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Scale-up of sulphur resistant promoted-vanadium oxide catalysts for self-regenerating catalytic filters in off-road diesel engines and domestic apparatus

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Abstract

Wall-flow catalytic filters were prepared by impregnation of porous cordierite honeycombs with Cs-Fe-V catalysts. The catalytic filters were tested at the exhaust of a gas-oil burner. Results reported indicate that the trapped soot begin to burn at a temperature around 300–320 °C allowing the self-regeneration of the filter. Performances were found to remain stable also under high SO_2 concentrations, making these catalytic filters suitable for soot removal in off-road diesel engines and domestic apparatus.

Keywords: Soot; Combustion; Catalytic filter

1. Introduction

Reduction of particulate emissions by diesel engines is one of the main challenge for a sustainable future in the next years. Engine modifications and/or a variety of exhaust after-treatments have been proposed for this scope [1,2]. Diesel particulate filters (DPFs) seem the more appropriate solution, being able to reduce particulate by 95% or more [3,4]. DPFs containing platinum-based catalysts have been recently introduced on a number of diesel car models. However, due to the low resistance to SO_2 poisoning of the noble metal catalysts, fuel with very low sulphur level (<50 ppm) is required. On the other hand, for small off-road engines (i.e. used in compressors, snow plows, portable generators, etc.) and domestic apparatus (i.e. gas-oil boiler) no regulation of the sulphur content exists at the present and fuels containing very large (as high as 5000 ppm) sulphur level are still used [5]. Metal oxides-based DPFs, which are more resistant to sulphur deactivation and also cheaper than platinum-based DPFs, could be the catalysed devices of choice for these apparatus.

In this paper, we have focused our attention on the Cs-Fe-V oxide catalytic system which has shown good properties for the soot combustion in laboratory tests with powdered catalysts [6,7]. Here we report data on the scale-up of this catalytic system impregnated within a porous ceramic honeycomb in order to develop a wall-flow self-regenerating catalytic filter for small off-road diesel engines and domestic apparatus. Performances of the device realised were tested in a pilot plant equipped with a gas-oil burner in order to simulate realistic conditions of functioning.

2. Experimental

2.1. Catalytic filter preparation

The catalytic filter (50 mm diameter, 62 mm long) was prepared by impregnation of a commercial porous honeycomb (Corning EX-80, having 100 cells per square inches of 0.017 in. wall thickness and 48% nominal porosity with a mean pore size of 12.5 μm) with an aqueous solution containing the catalytic precursors (NH_4VO_3, $FeCl_3$, CsCl) in the atomic ratio Cs:Fe:V of 2:2:1. The loading of the catalyst on the filter was around 0.5 wt.%. The filter was then dried and calcined at 500 °C in air for 4 h.

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To test the stability to sulphur, the filter was aged in air containing 1000 ppm of SO_2 for periods of time up to 72 h.

2.2. Samples characterization

X-ray diffraction studies were carried out with an Ital-Structures diffractometer using the Cu Kα radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. SEM analyses were carried out with a JEOL 5600LV electron microscope equipped with an EDX analyzer (Oxford series 3000).

2.3. Activity tests

Laboratory catalytic tests for the oxidation of soot on the filter traps were performed in a temperature programmed oxidation (TPO) apparatus as follows. The soot, coming from the gas-oil burner and previously collected on the filter, was oxidised in the TPO apparatus in the range 25–900 °C in flowing air (50 ml/min) at a heating rate of 10 °C/min. Differences between the sample temperature and the nominal value were found always less than 5 °C. The product gas stream was analyzed by a mass quadrupole spectrometer (Fisons-VG Quadrupole). The MS apparatus has been calibrated with respect to CO_2 before each measurement by means of a standard mixture.

2.4. Pilot plant tests

The continuous combustion of soot on the filter traps was tested in a pilot scale plant. The plant consists of a domestic gas-oil burner to generate combustion exhausts connected to a pipeline to convey the gas (Fig. 1). The pipeline was formed by a steel pipe discharge line (diameter = 4 in.) connected through a butterfly valve to a pipe (diameter = 1 in.) used as test line. The overall exhaust generated by the gas-oil burner was transported to the discharge pipe and partially diverted by the butterfly valve to the test line. The test line was electrically heated to control the gas temperature and equipped with a digital flow meter, thermocouples and the sample holder (Fig. 1). Flow rates and temperatures along the discharge pipe were monitored. The sample holder was a cylindrical stainless steel pipe (50 mm diameter, 80 mm long) flanged along the test pipe about 3 m from the burner and used to locate the cordierite diesel filter. Pressure drop between inlet and outlet extremities of the sample holder was monitored by means of a differential strain gage pressure transducer.

The fuel used in the performed tests was a commercially available diesel fuel (H/C molar ratio 1.7, sulphur content 0.05 wt.%) and it was fed to the burner at a flow rate of 2.5 l/h. Combustion air flow rate was regulated to 35 N m^3/h in order to maintain an air/fuel mass feed ratio of 21.

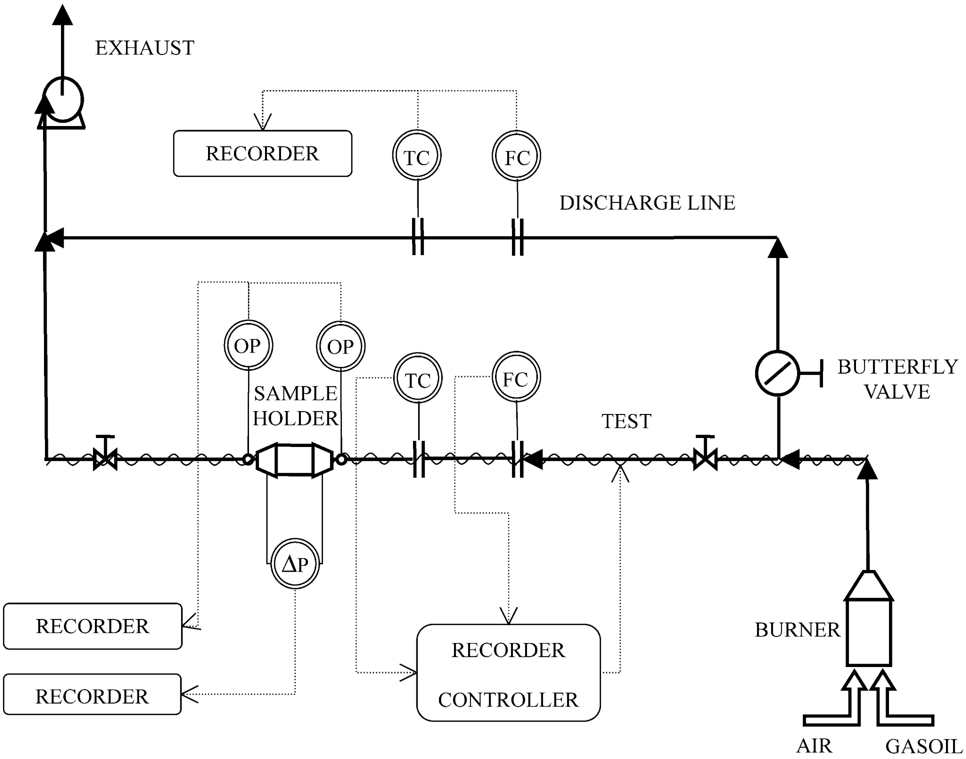

Fig. 1. Pilot plant set-up for continuous tests of the filter traps.

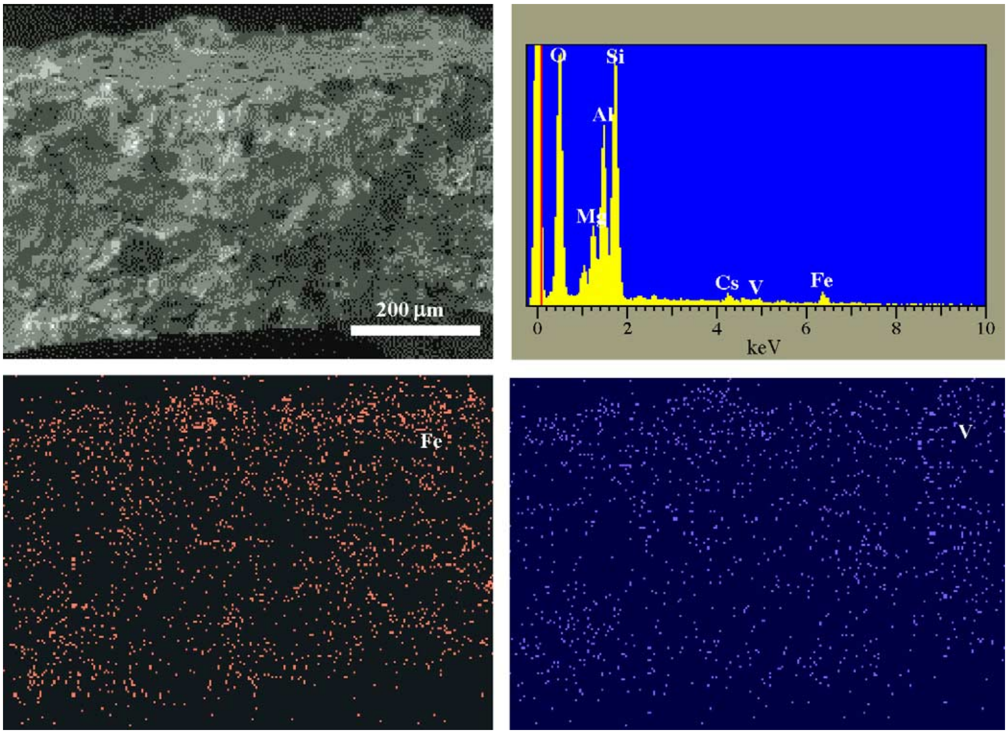

Fig. 2. SEM and elemental and EDX-mapping of the cross section of a catalytic filter wall.

3. Results and discussion

3.1. Catalytic filter preparation and characterization

Preliminary studies were devoted to the optimization of the preparation procedure (catalyst loading, calcination temperature, etc.) of the catalytic filter in order to: (i) form the desired catalytic active phase(s); (ii) obtain a homogeneous dispersion of the catalytic system inside the filter walls; (iii) preserve the filter porosity. This was checked by a complete morphological, microstructural and axial flow characterization of the catalytic device.

Fig. 2 shows the SEM micrograph of the cross-section of the catalytic filter wall. The elemental analysis and the corresponding EDX-mapping are also shown. It can be noted that, at the catalyst loading here considered (about 0.5 wt.%), the spatial distribution of the main elements of the active phases (iron and vanadium) is almost homogeneous. The complete coverage and uniform distribution of the catalyst within the honeycomb structure ensure a high activity and an homogeneous heat distribution during soot burning limiting thermomechanical stress and risk of failure [8]. Although a detailed microstructural characterization of the active phases was not possible, due to their low concentration, XRD analysis has shown the presence of low intensity diffraction peaks associated to Cs–Fe–V–O mixed oxides phases, which have been previously found to be active phases for the soot combustion [6,7].

Comparing the backpressure characteristics at different flow rate of the catalysed filter with respect to that of the uncatalysed filter (Fig. 3) we have not observed any appreciable decrease of the axial flow through the catalytic trap suggesting that the porosity of the filter was preserved after the impregnation step.

3.2. Catalytic activity

The results obtained in the laboratory scale oxidation of the soot collected on the uncatalysed and catalysed filter are reported in Fig. 4a–c. Fig. 4a and 4b shows SEM micrographs of the soot collected on the filters before TPO. Smaller soot particles (indicated by the arrow 1) are

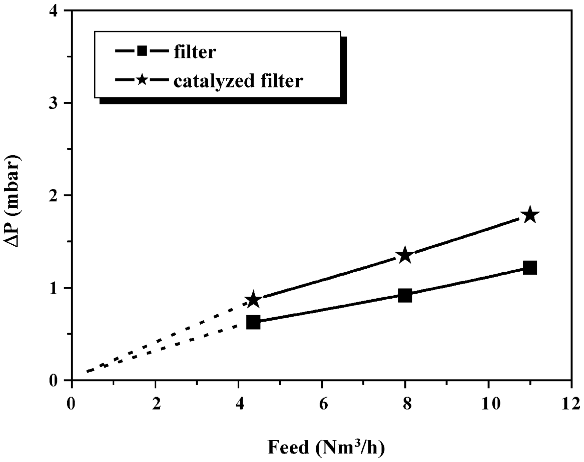

Fig. 3. Comparison of the backpressure characteristics at different flow rate of the catalysed filter with respect to the uncatalysed filter.

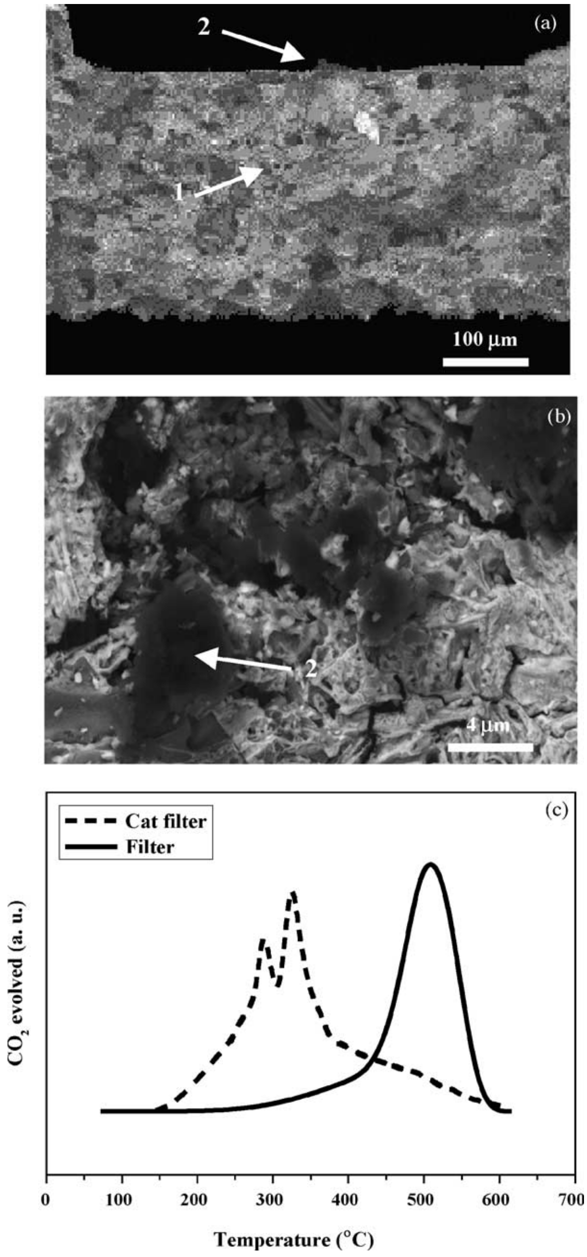

Fig. 4. (a) SEM image of the cross section of a catalytic filter wall and (b) of the surface wall, showing the location of the smaller (arrow 1) and larger soot particles (arrow 2). (c) Comparison of the TPO curves related to the combustion of soot trapped on the uncatalysed and catalysed filter.

trapped within the ceramic walls, whereas larger soot aggregates remain on the external surface (arrow 2).

Fig. 4c shows the TPO curves of the soot on the uncatalysed and catalysed filter. On the uncatalysed filter, the soot burns at temperatures >500 °C. The presence of the catalyst decreases the combustion temperature of about 200 °C as showed by the peaks of CO_2 production around 300 °C. Taking into account the SEM observations we can attribute these low temperature peaks to the soot particles burning in strict contact with the catalyst, likely inside the honeycomb walls. Only a minor fraction of soot, likely the larger soot aggregates trapped on the surface and therefore, little interacting with the catalyst, burns at higher temperature [9–12], as evinced by the TPO curve of the catalysed filter.

3.3. Pilot plant tests

Continuous filter performances were evaluated in a pilot plant under realistic condition of functioning of a domestic gas-oil burner. The evaluation test was performed with the catalytic filter, located in the sample holder along the test line, under a flow of 1 N m^3/h of exhaust gas generated at the burner.

The heat of exhausts increases the temperature on the filter as reported in Fig. 5, reaching after about 1 h of functioning a stationary value of about 340 °C. The pressure drop through the filter (ΔP) as a function of time and filter temperature is also shown. A very different behaviour was observed for the two filter traps tested. On the uncatalysed filter the drop pressure increases continuously, as a consequence of soot accumulation. In fact, the temperature of exhausts remain always lower than the uncatalysed combustion temperature of the soot. In such conditions, unacceptable back pressure can be rapidly reached.

On the catalysed filter the drop pressure initially increases at the same rate as on the uncatalysed filter. This is, however, a transitory state, because the initial low temperature of exhausts not allows soot burning. When the temperature of exhausts reach about 300–320 °C, the pressure drop begin to decreases. This onset temperature of the soot combustion is in agreement with that obtained by TPO experiments in laboratory tests. As also reported by other authors, this confirm that realistic information on such a complex system can be obtained from laboratory tests if the soot-catalyst physical contact is the same as in the true working condition of the filter [11].

At the stationary state, the temperature on the catalytic filter is above the catalysed combustion temperature of the soot, then it is promptly burned after trapping, decreasing

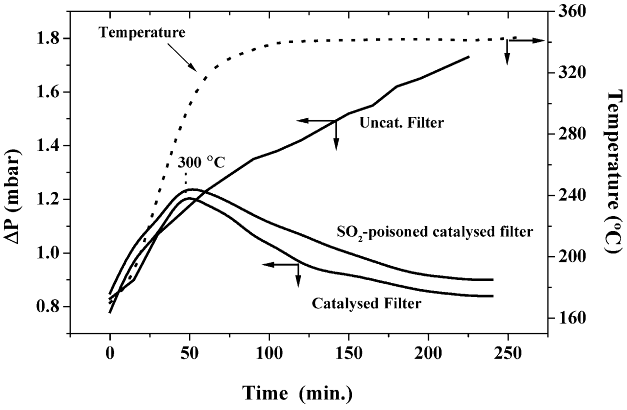

Fig. 5. Drop pressure profile for uncatalysed and catalysed filter as a function of time and exhausts temperature. Drop pressure profile for the SO_2-poisoned catalytic filter is also shown.

backpressure and allowing self-regeneration of the filter. The regeneration temperature is within the temperature range typical of diesel engine exhausts (150–500 °C), therefore the filter could operate without any additional heater device.

Because of the low sulphur content of the fuel used, to test the stability to sulphur of the catalysed device, it was aged up to 72 h in the presence of 1000 ppm of SO_2 before pilot plant experiments. Data obtained (see Fig. 5) are similar to that obtained on the fresh catalytic filter before aging in SO_2, indicating an excellent stability of the catalysed trap towards sulphur deactivation. This is in according with results reported by us on the same powdered catalyst samples [7] and other authors on similar metal-oxides catalytic systems [13]. This is a point of outmost importance because diesel fuels contains sulphur compounds which are released, after combustion, mainly as SO_2. It is well known that SO_2 can deactivate the catalyst, particularly when noble metals are present in the formulation, whereas metal oxides are more resistant than noble metals.

4. Conclusion

The results reported have shown the good performance of a self-regenerating Cs-Fe-V-promoted ceramic filter tested at the temperature of exhaust of a gas-oil burner. The filter performances, also when tested in the presence of high sulphur dioxide loading in the stream, show no alteration indicating an elevated resistance of the catalytic system to the sulphur poisoning. These good characteristics, and the low cost due to the lacking of precious metals in the catalytic formulation, make these self-regenerating catalytic filters promising for soot combustion in the exhausts of small off-road engines and domestic apparatus.

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