ELSEVIER

Catalysis Today 75 (2002) 471–478

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Performances of a catalytic foam trap for soot abatement

P. Ciambelli*, V. Palma, P. Russo, S. Vaccaro

Department of Chemical and Food Engineering, University of Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy

Abstract

A catalytic trap for soot particles was prepared by deposition of Cu–V–K–Cl catalyst on a ceramic foam. Catalytic trap performances were evaluated by treating the exhaust of a gas oil burner under different operating conditions. The results obtained showed that ceramic foam is a particularly suitable support for this application since it yields low gas pressure drop, good soot collection efficiency ("deep bed" filtration mechanism), high thermal shock resistance and good contact throughout the filter between soot particles and catalyst surface. In addition, the catalytic foam trap is able to spontaneously regenerate at operating conditions comparable to those typical of diesel engine exhaust and after more than 70 test hours it retains its activity towards soot oxidation.

Keywords: Catalytic foam; Diesel engine exhaust; Catalytic soot combustion

1. Introduction

The use of a catalytic trap at the diesel engine exhausts, performing both filtration and catalytic combustion of soot, appears effective for matching the future EU limits for car pollutant emissions. However, although the performances of catalytic traps are primarily affected by the catalyst activity [1–3] and by the soot–catalyst contact efficiency [4], the type of filter medium plays a relevant role too. It determines, indeed, the engine backpressure and the capability of soot accumulation when operating conditions are unfavourable for soot ignition even in the presence of a catalyst. In comparison with other filter media proposed in the literature, ceramic foams, operating according to the deep filtration mechanism, appears very promising [5,6]. They allow: (i) a better soot–catalyst contact; (ii) the treatment of relatively high gas flow rates with lower filter pressure drops [7]; and (iii) the retention of large soot quantities without dramatic increase of the filter pressure drop or trap thermal failure during regeneration steps. However, in front of these advantages, a generally lower filtration efficiency and a higher intrinsic fragility of the ceramic foam must be accounted for. Nonetheless, these unfavourable characteristics can become of scarce relevance by appropriate trap design. Actually, an appropriate trap fluid-dynamic design can markedly increase the trap filtration efficiency while specific construction details can minimise the effect of mechanical strength and vibrations on the trap integrity.

Beside those mentioned above, a catalytic trap for diesel exhaust treatment has to show also thermal and chemical stability in the combustion exhaust environment such that an economically long lifetime can be expected during which the catalytic activity is high enough to allow effective soot removal.

In this work a catalytic foam trap was prepared. Its performances in soot abatement and in trap resistance to real working conditions were evaluated by treating for 70 h the exhaust of a gas oil burner under various operating conditions.

* Corresponding author. Tel.: +39-089-964151; fax: +39-089-964057.
E-mail address: pciambelli@unisa.it (P. Ciambelli).

0920-5861/02/$ – see front matter
PII: S0920-5861(02)00098-6

2. Experimental

2.1. Materials

Two 0.34 dm^3 traps were prepared each with 11 alumina foam disks (75 mm in diameter and 7 mm in thickness) (Gimex) with 91% porosity and 65 ppi. In the case of the uncatalytic trap, foam disks were assembled together as received. Instead, in the case of the catalytic trap a Cu/V/K/Cl catalyst [8] was previously deposited over the alumina foam disks, through several cycles of impregnation with aqueous solution of catalyst precursor salts, drying at 120 °C and calcination at 700 °C overnight.

2.2. Physico-chemical characterisation

The ceramic and catalytic foam, either fresh or after 70 test hours at the exhaust of a gas oil burner, described below, were characterised by different techniques. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDAX) analysis of the traps were obtained with a Philips XL30 scanning electron microscope equipped with a LaB6 filament. Specific surface area was evaluated by N_2 adsorption at 77 K, carried out with a Sorptometer 1040 (Costech Instruments). Analysis of catalyst active species was performed by plasma atomic emission spectrophotometry (ICP-AES) of dissolved samples using a Varian Liberty II.

2.3. Apparatus setup

The traps were tested in a pilot scale plant, which includes a gas oil burner equipped with a nozzle giving a gas oil mass flow rate of 1.9 kg/h [9]. Commercial gas oil (H/C molar ratio of 1.75, sulphur content of 0.05 wt.%) was employed in the experiments. Air flow rate to the burner was adjusted in the range 28.5–45.6 m^3/h (STP) to obtain an air/fuel mass feed ratio (α) ranging from 23 to 37. The overall burner exhaust was conveyed to two stainless steel trap holders (20 cm in length, 10 cm ID) located, respectively, at 2 and 4 m from the burner outlet. Six special valves, resistant at operating temperature of 673 K, allowed the overall mass flow rate to pass through only one of the reactors or through both in series so also changing the length of the piping from the burner outlet to the reactors. External heaters contributed to the trap holders temperature control. In particular, the progressive heating of the trap from the test start-up was, generally, achieved by means of the exhaust gas sensible heat and, also, properly changing the length of the piping. In some cases, however, the external-heating device was employed to reach the needed temperature. The temperature of the trap inlet and outlet gas was measured by K-type thermocouples, while the trap pressure drop was monitored through differential strain gauge pressure transducers. The soot concentration upstream and downstream of the trap was measured by means of an opacimeter (Tecnotest).

3. Results and discussion

The typical behaviour of the aged catalytic trap is shown in Fig. 1, where the pressure drop, the inlet and outlet gas temperature and the soot removal overall efficiency (η) of the trap are reported as functions of trap operation time. Results in Fig. 1 show that during the whole test the measured removal efficiency was constant. In addition, from Fig. 1 it appears that from the test start-up the trap inlet and outlet gas temperature continuously increase with time at decreasing rates, asymptotically approaching an upper limit and, correspondingly, the trap pressure drop increases as the temperature increases and levels off at a constant value. In the view that constant trap pressure drop reflects a constant soot load in the trap, such results suggest that for a given burner operating condition it is possible to reach a trap temperature at which the rate of soot burning is equal to the rate of soot removal from the gas stream. Furthermore, when the burner operating conditions are changed, different asymptotic values of the trap pressure drop and of the temperature at which it occurs may be found. Such a temperature can be called "balance temperature" (T_b) and can be defined as the temperature at which the rate of soot catalytic combustion (i.e. the regeneration rate of the soot loaded trap) balances the net rate of soot deposition on the trap.

Tests specifically designed to measure T_b in relation to different burner operating conditions were performed. Results pertaining to the aged trap are summarised in Fig. 2, where T_b and η are reported as functions of α. Oxygen and soot concentrations, C_{O_2}

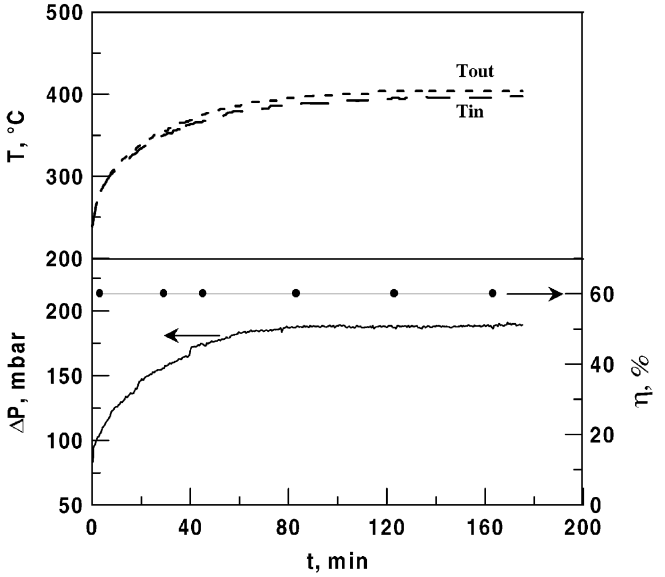

Fig. 1. Pressure drop, inlet (T_{in}) and outlet (T_{out}) gas temperature and soot removal efficiency as a function of time of operation for the aged catalytic trap. Operating conditions: $\alpha = 28$; $C_{BS} = 4.5$ g/h; gas flow rate = 34 Nm^3/h.

and $C_{BS,}$ respectively, measured in the same tests at the burner exhaust, are also shown in Fig. 2. When α decreases from 36 to 23, C_{O_2} decreases from 14.5 to 9 vol.%, C_{BS} increases by a factor slightly above 4, and T_b changes from 375 to 460 °C, i.e. in a range of temperature within that typical of diesel engine exhausts (150–500 °C). In addition, it is worth noting that T_b is below 400 °C for most of the operating α

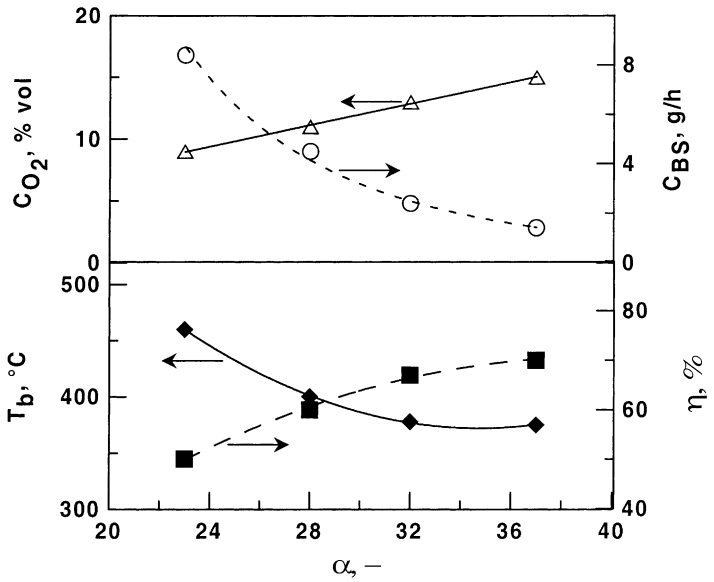

Fig. 2. Balance temperature (T_b) and soot removal efficiency (η) of the aged catalytic trap at various α and, correspondingly, soot and oxygen concentrations in the exhaust.

values. Fig. 2 also shows that on increasing α from 23 to 36 the overall net soot removal efficiency increases from 50 to 70%. Accordingly, simple calculations tell us that the amount of soot burned on the catalytic trap varied from 1 to about 4 g/h.

The trend of η with α in Fig. 2 agrees with previous findings [10]. It can be explained on taking into account that η is the product of the efficiency of particulate capture and the efficiency of retention of captured particulate on the collectors. In addition, increasing the air excess (that is α) results in a greater content of hydrocarbons adsorbed on the soot surface, which makes the soot more sticky and adhesive to the filter surface. Therefore, this leads to an enhanced retention efficiency and, hence, an increase of η.

The comparison between the behaviour of the aged catalytic trap and that of the uncatalytic trap at the burner exhaust is shown in Fig. 3. The gas pressure drop through the traps, made dimensionless with respect to the relevant initial value, and the traps temperature are reported as functions of trap operation time. As it is evident from the figure, the gas pressure drop through the uncatalytic trap increases continuously during all the tests. In particular, from the cold start-up, the trap pressure drop increases with time as a consequence of both trap temperature increase and soot accumulation, which influences the trap voidage. It is clear that in such conditions, unacceptable burner or engine backpressure can be rapidly reached. Instead, for the catalytic trap the pressure drop tends to level off as the trap temperature reaches a suitable value. In particular, at the test start-up the temperature is low and the trap pressure drop increases with a slope very similar to that pertaining to the uncatalytic trap. But later on, as the temperature increases, such a slope becomes progressively lower, eventually approaching zero as it was also observed in Fig. 1.

Another difference between uncatalytic and catalytic trap is that either increase (trap loading) or decrease (trap regeneration) of the trap pressure drop can be experienced during the test with the latter. This behavior can be observed in Fig. 4 in the case of a run where a previously soot loaded fresh catalytic trap was employed (i.e. relatively high initial trap pressure drop). Specifically, the figure shows that as the time increases from the cold start-up, the trap pressure drop increases as a consequence of both trap temperature increase and soot accumulation. However, as the temperature becomes high enough (i.e. about 320 °C), the trap pressure drop decreases, meaning that the trap is regenerating, and reaches a value lower than that at the beginning of the test although a much higher temperature is reached at the end of the test.

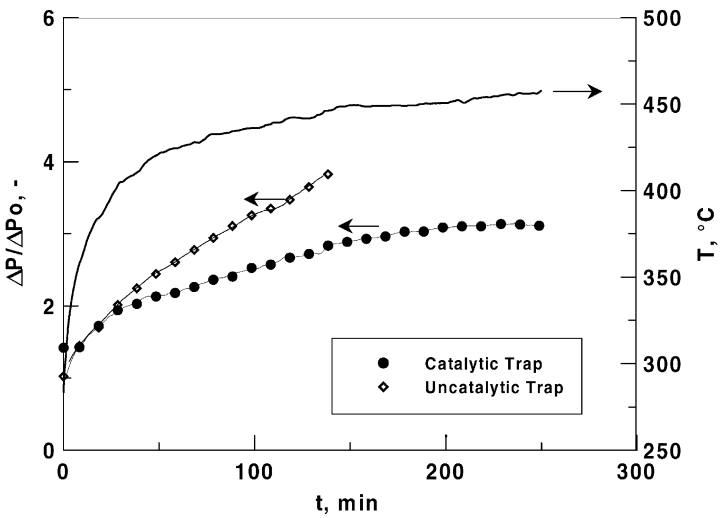

Fig. 3. Comparison between time profiles of trap pressure drop and temperature for the uncatalytic and the aged catalytic trap. Operating conditions: $\alpha = 23$; $C_{BS} = 9.5$ g/h; gas flow rate $= 30\,Nm^3/h$; $\eta = 50\%$.

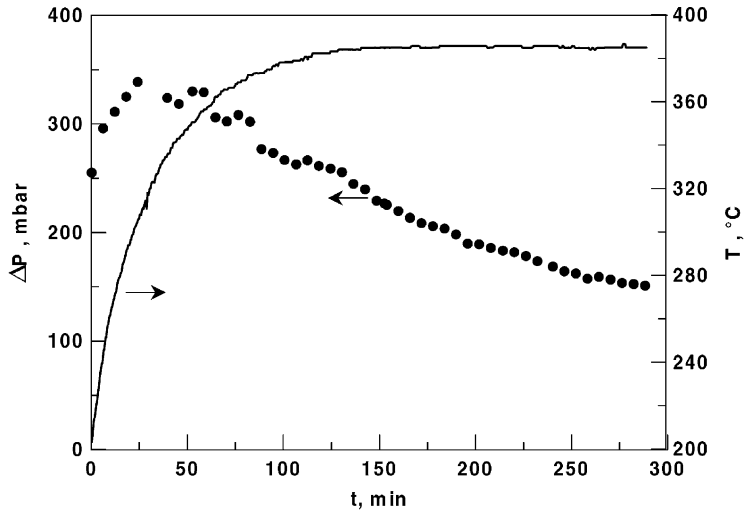

Fig. 4. Pressure drop and temperature as a function of time of operation for the fresh catalytic trap. Operating conditions: $\alpha = 23$; $C_{BS} = 9.5$ g/h; gas flow rate = 30 Nm^3/h; $\eta = 50\%$.

As mentioned, the results in Fig. 1 refers to an aged catalytic trap, but the typical behaviour of a fresh catalytic trap is substantially the same, the differences regarding the steady state values of trap temperature and gas pressure drop. Indeed, an attenuation of the activity of the catalytic trap shows up because of the trap operation in the burner exhaust environment. This attenuation can be appreciated by comparing results in Figs. 3 and 4. Specifically, from Fig. 4 it can be seen that operating the burner at $\alpha = 23$ with the fresh catalytic trap, T_b is below 400 °C. Instead, from Fig. 3 it appears that with the aged catalytic foam under the same α, T_b is about 460 °C. However, in any event it is within the range of operating diesel engine exhaust gas temperature (i.e. 150–500 °C).

SEM pictures of foam samples are reported in Fig. 5a–f. Specifically, Fig. 5a, c and e shows uncatalytic, fresh catalytic and aged catalytic (70 h of operation at the burner exhaust) foams, respectively. Fig. 5b, d and f show the same samples at higher magnification. At lower magnification (Fig. 5a, c and e) the typical three-dimensional cellular microstructure with highly interconnected voids of ceramic foam appears to be the same for all three analysed samples. At higher magnification the uncatalytic ceramic foam (Fig. 5b) appears constituted by 5 μm mean diameter grains and 1 μm mean diameter pores, while the catalytic foam (Fig. 5d) appears more homogeneous, smaller porosity disappeared as a result of uniform dispersion of the catalyst on the foam. Correspondingly, the specific surface area of the ceramic foam changes from 0.7 to 0.2 m^2/g as a consequence of catalyst deposition. Finally, the aged catalytic foam (70 test hours) shows segregated species on the surface visible at lower and higher magnifications (Fig. 5e and f) and, correspondingly, the measured surface area is only 0.5 m^2/g.

The percentage distribution, yielded by EDAX analysis, and the corresponding relative amount of the main catalyst atomic components on the surface of fresh and aged catalytic foams are reported in Table 1. A feature common to the fresh and the aged catalytic foams is the lack of chlorine which is one of the

Table 1
Relative abundance of relevant elements on the surface of fresh and aged catalytic foam (EDAX analysis)

Elements	Catalytic foam			
	Fresh		Aged	
	%	Relative amounts	%	Relative amounts
Cu	5.8	1	2.9	1
V	5.3	0.914	3.7	1.276
K	3.0	0.517	3.8	1.310
S	–	–	2.6	0.896

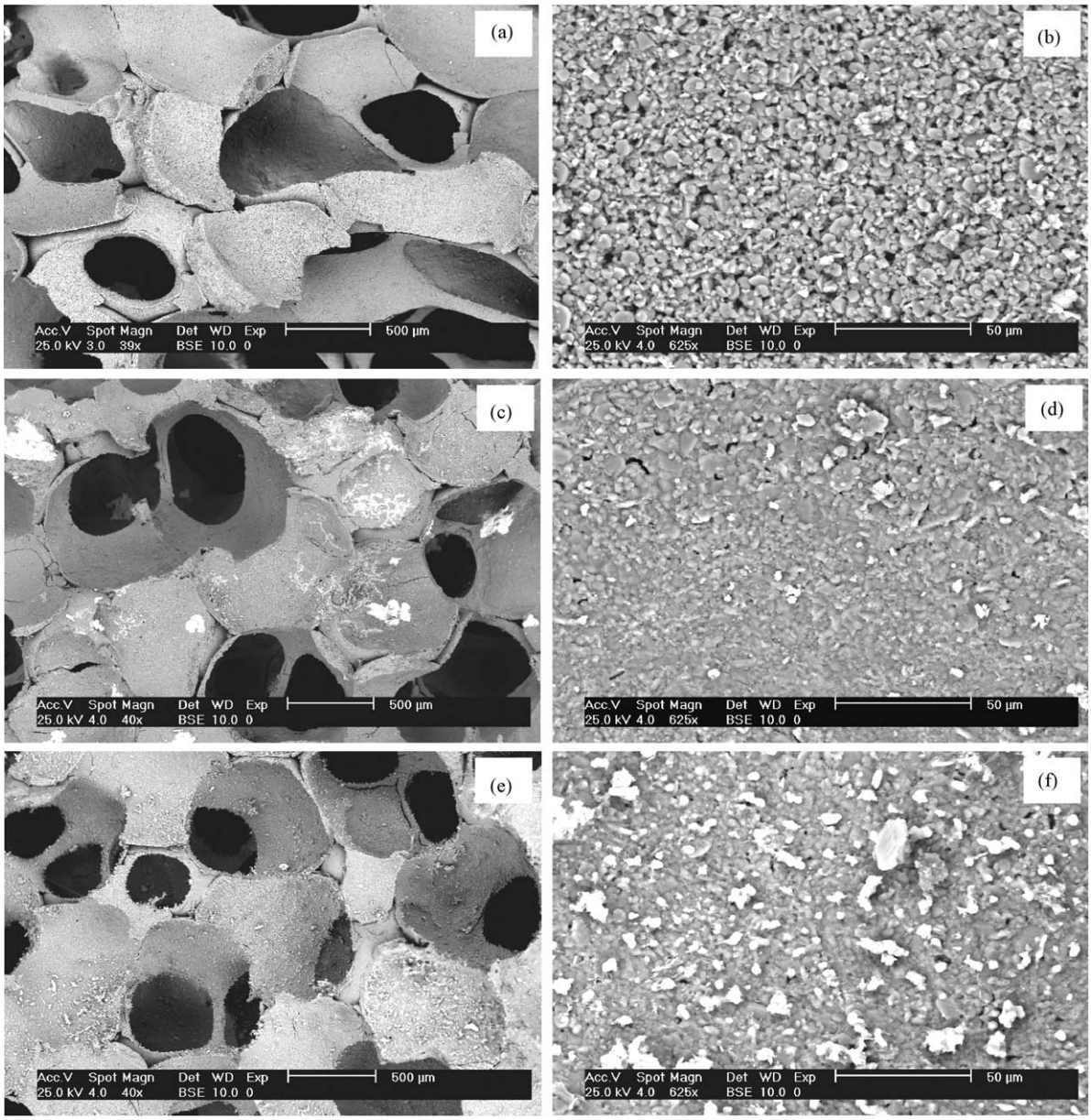

Fig. 5. SEM pictures of uncatalytic (a, b), fresh catalytic (c, d) and aged catalytic (e, f) foams at lower (a, c and e) and higher magnifications (b, d and f).

components of the catalyst precursors. This feature is particularly remarkable in that chlorine was, instead, previously observed by the authors when the same precursors were employed for preparing alumina or titania supported powder catalysts [2,8]. In any case, in comparison with the fresh catalytic foam, the aged one shows a generalised decrease of the percentage of all relevant elements but potassium. In addition, there is an increase, more marked for potassium, of the relative amounts of V and K with respect to Cu. Indeed, from

Table 2
Relative abundance of relevant elements on the bulk of fresh and aged catalytic foam (ICP-AES analysis)

Elements	Catalytic foam			
	Fresh		Aged	
	%	Relative amounts	%	Relative amounts
Cu	0.81	1	0.45	1
V	0.78	0.963	0.55	1.222
K	0.93	1.148	0.47	1.044

fresh to aged sample such relative amounts change from 0.914 to 1.276 in the case of V, and from 0.517 to 1.310 in the case of potassium (Table 1). Furthermore, in the aged samples the analysis reveals a significant amount of sulphur, which is absent in the fresh sample. It is worth noting that in a previous work the authors found that the chlorine present in the fresh catalyst was substituted with sulphur after catalyst operation in a real exhaust environment [9]. The lack of chlorine in the fresh catalytic trap appears particularly important since the presence of soot, of chlorine, and of metallic catalyst promotes the formation of dioxins in the range of temperatures 300–400 °C [11,12]. Nevertheless, some chlorine may be present in the commercial diesel fuel and, hence, the formation of dioxins could be promoted. However, it may be argued that this occurs mainly on the soot particles [11], and that the present catalyst is capable of promoting the combustion of every form of carbon, even the very stable one [13] and, therefore, it could help to burn the produced dioxins. However, the occurrence of this favourable possibility has to be investigated in the near future.

Table 2 reports the results of the relative abundance of the metallic elements in the bulk of the catalyst obtained by ICP-AES of solubilized catalyst. The relative abundance of Cu and V is the same as that on the catalyst surface either for the fresh or the aged catalyst. In contrast, the relative amount of K in the bulk is more than double that on the surface for the fresh catalyst, while it is slightly lower in the case of the aged catalyst.

Altogether, the EDAX and ICP-AES analyses indicate that: (i) some Cu, K and V are lost during trap operation and the loss of Cu is larger than that of the other two metals; (ii) the relative abundance of Cu and V are the same on the surface and in the bulk of the catalyst; (iii) in the fresh sample, potassium concentrates prevalently in the bulk of the catalyst, while in the aged sample it is more homogeneously dispersed in the bulk and on the surface. The distribution map of the elements on the surface of a given area of the sample, yielded by EDAX analysis, indicates that sulphur enters the catalyst by reacting with potassium. Indeed, the maps of the relative abundance of sulphur and potassium in the investigated area are very similar.

However, it should be established if the catalyst employed is inherently unstable under practical conditions of operation or if it stabilises after modifications due to the interaction with the various exhaust gas components. Actually, the authors do not have information about this but this topic will be investigated in the near future.

4. Conclusions

A ceramic foam catalytic filter, obtained by deposition over ceramic foam of a Cu/V/K/Cl catalyst and operated for 70 h at the exhaust of a gas oil burner, allows:

- the abatement of relevant amounts of soot from the exhaust of a gas oil burner;
- the steady state operation of the trap in terms of temperature and pressure drop depending on the burner operating conditions;
- the spontaneous operation of the trap at a steady state temperature always within the temperature range typical of diesel engine exhausts, making this system attractive for the treatment of diesel engine exhaust.

The operation at the exhaust of a gas oil burner leads to the sulphation of the catalyst mainly by reaction with potassium.

References

[1] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B 8 (1996) 57.
[2] P. Ciambelli, P. Corbo, M. Gambino, V. Palma, S. Vaccaro, Catal. Today 27 (1996) 99.
[3] G. Saracco, C. Badini, N. Russo, V. Specchia, Appl. Catal. B 21 (1999) 233.

[4] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, Stud. Surf. Sci. Catal. 116 (1998) 635.
[5] J.P. Gabathuler, T. Mizrah, L. Eckert, A. Fisher, P. Kaser, A. Maurer, SAE Paper 910 325 (1991).
[6] B.A.A.L. van Setten, J. Bremmer, S.J. Jelles, M. Makkee, J.A. Moulijn, Catal. Today 53 (1999) 613.
[7] Y. Watabe, K. Irako, Y. Murakami, SAE Paper 830 082 (1983).
[8] P. Ciambelli, P. Corbo, M.R. Scialò, S. Vaccaro, Italian Patent No. 1 221 416 (1990).
[9] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, Ind. Eng. Chem. Res. 39 (2000) 4914.
[10] P. Ciambelli, P. Corbo, V. Palma, P. Russo, S. Vaccaro, B. Vaglieco, Top. Catal. 16/17 (2001) 279.
[11] H. Huang, A. Buekens, Chemosphere 31 (1995) 4099.
[12] P. Weber, E. Dinius, L. Stieglitz, Chemosphere 42 (2001) 579.
[13] P. Ciambelli, V. Palma, S. Vaccaro, Combust. Sci. Techol. 103 (1994) 337.