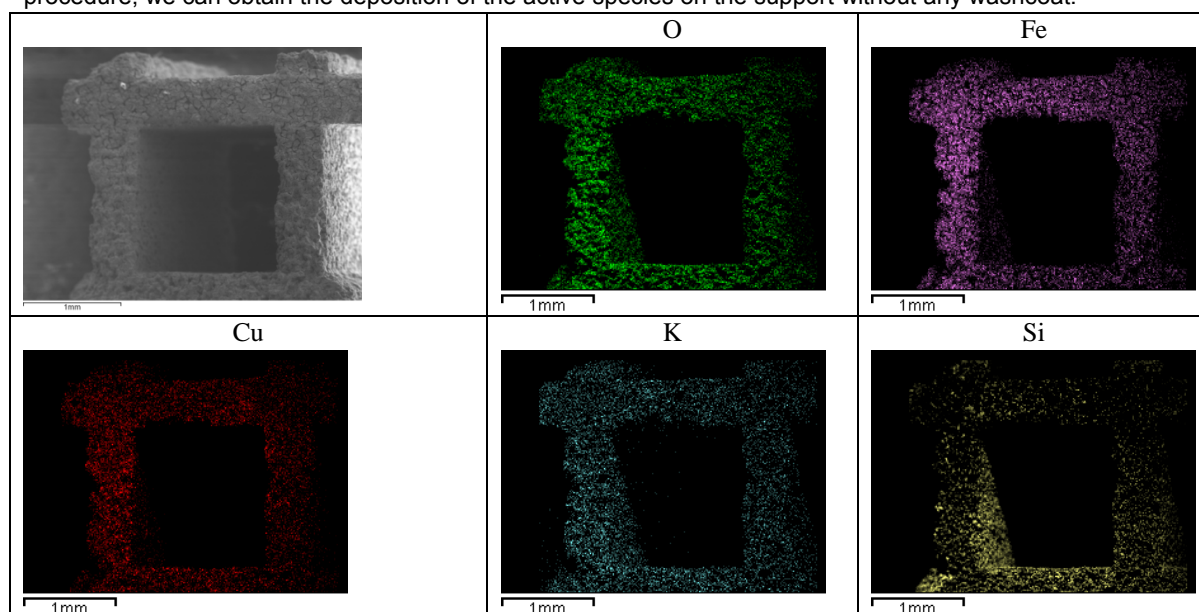


Figure 2: SEM image and distribution of elements, as obtained by EDX element mapping, for the the 15 %wt $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ catalysed filter

3.4 Specific Surface Area

The Specific Surface Area (SSA) of the filters has been obtained by means of the SORPTOMETER Kelvin 1040 Costech instrument, applying BET method for its calculation. The values are summarized in Table 1.

Table 1: Specific Surface Area of uncatalytic and catalysed SiC monoliths

Load of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$	BET Surface Area [m^2/g]
0 %	0.3
15 %	1.2
20 %	1.3
25 %	1.6
30 %	2.3

The values in table 1 show that the growing catalyst load over the bare monoliths induces an increase of the BET specific surface areas; this is an expected result, since the deposition of the active species on a support characterized by low values of specific surface area, such as SiC, results in the increase of surface roughness, without plugging pores.

3.5 Hg porosimetry tests

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 2.

Table 2: porosimetric characteristics of the catalysed and uncatalysed filters

	Median pore diameter (μm)
Uncatalytic SiC DPF	17.0
Catalytic DPF with 15%wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$	15.7
Catalytic DPF with 25%wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$	14.9
Catalytic DPF with 30%wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$	11.0

From these data, it is evident that the increase of the active species load results in the median pores diameter decrease. In particular, by analyzing the changes of this value, is evident that the increase of the active species load doesn't result in the occlusion of the pores, but only in their diameter decrease, from 17 μm to 11 μm . 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.

3.6 H_2 TPR Analysis

The H_2 -TPR analysis was carried out using a SiC monolith catalysed with 15 %wt and 30 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ from room temperature to 900 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C min}^{-1}$ in 5 % H_2/N_2 flow. The reaction parameters (temperature and concentrations) have been monitored by means of an HIDEN Analytical system, including a mass spectrometer.

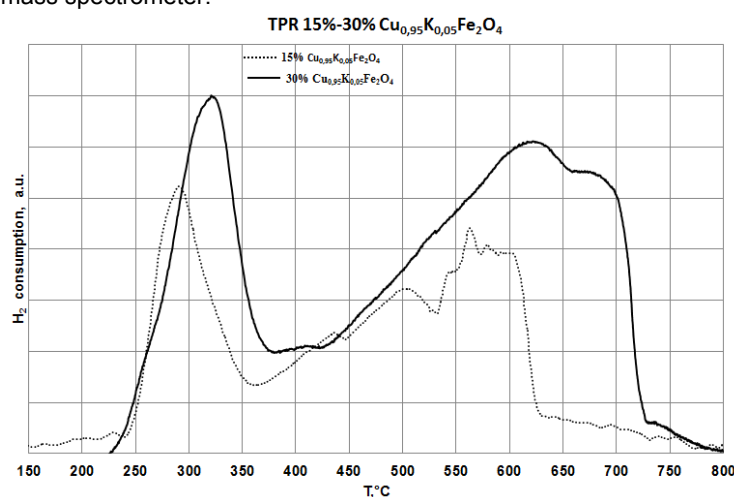
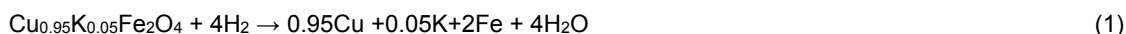


Figure 3: H_2 -TPR profiles of a SiC monolith catalysed with 15 %wt and 30 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$

Figure 3 shows the H_2 -TPR profiles: two pronounced reduction peaks were observed in the range 200 $^\circ\text{C}$ - 375 $^\circ\text{C}$ and 450 $^\circ\text{C}$ - 700 $^\circ\text{C}$ for the two samples; these peaks are attributed to the reduction of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ to Cu and Fe_3O_4 , and subsequently to Fe and K. As evident, the increase of the catalyst load, results in the shift of the peaks to higher temperature values. The total amounts of H_2 consumed for Cu mole (H_2/Cu ratio) were 5 and 4.35, for the 15 %wt and 30 %wt catalyst loaded monoliths, respectively. These values are consistent with that for the complete reduction of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ to Cu and Fe.

The overall reaction is:



The values of 5 and 4.35 corresponds to about 18 %wt and 31 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$, that are in a quite good agreement with the estimated 15 %wt and 30 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ on the monolith. As shown in literature (Kameoka et al., 2005), after the reduction, mixture of Cu and Fe is favorable for the formation of CuFe_2O_4 at about 800 $^\circ\text{C}$ in air, even if not all in the same crystalline form. So we can say that through redox process, the $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ completely reduces to Cu, Fe and K, and then returns to $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$, even if not in the exactly same crystalline form, confirming that it is a very good oxidation catalyst.

3.7 Catalytic activity tests

Preliminary activity tests were performed on two catalytic monoliths, loaded with 15 %wt and 30 %wt of catalyst, respectively. In order to verify the effect of K addition to our catalyst formulation, in terms of catalytic activity with and without NO_x in the exhaust stream, as reported in literature (Liu et al., 2003) in the case of a DPF loaded with a K-doped Copper ferrite ($\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$), some activity tests were performed using a gas

stream with the typical composition of a diesel engine exhaust. In particular some Temperature Programmed Oxidation (TPO) tests were performed using a SiC monolith catalysed with 30 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ from room temperature to 800 °C at a heating rate of 5 °C min^{-1} in 5 % O_2/N_2 flow and then with the addition of about 550 ppm of NO_x . These tests were performed shaping and entrapping the monoliths, on which the soot was previously deposited, into a tubular reactor. The reaction parameters (temperature and concentrations) have been monitored by means of an HIDEN Analytical system, including a mass spectrometer. The comparison of the performances of the samples with different catalyst load are reported in Figure 4.

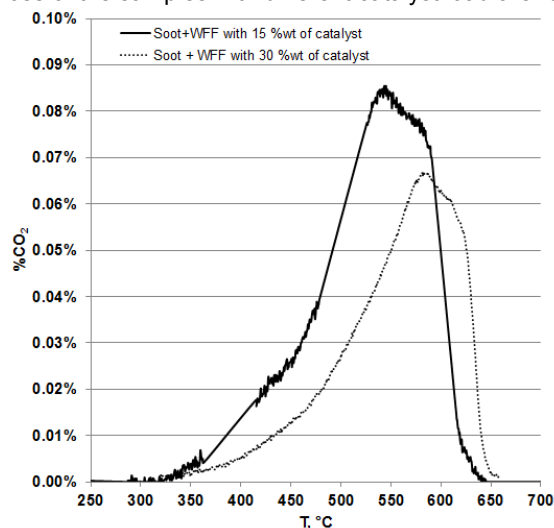


Figure 4: TPO profiles of a soot loaded SiC monolith catalysed with 15 %wt and 30 %wt of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$

The data reported in Figure 4 confirm the results obtained in the TG tests; in particular it is evident that the increase of the active species load doesn't result in the decrease of the ignition temperature, that is of about 350 °C, so confirming also the good oxidation property of this formulation.

The comparison of the performances of the samples in a stream with and without NO_x , is reported in Figure 5.

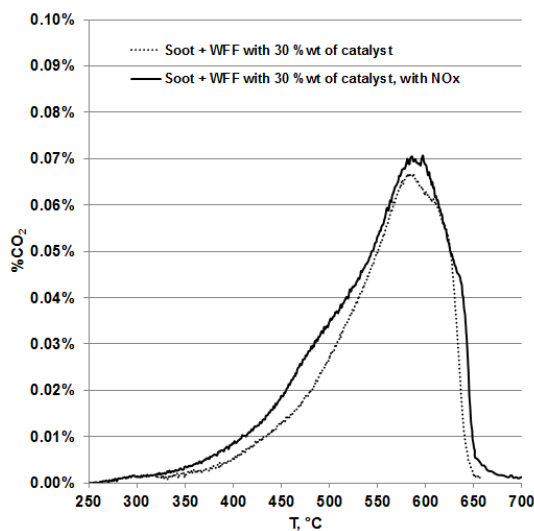


Figure 5: TPO profiles of a 30 %wt $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ loaded DPf in presence of a 5 % O_2/N_2 and with 550 ppm NO_x flow

Figure 5 shows that the presence of NO_x has a positive result on the catalytic activity of the catalyst towards the soot oxidation, since NO_2 is a better oxidant than O_2 , so allowing an ignition temperature decrease of about 80 °C, and a faster reaction rate. These very promising results will be verified in the future by performing activity tests directly at the exhaust of a diesel engine. It is important to note that the use of our proposed

catalyst, doesn't lead to an increment of manufacture cost of the filter, that is actually of about € 1000,00 for light duty diesel vehicles.

4. Conclusions

In this work the performances of a K-doped copper ferrite ($\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$) catalysed SiC Wall Flow Filter was verified in terms of diesel soot oxidation, at various catalyst loads, even in presence of NO_x . The analysis performed on the prepared samples showed that the increase in the load of active species up to 30 %wt resulted in increased reaction rate, in decreased median pore diameter, even if not in lower soot oxidation temperature. 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 Cu, K and Fe, the catalyst active species, homogeneously distributed on the support and in its porosities. The specific Surface Area analysis showed that the growing catalyst load over the bare monoliths induces an increase of the BET specific surface areas, as expected, since that with the deposition of active species on a support we increase surface roughness to the composite, without plugging pores. The H_2 -TPR measurements showed two pronounced reduction peaks attributed to the reduction of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ to Cu, K and Fe in two steps. As shown in literature, after the reduction, mixture of Cu, K and Fe is favorable for the formation of $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ at high temperature (about 800 °C in air), even if not all in the same crystalline form. So we can say that through redox process, the phase transition from $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ to Cu, K and Fe, and finally return to $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ implying that $\text{Cu}_{0.95}\text{K}_{0.05}\text{Fe}_2\text{O}_4$ is a very good oxidation catalyst. The catalytic activity tests performed using a catalytic DPF with 15 % and 30 %wt catalyst load showed that the increase in the active species load resulted in a higher reaction rate, even if it has no effect on the ignition temperature (about 350 °C), so confirming the TG-DTA results. Furthermore the tests performed in presence of NO_x evidenced the positive effect of NO_x on the catalytic activity of the catalyst, allowing an ignition temperature decrease of about 80 °C. In the future we will evaluate the performances of a DPF loaded with this new catalyst formulation directly at the exhaust of a diesel engine. It is important to note that the use of our proposed catalyst, doesn't lead to an increment of manufacture cost of the filter, that is actually of about € 1000,00 for light duty diesel vehicles.

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