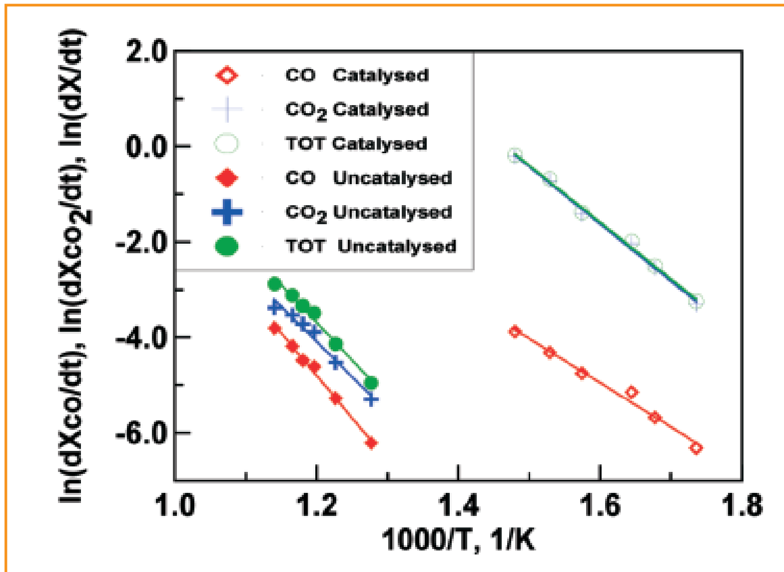

Arrhenius plot for catalytic and uncatalytic oxidation of soot [6]

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CARBON MATERIALS AND CATALYSIS

Part 2: Catalytic Destruction

A catalytic filter based on a Cu/V/K/cl catalyst on ceramic foam was developed for soot abatement at diesel engine exhaust. The filter performances were evaluated and compared with an uncatalytic filter in lab and engine bench scale test. Microwaves assisted filter regeneration was also investigated.

Diesel particulate matter is the most complex of diesel emissions: the basic fractions are elemental carbon, heavy hydrocarbons derived from the fuel and lubricating oil, and hydrated sulphuric acid derived from the fuel sulphur. It contains a large portion of the polynuclear aromatic hydrocarbons found in diesel exhaust. Diesel particulates has a bimodal size distribution which includes small nuclei mode particles of diameters below 40 nm and their agglomerates of diameters up to 1 μm. The characteristics of soot depend very significantly on the engine operation conditions.

Devoted to prof. Elio Santacesaria in honour of his 65th birthday and of his constant contribution to innovative new processes development in industrial chemistry.

The more stringent limits for NOx and particulate of future Euro V standards with respect to Euro IV will require necessarily aftertreatment systems. At present, the only solution for diesel particulate reduction is the Diesel Particulate Filter (DPF).

The first system allowing for a continuous trap regeneration (CRT) was developed by Johnson Matthey, combining a catalyst for the oxidation of NO to NO_2 and a wall flow monolith acting as a particulate filter [1]. However, the high activity of Pt catalyst towards the oxidation of SO_2 results in H_2SO_4 formation and, hence, increased particulate emission [2]. Expected lower sulphur content in fuel should support this solution. More recently a system based on organometallic fuel additives has been commercialised by Peugeot-Citroen (PSA) [3]. A novel after-treatment system, DPNR (Diesel Particulate-NOx Reduction), has been developed by the Toyota group [4], allowing to simultaneously abating soot and NOx, under cyclic lean and rich conditions.

The key parameter for the regeneration of passive DPF (occurring by hot exhaust gas) is the exhaust gas temperature, typically lower than that required to burning off the collected particulate on the filter. The application of catalytic filters could overcome this limitation lowering the soot ignition temperature and allowing for low temperature regeneration or continuous self-regeneration. In the past decade numerous catalysts for the total oxidation of soot have been investigated in laboratory tests [5-12]. The most active catalysts are based on mixed transition metal oxides [7, 8, 10].

Cu/V/K/Cl catalyst: activity and reaction mechanism

A Cu/V/K/Cl catalyst supported on alumina powder so far formulated by us [6] is very active in the combustion of various carbonaceous materials [9], allowing soot burned out in the range of temperatures 300-400 °C [6]. Moreover, with respect to the uncatalysed combustion the reactivity of soot increases of some orders of magnitude while the apparent activation energy is less than half (Fig. 1) [6].

We associate the high activity of the Cu/V/K/Cl catalyst to its redox properties: catalyst reduction by soot occurs in all the range of temperature investigated (up to 700 °C), while the re-oxidation process appears strongly activated. Hence, the catalyst threshold temperature is related to the catalyst re-oxidation step while the carbon oxidation rate is closely dependent on the catalyst reduction rate [13].

Influence of secondary exhaust gas components on catalyst activity

In the practical application of diesel exhaust treatment by a catalytic trap various aspects must be taken into account such as the thermal and chemical stability in the combustion exhaust environment allowing for an economically long lifetime. Therefore, the influence of secondary exhaust gas components such as NO_x, SO_2 and H_2O on catalyst performances and/or deactivation has been investigated [14, 15]. Improvement of the soot combustion process likely related to the presence of NO_x in the exhaust was found. Moreover, NO_2 plays a significant role in the oxidation of carbon at relatively low temperature [1, 2] and reduction of NO with carbon occurs in the presence of oxygen [16].

The Cu/V/K/Cl catalyst is capable of activating the oxidation of both soot and NO. The promoting effect of H_2O could be attributed to the presence of potassium, a typical catalyst for carbon gasification by steam. Test performed after sulphation of the catalytic filter evidenced a marked loss of activity. However, in the presence of NO and H_2O the activity of soot oxidation was mostly preserved [15].

Realization of a catalytic filter

The filter itself must fulfil some requirements crucial for the application such as thermal shock resistance, low pressure drop, high soot filtration efficiency, high soot-catalyst contact efficiency.

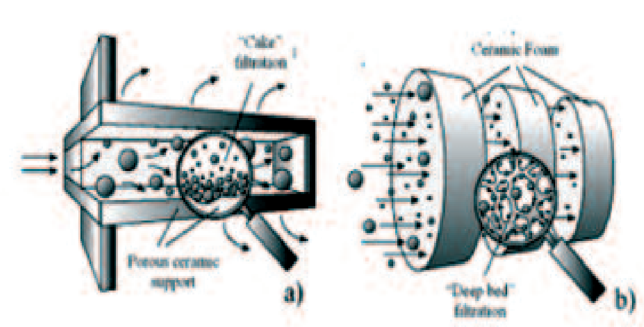

Fig. 2 - Diesel particulate filter working principle: a) cake filtration; b) deep bed filtration [18]

Cordierite and silicon carbide wall-flow filters have been developed with high (>90%) filtration efficiency [17] and are used in new cars. Ceramic foams, characterised by a three dimensional cellular microstructure with highly interconnected voids, have been recently proposed as an alternative filter media (Fig. 2) [18]. Ceramic foams, working according to the deep filtration mechanism, allow: (i) better soot-catalyst contact; (ii) retention of large soot quantities with lower increase of the filter pressure drop even at high gas flow rate [5] and without trap thermal failure during regeneration steps [19].

We have built and tested filters prepared by depositing the Cu/V/K/Cl catalyst on ceramic foam as support. Regeneration performances were first investigated in a lab scale, then in a bench

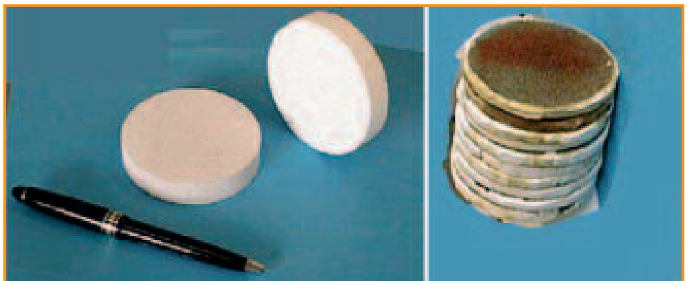

Fig. 3 - Axial flow trap made of 75 mm OD, 7 mm thick, 91% porosity and 65 ppi alumina foams [21]

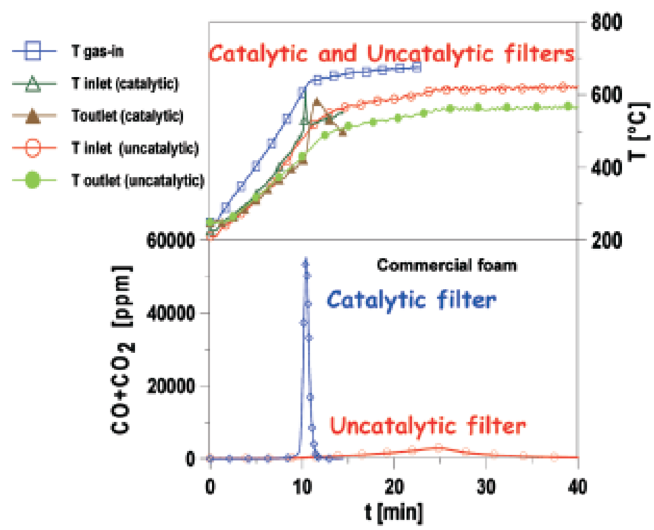

Fig. 4 - Regeneration test on uncatalytic and catalytic ceramic foams in laboratory scale tests [20]

scale apparatus based on a gasoil burner, finally in full scale at the exhaust of a diesel engine.

Catalytic filter regeneration at lab-scale

In lab scale tests the filter was made of 3 alumina foam disks (Fig. 3). Typical results of cyclic loading and regeneration for both catalytic and uncatalytic foam filters are reported in Fig. 4 [20]. Regeneration was carried out with gas stream heated at 50 °C/min. up to 700 °C. Results show that the catalytic foam filter is able to self-regenerate completely (99% regeneration efficiency) with respect to the uncatalytic regeneration (73% efficiency) in a shorter time (12 min. with respect to 38 min.) and with a higher selectivity towards CO_2 (CO_2/CO ratio 3 with respect to 1.3).

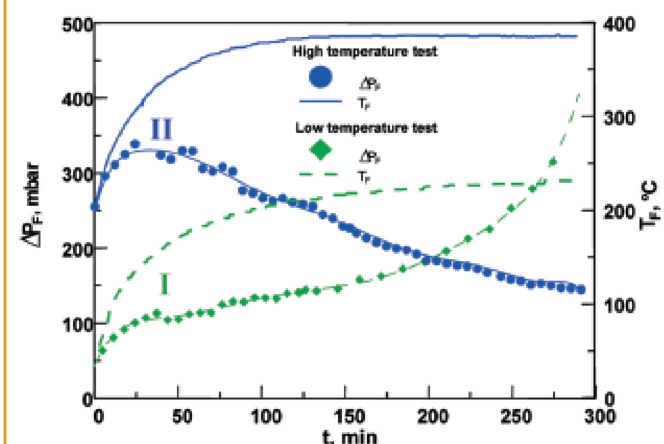

Fig. 5 - Pressure drop and mean temperature of catalytic foam trap as a function of time. Low (I) and high (II) temperature tests at the exhaust of gasoil burner. (Operating conditions: α=23; CBS=9.5 g/h; gas mass flow rate: 30 Nm^3/h; η=50%) [21]

Continuous filtration and regeneration tests at the exhaust of a gasoil burner

The experimental apparatus for continuous soot loading and regeneration test of traps comprised a gas-oil burner generating soot particulates. Axial flow catalytic foam trap (0.34 dm^3) made of 11 alumina foam disks (Fig. 4) were tested changing filter temperature and air/fuel mass feed ratio (α) [21]. In the higher-temperature test (Fig. 5) the monotonic decrease of ΔP_F starting from 600 K indicates that the filter was able to burn more soot than that captured and retained on it, i.e. to regenerate spontaneously. Instead, at lower temperature ΔP_F curve and its slope increased continuously during the test (Fig. 5). Therefore, the catalytic foam filter allows: i) the abatement of relevant amounts of soot from the exhaust; ii) the steady state operation of the trap in terms of temperature and pressure drop depending on the burner operating conditions; iii) the continuous operation of the trap at steady state temperature values close to the typical range of diesel engine exhausts, making it attractive as aftertreatment system.

Continuous filtration and regeneration tests at the exhaust of diesel engines.

The same filter was located at the exhaust of a single cylinder 436 cm^3 DI diesel engine operating at different α values. Filter performances were evaluated by monitoring (i) the pressure drop through the filter, and (ii) the soot removal efficiency.

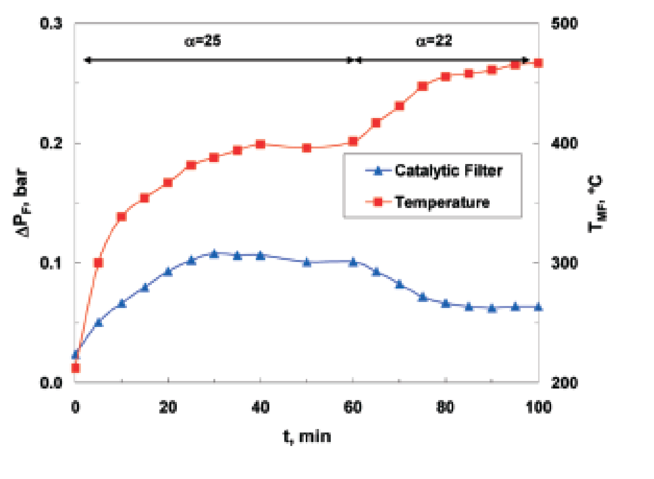

Fig. 6 - Filter pressure drop and temperature as function of time in a test at the single cylinder engine exhaust [22]

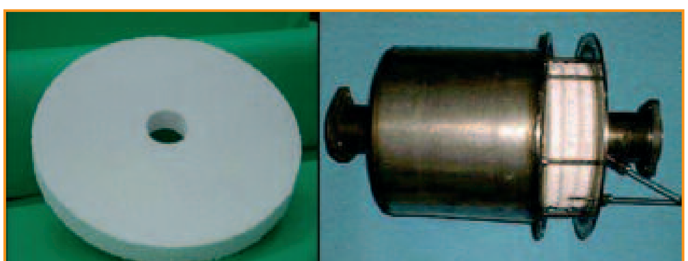

Fig. 7 - Radial flow trap made of OD=177.8 mm, ID=30.48 mm, 15.24 mm thick, 91% porosity and 65 ppi alumina foams [23]

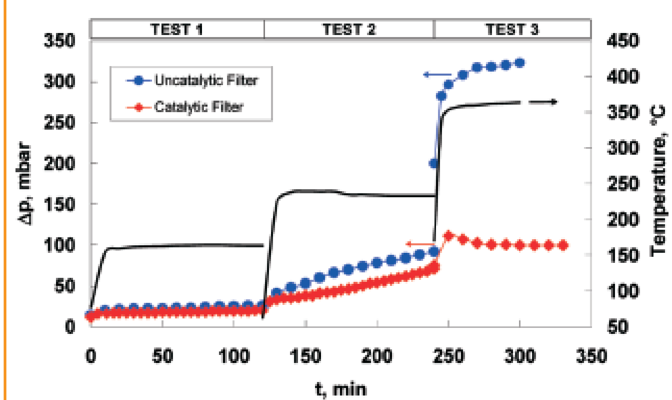

Fig. 8 - Results of Tests at the Common Rail Diesel Engine Exhaust [23]

We found that the catalytic filter is able to regenerate spontaneously: above 350 °C, it is able to reach a working regime where ΔP_F remains unchanged. At α=22 and 470 °C not only the soot currently captured but also that previously accumulated is burned out (Fig. 6) [22]. However, in front of these advantages, a lower filtration efficiency and a higher intrinsic fragility of the ceramic foam must be accounted for. Nonetheless, these unfavourable characteristics can be overcome by optimising the trap design either improving trap fluid-dynamics and introducing specific construction details to minimise the mechanical effects on the trap integrity.

To this purpose radial flow ceramic foam traps were prepared from hollow disks (Fig. 7) and tested for soot removal from the exhausts of a 1.91 dm^3 JTD common rail diesel engine [23]. Trap temperature, filter pressure drop and soot removal efficiency were measured at different test conditions.

Soot filtration (efficiency of 70%) and combustion are efficiently performed with a 2.94 dm^3 radial flow alumina foam trap modified with Cu/V/K/Cl catalyst. Catalytic trap self-regeneration is achieved at 300-350 °C. Above such a temperature while the pressure drop through the uncatalytic trap increases continuously because of soot load, that through the catalytic trap reaches a steady-state value where the soot amounts captured and burned on the trap are equivalent (Fig. 8) [23].

Microwave assisted regeneration of particulate filter

The catalysed regeneration of filter is obviously not feasible at the engine start up, while auxiliary power supply is required to achieve filter regeneration independently of the engine operating condi-

Materiali carboniosi e catalisi. Parte 2: distruzione catalitica RIASSUNTO

È stato sviluppato un filtro catalitico a base di Cu/V/K/Cl su schiuma ceramica per l'abbattimento del soot allo scarico di motori diesel. Le prestazioni sono state confrontate con un filtro non catalitico in test di laboratorio ed al banco motore. È stata studiata la rigenerazione del filtro assistita da microonde.

tions. Microwave MW heating is very attractive for its characteristics of body and selective heating [24]. In particular, temperature controlled regeneration can lead to oxidation of particulate minimizing the thermal stresses of the filter [25].

In the past the regeneration of diesel soot filters by MW was investigated [24], but only few attempts combined this heating technique with catalysis [26-29]. Indeed combining catalytic and permittivity properties of the filter components (catalyst and support material) with the MW absorbing properties of soot should result in enhanced regeneration performance.

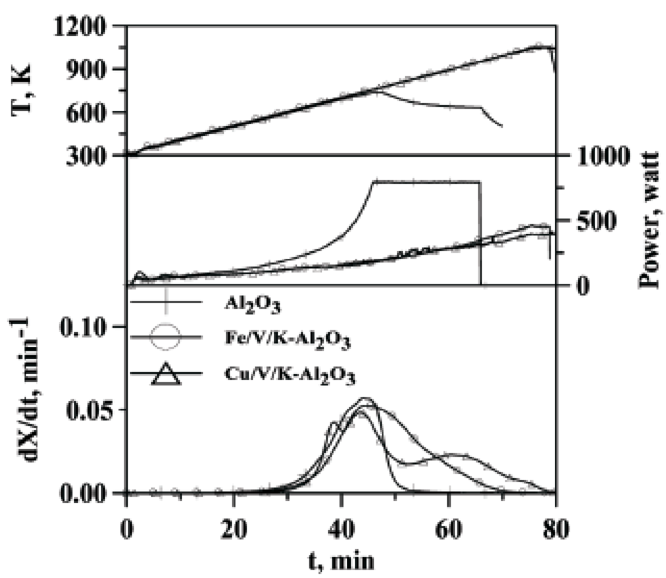

Fig. 9 - Overall carbon reactivity (dX/dt), filter temperature (T) and the microwave power supplied for microwave regeneration of catalytic and uncatalytic foams [29]

Recently, we reported [28, 29] results on the MW assisted regeneration of a ceramic foam filter for soot particulate with a specially designed single-mode MW cavity. We found that a combined system of catalytic filter and MW heating allowed to perform regeneration at the temperature typical of diesel exhaust. In particular, the presence of catalyst assures lower soot ignition temperature, higher selectivity to CO_2, higher soot combustion rate and higher MW energy saving (Fig. 9) [29].

Conclusions

A catalytic filter able to efficiently realize filtration and combustion of soot particles at the exhaust of diesel engine was developed. Catalytic trap self-regeneration was achieved at 300-350 °C. When the exhaust temperature is not high enough for catalysed regeneration the auxiliary power supplied by a MW source under controlled generation allows the filter regeneration in a very short time.

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References

[1] B.J. Cooper *et al., SAE Paper,* 890404, 1989.
[2] W.A. Majewsky *et al., SAE Paper,* 950374, 1995.
[3] P.J. Richards *et al., SAE Paper,* 2000-01-0474, 2000.
[4] Toyota Patent, *Eur. Pat. Appl.* n. 01107629.6, 2001.
[5] Y. Watabe *et al., Tech. Pap. Ser.,* 830082, 1983.
[6] P. Ciambelli *et al., Thermochim. Acta,* 1990, **162,** 83.
[7] A.F. Ahlstrom *et al., Appl. Catal.,* 1990, **60,** 143.
[8] E. Xue *et al., Appl. Catal. B: Environ.,* 1993, **2,** 183.
[9] P. Ciambelli *et al., Catal. Today,* 1993, **17,** 71.
[10] J.P.A. Neeft *et al., Appl. Catal. B: Environ.,* 1996, **8,** 57.
[11] B.A.A.L. van Setten *et al., Appl. Catal. B: Environ.,* 1999, **21,** 51.
[12] D. Fino *et al., Chem. Eng. Sci.,* 2002, **58,** 951.
[13] P. Ciambelli *et al., J. Mol. Catal. A: Chemical,* 2003, **204-205,** 673.
[14] J. Oi-Uchisawa *et al., Appl. Catal. B,* 1999, **21,** 9.
[15] P. Ciambelli *et al., Catal. Today,* 2000, **60,** 43.
[16] T. Suzuki *et al., Ind. Eng. Chem. Res.,* 1994, **33,** 2840.
[17] M.P. Walsh, *SAE Paper,* 990107, 1999.
[18] J.P. Gabathuler *et al., SAE Paper,* 910325, 1991.
[19] L. Montanaro *et al., SAE Paper,* 980540, 1998.
[20] P. Ciambelli *et al., Top. Catal.,* in press.
[21] P. Russo *et al., Top. Catal.,* 2003, **22,** 123.
[22] P. Ciambelli *et al., Top. Catal.,* 2001, **16-17,** 279.
[23] P. Ciambelli *et al., Catal. Today,* 2002, **73,** 363.
[24] Z. Ning *et al., SAE Paper,* 991470, 1999.
[25] V. Palma *et al., Comb. Sci. Technol,* 2002, **174,** 11.
[26] J. Ma *et al., Appl. Catal. A,* 1997, **159,** 211.
[27] Y. Zhang-Steenwinkel *et al., Top. Catal.,* 2004, **30/31,** 257.
[28] V. Palma *et al., Top. Catal.,* 2004, **30/31,** 261.
[29] V. Palma *et al.,* 7th WCCE Glasgow, UK, July 10-14, 2005.